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Elemental Composition of Soils in the Heterogeneous Geological Setting of the Mzymta River Basin on the Russian Black Sea Coast

Lalita Zakharikhina[1,*], Vadim Kerimzade[1], Yury Litvinenko[2]

[1]Federal Research Center the Subtropical Scientific Center of the Russian Academy of Sciences, 2/28 Jānis Fabriciuss, Krasnodar Krai, Sochi, 354002, Russian Federation
[2]EcoGeoLit Ltd., 17 B Mosfilmovskaya St., Moscow, 119330, Russian Federation

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Abstract This study examines the regional geochemical anomalies in the soil of the Mzymta River valley in Russia, which was affected by large-scale construction works for the 2014 Winter Olympics. The study found that the elemental composition of soils not affected by human activity is influenced by the chemically rich parent rock and the presence of mineralized zones. The abundance and concentrations of excess and deficient elements in the soil were determined using mass spectrometry for 61 elements, and factor analysis was used to identify the causes of the variations observed. The study identified geochemical indicators that can predict soil-forming factors and revealed both natural and anthropogenic sources of chemical elements in the valley soils. Natural sources include geochemically rich rocks that contributed most significantly to the soil chemistry. The anthropogenic sources of elemental variation in the soil were a result of the construction of Olympic transit infrastructure using local geochemically rich materials. The heavy crushing and subsequent intense weathering of this material resulted in an increase in the concentration of excess elements in the soil compared to the parent rock or mineralized zones. This indicates a significant alteration of the soil's elemental composition due to construction activities in the area. The findings of this study can be applied to predict potential soil contamination in similar river valleys that are experiencing both natural and anthropogenic pressures.

Keywords Geochemistry, Soil Ecology, Elemental Provenance, Rare Earth Elements

1. Introduction

Understanding the quantitative geochemical characteristics of soils and the factors that impact them is crucial for evaluating the extent of chemical contamination in a particular area and determining the soil's residual ecological potential. With increasing urbanization, it becomes more difficult to pinpoint all sources of chemical pollution, but it is necessary to do so in order to develop effective methods for preserving the ecological function of the soil. This is important for maintaining biodiversity, preserving soil fertility, and protecting human health. Conducting a thorough study of the properties of both disturbed and undisturbed soils formed under different natural and human-induced conditions is essential for gaining a comprehensive understanding of the issues and devising effective solutions.

In recent years, there has been significant discussion and research on the geochemical transformations of soils in urban environments. The alkalinization of soils due to the

influx of metal salts associated with urban anthropization has been observed in many locations [1,2]. The contaminants found in environments with varying degrees and nature of anthropogenic impacts often contain the same chemical elements: Cd, Cr, Ni, Zn, Cu, Pb, As, Fe, V [1,3-5]. However, the concentrations of these elements can vary by 2-4 orders of magnitude, depending on the type of land use [4,6,7]. Geochemical anomalies in urban environments caused by the natural regional geochemical specialization of soil-forming rocks and unrelated to anthropization have also been frequently observed [8,9].

In order to fully understand the impact of urbanization on soil chemistry, it is important to assess ongoing changes in soil chemistry associated with urbanization and to characterize soil-forming processes under specific regional conditions, using up-to-date information on a wide range of chemical elements. Additionally, it is important to evaluate and compare the natural geochemical background with man-made anomalies that are not directly linked to the natural enrichment of chemical elements in rocks and soils.

Studying soil contamination can be challenging due to limitations in analytical capabilities and methods used, which can result in a narrow focus on certain elements and exclude a large group of rare, dispersed, and radioactive elements from the research. To improve our understanding of soil geochemistry, it is essential to study a wide range of chemical elements and take into account both natural factors and anthropogenic influences.

This study aimed to analyze soils in the Mzymta river basin on the southern slopes of the Caucasus Mountains, an area characterized by highly heterogeneous and contrasting bodies of rock including argillites, siltstones, clay shales, carbonate formations, clay-carbonate rock suites, and igneous rocks [10]. Additionally, the area has multiple polymetallic, auriferous, sulfide, and rare earth mineralizations [11, 12]. The goal of the study was to examine the soils formed in these areas of contrasting geology, including areas of established anthropogenic impact, for a wide range of major, minor, and dispersed elements.

2. Materials and Methods

2.1. Study Area

The entire length of the river valley, from the headwaters to the estuary, was divided into seven survey sites (SS) based on known geochemical patterns (Figure 1). Soil sampling at each site was conducted at 10 sampling points located at 20-30 m intervals across the valley. The coordinates of the survey sites are provided in Table A1.

The composition of the rock that forms the soil is a major factor that determines the geochemical properties of the soil. In the Mzymta River basin on the Black Sea coast, the soil-forming rocks include argillites, siltstones, and sandstones, with a lesser presence of carbonates and occasionally igneous rocks. Limestones are commonly found in the middle reaches of the rivers. Additionally, there is a geological transition from argillites and silts to carbonate marls that occurs along the length of the Mzymta River from the headwaters to the estuary [13].

The Mzymta River valley is divided into four primary subregions based on the composition of soil-forming rocks. These subregions are depicted in Figure 1. The first survey site, located at an elevation of 1838 meters above sea level, is characterized by soils that have developed from igneous rocks such as Jurassic gabbro-diorites and granites. The second, third, and fourth survey sites consist of Jurassic mudstones with interlayers of siltstones, sandstones and siderites with pyrite concretions. The fifth survey site is characterized by soils that have formed on Cretaceous marls with sandstone interbeds. Further downstream, at the river mouth, modern alluvial deposits overlie Paleogene and Neogene clays, marly clays with siltstones, and sandstones at survey sites 6 and 7.

The first survey site is located within the Caucasus State Nature Biosphere Reserve, as depicted in Figure 1. The second, third, and fourth survey sites are located upstream and downstream, respectively, of a potential source of pollution, the mountain recreation and sports tourism complex known as Krasnaya Polyana. The fifth and sixth survey sites are situated downstream of the Mzymta tributaries Chvizheps and Kepsha, and their eponymous villages. The seventh survey site is located above the mouth of the Mzymta River, in proximity to the village of Moldovka. The highway and railroad from Adler to Krasnaya Polyana, constructed for the 2014 Olympics, run along the river bank between the third and sixth survey sites. The soils studied in the Mzymta River watershed were classified as alluvial gray humus (sod) soils [14], or fluvisols, according to the international classification system [15]. These soils were characterized by slightly acidic reactions in the upper valley and close to neutral reactions in the mid- to lower valley. The humus content was high, varying from 3.3 to 5.7%, and the base saturation percentage was mostly high at about 90%, with the exception of the headwaters area where it was 46% (as per Table A2).

2.2. Sampling and Analysis

The upper organo-mineral soil horizon at each survey site was sampled using the envelope method. This method involved forming a composite sample by combining five individual samples that were taken at the corners and center of a 5-meter square at each survey site. The composite sample was then packaged and shipped to a laboratory for analytical studies.

The total elemental contents in the samples were determined for 61 chemical elements by quantitative techniques, including inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma

atomic emission spectroscopy (ICP-AES), using XSeries I mass spectrometer (Thermo Scientific, USA) and iCAP 6500 Duo atomic emission spectrometer (Thermo Scientific, USA). The analysis was performed according to the certified methodology of the Russian Federal Standard NSAM #499-AES/MS, specifically the method of "Determination of the elemental composition of rocks, soils and sediments by atomic emission method with inductively coupled plasma and mass spectral method with inductively coupled plasma".

The samples were digested using a mixture of acids (HF, HNO_3, HCl, and $HClO_4$) in an open system. The chemical yield for the elements by this method typically ranges within 90-100 %. The margin of error for the elements determined by this method relative to an external standard was ⩽6 %. The limits of detection (LODs) of the method for trace elements in soil were 1/100 of a microgram per gram (μg/g) and several hundredths of a percent for macro-components. The LODs for chemical elements in soils were determined by measuring control samples (at least three per batch) and are listed in Table A3.

Standard basalt samples, Hawaii Volcanic Observatory BHVO-2 (U.S. Geological Survey), were used to verify the accuracy of the analysis (discussed below in Section 3). The concentrations of the chemical elements of interest in the standard samples were also determined. The agreement with the certified values was, on average, 1-3 %.

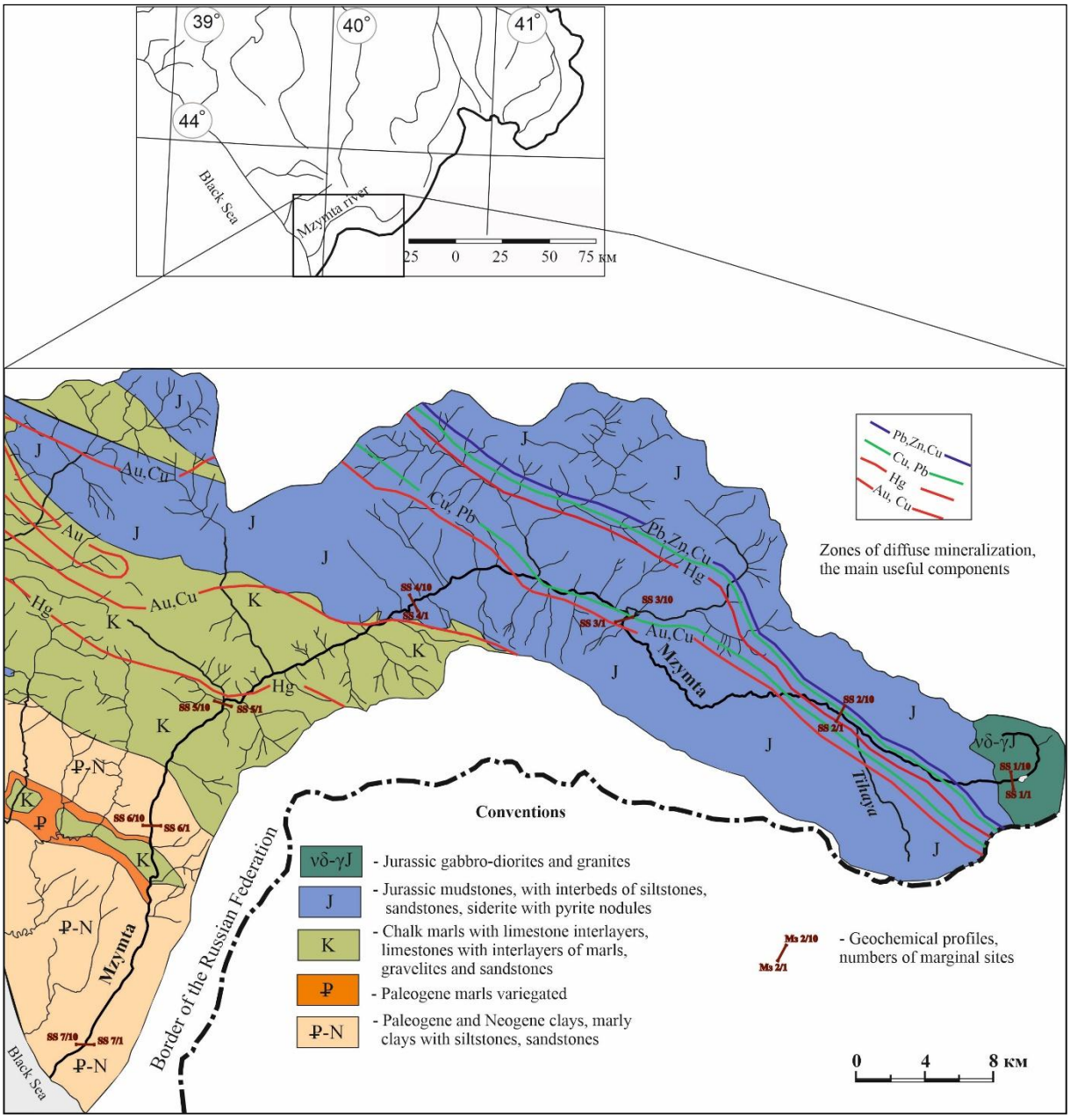

Figure 1. Geological map of the Mzymta River and Geochemical profiles, numbers of marginal sites

2.3. Assessment of Geochemical Characteristics and Contamination of Soil

The element concentrations in the soils under study were calculated relative to clarke numbers (Cc) using the formula Cc=Cb/C, where Cb is the average background content of the element in the study area and C is the average abundance of the element in continental soils [16]. Values of Cc >1 indicate excess chemical elements and Cc <1 indicate deficient elements. Geochemical formulas for the studied soils were constructed by ranking and grouping chemical elements according to the Cc value.

To determine the degree of soil contamination, the total pollution index $Zc = \sum Cci - (n-1)$ [17,18] was calculated, where Cci is the concentration coefficient of the i-th element in the soil, equal to the ratio of its actual content at a survey site (Ci) to the local background content (Cb). The background values were assumed to be the average element concentrations in the upper reaches of the Mzymta river at survey sites 1 - 3. The indicative assessment scale of soil pollution hazard according to the total pollution index Zs consists of the following categories: permissible (less than 16); moderately dangerous (16-32); dangerous (32-128); and extremely dangerous (more than 128) [17].

Elemental chemical contents as fractions of maximum permissible concentrations (MPC) and tentatively permissible concentrations (TPC) based on the Russian hygienic standards (Russian Federal Hygienic Standards 2.1.7.2041-06; Russian Federal Hygienic Standards 2.1.7.2511- 09) were established. MPC is a Russian standard that established limits for the maximum permissible concentrations of chemical elements for all soils, while TPC established limits for soils with heterogeneous granulometries. In this study TPC limits for soils with clay texture were used. The permissible total concentrations of the elements of interest in soils were: MPC: Sb - 4.5 mg/kg; Mn - 1500 mg/kg; V - 150 mg/kg; Pb - 32 mg/kg; As - 2.0 mg/kg; and TPC: Pb - 130 mg/kg; As - 10.0 mg/kg; Cd - 2.0 mg/kg; Cu - 132 mg/kg; Ni - 80 mg/kg; Zn - 220 mg/kg.

Given the heterogeneous geological setting of the Mzymta Valley, correlation coefficients between survey sites were calculated from soil chemical element Cc values to determine similarities or contrasts in the geochemical properties of soils in the subregions identified. This can help determine geochemical properties of the soil and understand the source of any potential pollution.

Additionally, rank correlation coefficients between Cc values of chemical elements in graded embankments and at survey sites were calculated to assess the role of highway and railroad embankments as possible sources of soil contamination in the anthropogenic impact zone.

A factor analysis of assay results was performed to establish hidden dependencies between chemical element contents in the data set, reduce the feature space, and identify factors that determine the geochemical composition of alluvial soils in the Mzymta River basin. The logarithmic concentrations of the elements were used in the calculations. The principal component method was applied and the factor analysis was performed using the Gold Digger software. Gold Digger is a software suite for complex processing of geological and geochemical data developed at the Department of Geochemistry, Faculty of Geology, Moscow State University [19].

2.4. Statistical Analysis

The chemical composition data sets obtained reflected the soils formed under highly divergent conditions. Significant differences between concentrations of chemical elements were tested using Student's t-test at $p < 0.05$. Statistical descriptions and data analysis were prepared using the Microsoft Office 2010 software suite (Microsoft, Inc., USA). Confidence intervals and least significant difference (LSD) values were calculated and are given in Table A3.

3. Results

The study found significant variations in both the relative abundances and prevalence in the chemical elements occurring in soils overlying different types of rocks in the Mzymta river system (Table 1). The geochemical properties of soils overlying igneous and sedimentary rocks showed varying degrees of similarity or dissimilarity based on Cc rank correlation coefficients. Survey sites 2-7 had close correlations, with values ranging from 0.69 to 0.98. Survey site 1 had a weak correlation ($r < 0.46$, r 5 % crit = 0.28) and survey site 3 had a negligible correlation ($r = 0.26$) (Table 2). These results indicate that the geochemical properties of soils over igneous and sedimentary rocks were closely related in survey sites 2-7, weakly related in survey site 1, and not related in survey site 3.

Table 1. Geochemical formulas of soils in the Mzymta river valley according to Cc index

Cc >5	5 - >2	2 - >1	1 – > 0.5	0.5 - >0.2	0.2- >0.1
headwaters, SS-1 (igneous rocks, gabbro-diorites and granites)					
–	–	Sn(2.0)-U(1.9)-Be(1.8)-Mn(1.7)-Zn(1.6)-Sc,Bi(1.4)-Ho,Co(1.3)-W,Cd,Er(1.2)-Ni,Gd(1.1)	V,Th,Tb,K,Fe,Sm Eu(1.0)-Lu,Ce,Nb,Al,As, Y(0.9)-Ga,Tm,Ta,Dy,Mo,Tl,Rb,Pb,Yb,Ca,Pr (0.8)-Cr,Nd,Cs,Cu(0.6)	La,Sr(0.5)- Li,Sb,Na, Ba(0.4)-Hf,Hg(0.3)	Zr,Mg(0.2)-P, Ag,S(0.1)
upper reaches, SS-2 (sedimentary rocks, mudstones with interlayers of siltstones)					
	As(4.6)-Mn(3.7)-Cs(3.0)-Ni(2.9)-Zn(2.8)-Pb(2.6)-Sn(2.5)-Co(2.5)-Cu(2.4)-Bi, Sb(2.3)	Sc(1.8)-Rb,K,Tl(1.7)-Be,V,Cr(1.6)-W(1.4)-Fe,Al(1.3)-Cd,Nb(1.1)	Mo(1.0)-Hg,Th,Ga, Eu(0.9)-Sm,Gd(0.8)-Ba, Ce(0.7)-Ho,Tb,U,Ta, Ag(0.6)	Er,Pr,Nd, Ca(0.5)-Dy,Sr,Y,Lu, Tm(0.4)-La,Yb(0.3)	P,Na,Mg, Hf(0.2)-Zr, S(0.1)
upper reaches, SS-3 (sedimentary rocks, mudstones with interlayers of siltstones)					
As (10.1)-Mn (6.6)	Cu(4.0), Ni(3.8)-Cs(3.7)-Co(3.1)-Li(3.0)-Bi(2.8)-Zn(2.5)-Sb(2.3)-Pb,Tl(2.2)	Rb,Sc,K(2.0)-V(1.8)-Mo, Cr(1.7)-W(1.6)-Hg,Nb(1.5)-Al,Fe(1.4)-Sn(1.3)-Th,Eu(1.1)	Ga,Cd,Sm(1.0)-Gd(0.9)-Ba,Ta,Ce(0.8)-Tb(0.7)-Ho, Pr,Nd,U(0.6)	Sr,Er,Dy, Ca(0.5)-Y,La,Tm, Ag(0.4)-Lu,Yb(0.3)	Mg,Na, P(0.2)-Hf,Zr, S(0.1)
middle reaches, SS-4 (sedimentary rocks, mudstones with interlayers of siltstones)					
	As(4.1),Ni(3.4)-Zn,Mn(2.7)-Bi(2.3)-Cu(2.2)-Co,Li(2.1)	Cr,Sb,Cs(2.0)-Sc(1.9)-W(1.8)-Pb,Rb(1.7)-V,K,Tl(1.6)-Be, Sn(1.4)-Fe,Al(1.3)	Ca,Nb(1.0)-Th,Ga,Eu, Cd(0.9)-Mo,Sm,Gd(0.8)-Ba,Hg,Ho,Ce(0.7)-Tb,Ta,U,Sr,Er(0.6)	Pr,Nd,Dy (0.5) -Y,Tm, Lu(0.4)-La,Yb(0.3)	Ag,Mg, Na(0.2)-P, Hf, Zr,S(0.1)
middle reaches, SS-5 (sedimentary rocks, Cretaceous marls with limestone)					
	As(4.1), Ni(3.4)-Mn(2.8)-Cu(2.3)-Co(2.2)-Zn(2.1)	Li(2.0)-Sc,Bi(1.9)-Cs,Cr(1.8)-Ca,W(1.7)-Rb,K,V,Tl,Sb(1.6)-Sn(1.5)-Be,Fe(1.4)-Pb(1.3)-Al,Nb, Th(1.2)-Eu(1.1)	Sm,Ce,Gd,Cd(0.9)-Ho,Ba,U,Hg(0.8)-Tb,Pr, Mo,Ta, Er,Ng(0.7)-Sr,Y,Dy(0.6)	La,Lu,Tm (0.5)-Yb, Ag(0.4)	Mg,Na,Hf, Zr(0.2)-P,S (0.1)
lower reaches, SS-6 (sedimentary rocks, clays with siltstones, sandstones)					
	As(3.6)-Ni(3.4), Mn(2.9)-Cu,Zn(2.5)-Co(2.2)-Li(2.1)	Cs,Bi(2.0)-Sc(1.9)-Sb,Tl, Rb(1.7)-K,W,Cr,V(1.6)-Sn,Pb(1.5)-Be,Nb(1.4)-Fe,Al,Th (1.3)-Cd(1.2)	Eu,Ca,Ce,Sm,Gd(1.0)-Ga,U,Ho(0.9)-Ba,Mo, Tb,Pr,Er(0.8)-Ta,Hg,Nd(0.7)-Dy, Y,Lu,Sr,La(0.6)	Tm,Yb(0.5)-Ag(0.4)	Mg,Hf,Na, Zr(0.2)-P,S (0.1)
estuary, SS-7 (sedimentary rocks, clays with siltstones, sandstones)					
	Nb(3.6)-Mo(3.5)-Ni,As(3.2)-Mn(3.0)-Cu, Sb(2.4)-Zn(2.3)-Ca, Li(2.2)-Cr,Bi(2.1)	Tl,K(1.9)-Co,V,Rb,Sc(1.8)-W(1.6)-Al,Fe,Be(1.4)-Pb(1.2)	Th,Eu(1.0)-Sm,Ga,Gd,Ce, Cd(0.9)-Ho,Tb(0.8)-Sr,U,Sn,Hg,Er,Cs(0.7)-Pr,Ta,Nd,Dy(0.6)-Tm,Y,La, Lu(0.5)	Yb(0.4)-Ba,Mg, Na(0.3)	Zr,Hf(0.2)-P,Ag,S(0.1)

Table 2. Correlation coefficients between survey sites the Cc indicator ($r_{5\%crit}$ = 0.28)

	SS-1	SS-2	SS-3	SS-4	SS-5	SS-6	SS-7
SS-1	1						
SS-2	0.414	1.000					
SS-3	0.265	0.914	1.000				
SS-4	0.397	0.952	0.887	1.000			
SS-5	0.426	0.918	0.892	0.974	1.000		
SS-6	0.462	0.943	0.883	0.979	0.984	1.000	
SS-7	0.328	0.693	0.687	0.776	0.789	0.790	1.000

Alluvial soils on igneous rocks were characterized by poor elemental contents, with Cc values below one for most of the elements studied (39 out of 55). In contrast, sedimentary rock soils had few deficient chemical elements (25-30 out of 55). Sedimentary rock soils even had elements with Cc > 2, which was never the case on upstream igneous rock soils. The variety of excess chemical elements in the upstream soils also greatly distinguished them from the soils elsewhere in the valley.

The study found that certain elements had higher Cc values in soils developed on igneous rocks, such as Sn, U, Be, Mn, Zn, Sc and Bi. These elements also had higher clarke numbers in igneous rocks than in sedimentary rocks.

Elements such as As, Mn, Sb, Ni, Bi, Cu, Co, Zn, and Cs had consistently high Cc values in soils formed over sedimentary rocks. Importantly, these elements also had significantly higher Cc values and clarke numbers in sedimentary rocks than in igneous rocks. For example, the clarke number of As in sedimentary rocks was 7.6 mg/kg, while in igneous rocks it was 1.7 mg/kg [20].

We found that the deportment of the rare earth group of elements (REEs) was of particular interest as it can provide insights into the geochemical processes that have shaped the soils on different parent materials. REEs have similar geochemical properties, and thus exhibit similar deportment in many geological processes. REEs undergo significant fractionation during rock altering earth surface processes, causing individual elements to exhibit distinct anomalies relative to standard reference materials [21-23]. Importantly, these fractionation anomalies exhibited by an individual REE in soils are similar to those exhibited by the same element in parent rocks.

To understand the geochemical processes that shaped the soils on different parent materials, the study divided the REEs into three groups: light REEs (La, Ce, Pr, Nd), medium REEs (Sm, Eu Gd, Tb, Dy) and heavy REEs (Ho, Er, Tm, Yb, Lu, and Y) according to Aubert et al. [24]. We found that the concentrations of REEs normalized to the North American Shale Composite (NASC) had a fractionation pattern in which the soils formed on sedimentary rocks were consistently enriched in the medium rare earth elements (MREE) (Figure 2). A similar fractionation pattern characterized the deportment of REEs in the river channel sediments and the country rocks of the study area [10]. Moreover, this fractionation pattern was consistent across multiple other samples such as surface waters [10], plants [25], and even the soft tissues of the Mediterranean mussels found in the coastal zone near the Mzymta River mouth [26].

A different pattern was dominant in soils overlying igneous rocks in the headwaters. Here, moderate and heavy REEs predominated, and total REE content was on average 21 % higher than in soils overlying sedimentary rocks, which is typical in soils developed over igneous rocks [20]. This pattern was also confirmed by the distribution of REEs in river channel sediments, where upstream sediments contained 30 % more total REEs than midstream and downstream sediments [10]. Thus, rare earth total concentrations and fractionation patterns in soil can be considered a reliable indicator of the sedimentary or igneous origin of soil-forming rocks.

The differences between soils formed on argillites and carbonate rocks were most evident in their Ca content: high Ca content (Cc = 1.7) was observed in soils formed on carbonate rocks at SS-5 and in marly clay and sandstones downstream from that point (SS-6, Cc = 1.0; SS-7, Cc = 2.2), while Ca was deficient (Cc ~ 0.5) in soils formed on argillites upstream of SS-5. This implies that the Ca content of the soils can be used as an indicator to distinguish between soils formed on argillites and carbonate rocks.

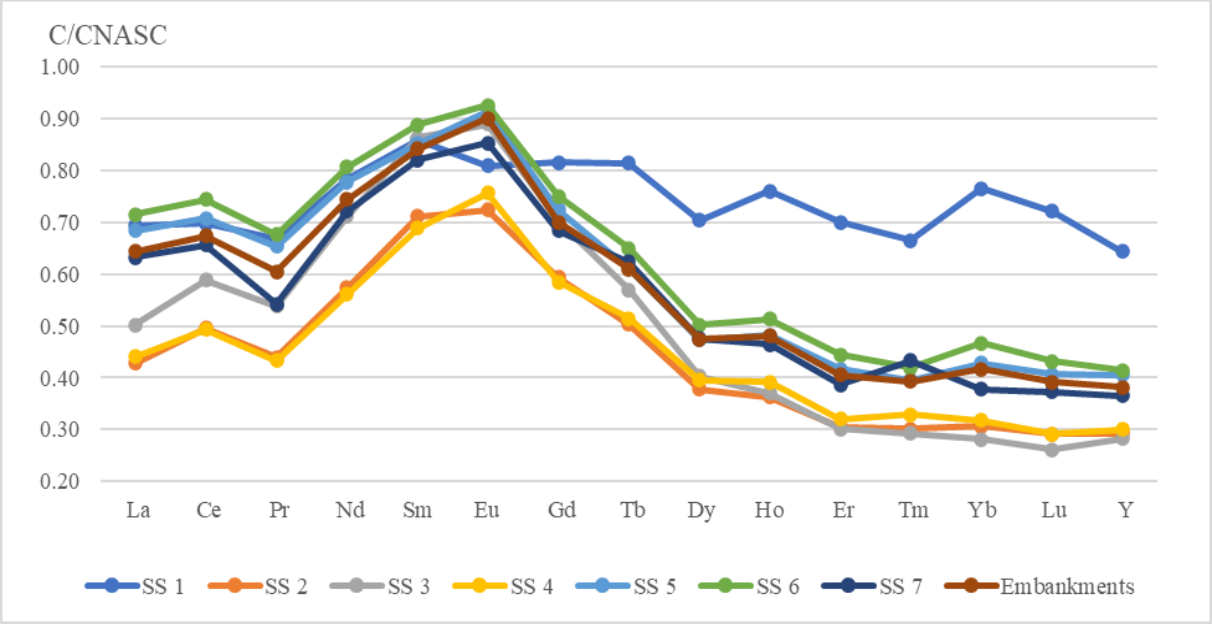

Figure 2. REE concentrations in soils and in man-made embankments normalized to North American Shale Composite (NASC)

The area downstream of SS-5 also had elevated Mg content, although it was not as high as the Ca content. This is due to the highly dissimilar clarke numbers for Ca and Mg in the clayey and carbonate sedimentary rocks. The clarke number for Ca in the carbonate rocks (325.00 mg/kg) is 11 times higher than in the clayey rocks (29.40 mg/kg), while the clarke number for Mg (46.00 and 15.40 mg/kg in the clayey and carbonate rocks, respectively) is only 3 times higher [10]. The soils retained the same ratios of the two elements as in the parent rocks. In the study area, the average Ca/Mg ratio in soils formed on argillites in the upper and middle reaches of the river was 0.7, and 1.6 in soils formed on marls. The means that the Ca/Mg ratio can be used as a diagnostic geochemical signature in identifying the provenance of soils from either clayey or carbonate parent rocks.

4. Discussion

4.1. Effects of Mineralized Zones on Soil Elemental Composition

The most common sedimentary rock soils in the studied watershed showed a consistent prevalence of excess chemical elements As, Mn, Ni, Zn, Cu, and Co.

The accumulation of these elements in soils is due to the presence of multiple mineralization zones throughout the area. These zones include polymetallic zones containing Zn, Cu, Pb, and Hg (Fig. 1), auriferous zones that are always associated with As [11], sulfide zones, and rare metal and rare earth zones [12]. The mineralized zones have a significant impact on the composition of soils, as demonstrated by the higher concentration of As found in these soils, with Cc values ranging from 3.2 to 10.

The areas of dispersed mineralization have a correlation with high concentrations of Zn, Cu, Co, and Ni that are commonly found in alluvial soils of the Mzymta River valley, with Cc ranging from 2 to 3, on average.

The presence of excess chemical elements in the soil is likely due to influx from mineralized zones, as indicated by similarities in their distribution. For example, a strong correlation was found between As and Co, Cu, Ni, and Zn with correlation coefficients of 0.95, 0.92, 0.68, and 0.52, respectively, with r5 %crit = 0.22, which supports the notion that these elements are coming from the same sources.

In addition, a close correlation between ore-bearing rock elements (Fe and Al) and associated elements (As, Co, Pb, Cu, Ni, Bi, Sb, and Zn) was observed as illustrated in Figure 3.

The binding of associated elements to iron can be explained by the increased sorption capacity of iron hydroxide which results from the supergene alteration of pyrite, a common mineral in mineralized zones.

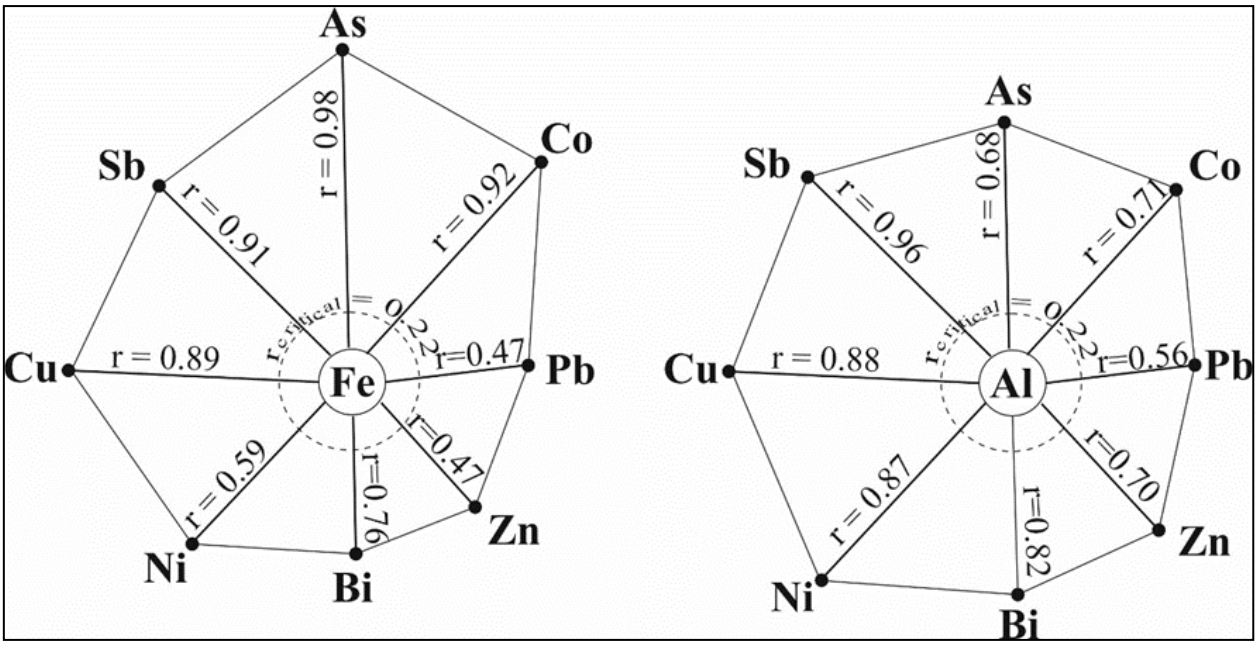

Figure 3. Correlations of Fe and Al with concomitant chemical elements of mineralization zones

The Mzymta River basin is known for having excess concentrations of Al in the clayey rocks that are widely distributed in the area. This element migrates into the absorbing minor clay minerals to accumulate in high concentrations during the process of rock weathering. Additionally, Al may also be present in high concentrations in minor clay minerals that form due to weathering of acidic igneous rocks. In the supergene zone, mineral elements are adsorbed onto iron hydroxides and minor clay minerals as intermediate storage sites and eventually enter the soil in large quantities.

4.2. Shared Local Soil Characteristics

Two distinct features have been identified in the soils of the Mzymta river valley. The first feature is that the soils have a consistent prevalence of the same deficient elements, as indicated by low Cc values (<0.5) for P, Ag, S, Hf, Mg, Na, and Zr. The spectrum of deficient elements also includes rare-earth elements with Cc values around 0.5. The second feature is the absence of contrasting geochemical anomalies. The chemical composition of the river channel sediments in the valley mirrors that of the country rocks, with elevated concentrations of elements such as Mo, Nb, As, Zn, Se, Cr, Li, Pb, Ni, Sb, Mn, Bi, V, Al, Sc, Cu, Ga, Fe, K, Rb, Na, Co, Be, Ti, Mg, and Eu [10]. High concentrations of most of these elements are typical of soils developed on sedimentary rocks.

A strong correlation exists between the relative element abundances in the alluvium of the Mzymta River valley and the channel sediments, as demonstrated by a rank correlation coefficient (r) of 0.72, as per the equations below, with a critical value of 0.282.

A statistical method known as factor analysis was utilized to examine the elements present in the soils of the Mzymta River watershed, and it was determined that six major factors explain 90.2% of the total variance of the baseline data. This implies that the majority of the variation in element concentrations can be attributed to these six factors.

Factor 1 – 44.6 % Li $_{0.93}$ (Rb, Sb, Cu, Pb, As, Tl, Ni, Bi) $_{>0.8}$ (V, K, Al, Co, Mn, Cr) $_{>0.7}$ (Fe, Zn) $_{>0.6}$ (Sc, Ga) $_{>0.5}$ W $_{0.34}$ Cs $_{0.27}$ (Yb, Lu, Er, Y, Ho, Tm) $_{<-0.9}$ (Dy, U, Hf) $_{<-0.8}$ Tb $_{-0.78}$ (Na, La) $_{<-0.6}$ (Pr, Gd, Ce) $_{<-0.5}$ (Ta, Nd) $_{<-0.4}$ Sm $_{-0.31}$ Ca $_{-0.24}$

Factor 2 – 16.3 % (Nd, Sm, Gd, Pr, Ce) $_{>0.9}$ (La, Tb) $_{>0.8}$ (Eu, Dy) $_{>0.7}$ (Ho, Ta, Y, Th, Er, Lu) $_{>0.6}$ (Yb, U, Tm) $_{>0.5}$ Hf $_{0.47}$ (Ga, Be, Nb) $_{>0.22}$ (Pb, Sb) $_{<-0.3}$ Zn $_{-0.28}$

Factor 3 – 11.5 % (Ba, Cs) $_{>0.8}$ Sn $_{0.72}$ Cd $_{0.54}$ (Be, Ag) $_{>0.4}$ Pb $_{0.31}$ (Mn, Co, Th) $_{>0.22}$ Nb $_{-0.81}$ (Mg, Mo, Ca) $_{<-0.6}$ Sr $_{-0.59}$ Cr $_{-0.41}$ (Sb, V, Na, Fe, Al) $_{<-0.22}$

Factor 4 – 7.6 % Be $_{0.76}$ Mo $_{0.63}$ (Ga, Na, Bi) $_{>0.4}$ (Al, K) $_{>0.3}$ (Mn, Nb, Cd, Tb, Tl, Sm, Gd) $_{>0.22}$ Ca $_{-0.56}$ Ag $_{-0.47}$ (Ba, Sr, Sc, W, Mg, Cs) $_{<-0.3}$ Ni $_{-0.27}$

Factor 5 – 6.0 % (Ag, Ta, Th) $_{>0.4}$ (Nb, Mo) $_{>0.3}$ As $_{0.2}$ (Sn, Mg, Cd, Sr, Na) $_{<-0.4}$ (V, Al) $_{<-0.3}$ (Fe, Ca, Tm, Ba, Tb) $_{<-0.2}$

Factor 6 – 4.2 % (Th, U) $_{>0.4}$ (W, Hf) $_{>0.3}$ K $_{0.29}$ Eu $_{-0.58}$ Sc $_{-0.49}$ (Fe,Mn,Co,V) $_{<-0.3}$ Sr $_{-0.25}$

Out of the six major factors identified through factor analysis, Factor 1 accounts for 44.6% of the total variance in the geochemical composition of the sediments in the Mzymta River basin. This factor illustrates the significant differences between soils formed on igneous and sedimentary rocks, and confirms that the unique characteristics of the soils in the area are primarily related to their geochemistry. Factor 1 reflects the opposing relationship between elements typically found in soils formed on sedimentary rocks, which have positive factor loadings, and elements typically found in soils formed on igneous rocks, which have negative factor loadings. This suggests that the differences in parent rocks account for 44.6% of the total variance in the elemental composition of the alluvial soils in the Mzymta River valley, with the primary distinction being the origin of the elements from either sedimentary or igneous rock classes. The same explanation also applies to the sediments of the river channel, accounting for 64.6% of the total geochemical variance in those sediments [10].

Factor 2 accounted for 16.3 % of the total variance in elemental composition. This factor is associated with rare earth elements and has positive factor loadings for elements such as Ta, Lu, Hf, Ga, Be, Nb, U, and Th, and slightly negative factor loadings for polymetals and antimony. It is noteworthy that rare earth elements were not previously recognized as a factor in the composition of river water or fluvial sediments in the region [10].

Factor 3 contributed 11.5 % to the total variance in the elemental composition of the soils in the Mzymta River watershed. This factor is positively correlated with typical anthropogenic soil contaminants whose origin from local country rocks is unconfirmed, such as Sn, Cd, Ag, Pb, Mn, Co, and Th. On the other hand, it has a negative correlation with local rock-derived elements such as Mg, Ca, Na, Fe, Al. This indicates that the accumulation of these trace elements in soils is not dependent on local country rocks and is likely associated with anthropogenic and technogenic impacts. For river channel sediments, the contribution of this factor to the total variance in elemental composition was 5.5 % [10].

Factor 4 accounted for 7.6 % of the total variance. Elements that are typically found in higher concentrations in clays and clayey shales were positively correlated with this factor [20]. Conversely, elements typically found in a variety of sedimentary and igneous rocks were negatively correlated with this factor. This characteristic factor structure can be interpreted as reflecting the dominant influence of siltstones and mudstones in shaping the geochemical composition of the soils in the Mzymta River watershed.

Factor 5, which accounted for 6.0% of the total variance, may be related to the impact of dispersed gold-silver mineralizations present in the basin, as Ag was found to have a significant correlation with this factor. The overlying distribution pattern of these mineralizations determined the negative correlation between this factor and petrogenic chemical elements.

Factor 6, with a small contribution of 4.2% to the total variance, is positively correlated with elements such as Th, U, W, Hf, and K, typical of granite. Elements negatively correlated with this factor are typical of basalt, reflecting the antagonism between acid and basic rock debris in the geochemical matrix of the river valley. In channel sediments, the contribution of Factor 6 to the total variance is 9.6% [10].

The geochemical parameters identified, such as the percentages of rare earth elements and Ca/Mg ratios, were relatively simple to discern as indicative of the diverse nature of soils formed on different types of parent rock. However, it is anticipated that further and more detailed soil sampling with an emphasis on geochemical barriers in the future will uncover additional geochemical properties of soils formed on contrasting rock types, and thereby contribute to a more comprehensive understanding of the geochemistry of soil formation.

4.3. The Nature of Soil Contamination

A comparison of the elemental composition of alluvial soils in the Mzymta basin with background values revealed that the overall level of soil contamination at all sites was within acceptable limits (less than Zc16, Table A3, last row) and no contrasting geochemical anomalies were detected. The range of excess elements in soils downstream of SS-4 (below the Krasnaya Polyana mountain recreation complex and the new transit infrastructure) did not deviate significantly from the background range (Table 3), with calcium being the most abundant excess element. A similarity in the geochemical composition of the soils in the middle and lower reaches of the Mzymta River was observed in the elevated content of rare earth elements such as La, Ce, Pr, Eu, and Sm. These elements were also found in high concentrations in mudstones, which are the most common rocks in the region [25].

Table 3. Coefficients of concentrations of chemical elements (Cc are given in parentheses) for soils and their rank correlation coefficients (r) for Cc with man-made embankments (r5%crit = 0.28)

Survey sites	Cc<1	r
SS-1	U (1.8) – Lu, Yb (1.7) – Er, Y, Hf, Tm (1.6) – Na, Ho, Zr (1.5) – Dy (1.4) – Ca, Tb, La (1.3) – Pr, Ce, Gd (1.2)	- 0.036
SS-2	Ag (1.8) – Pb, Sb (1.4) – Cs, P, Zn, S (1.2)	0.062
SS-3	As (1.9) – Cu, Hg (1.7) -Mn (1.6) – Cs, Mo, Ni (1.5) – Sb, Tl, Co (1.4) – Rb, Ba, Cr, Bi, K, Nb (1.3) – V, Pb, Al, Fe, Sc (1.2)	0.009
SS-4	Ca (1.8) – Cr (1.6) – Ni, W, Mg (1.3) – Sb, Sr, Zn, Ba (1.2)	0.780
SS-5	Ca (3.0) – Cr, Sr (1.4) – Ni, Ba, La (1.3) – W, Mg, Pr, Ce, Th (1.2)	0.958
SS-6	Ca (1.9) – La, Ni, Ba, Ce, Zr (1.3) – Cr, Pr, Th, Nb, Sr, Ag, Nd, W, Eu (1.2)	0.906
SS-7	Ca (4.0) – Nb (3.1) – Mo (3.0) – Cr (1.7) – Sr (1.6) – Mg, Zr (1.4) – Ni, V, Tl, K, Rb, Al, W, Fe, La (1.2)	0.579

Table 4. Total concentrations of trace elements in fractions of MPC (p) and TPC (o)

Survey sites	V	Mn	Ni	Cu	Zn	As		Cd	Sb	Pb	
	p	p	o	o	o	p	o	p	p	p	o
SS-1	0.62	0.57	0.27	0.10	0.43	2.76	0.55	0.10	0.08	0.49	0.12
SS-2	0.94	1.25	0.74	0.42	0.75	13.89	2.78	0.09	0.45	1.61	0.40
SS-3	1.09	2.21	0.94	0.70	0.68	30.44	6.09	0.08	0.47	1.39	0.34
SS-4	0.98	0.90	0.84	0.38	0.75	12.46	2.49	0.07	0.40	1.08	0.27
SS-5	0.94	0.94	0.86	0.41	0.57	12.28	2.46	0.07	0.31	0.83	0.20
SS-6	0.94	0.96	0.85	0.43	0.67	10.91	2.18	0.09	0.34	0.92	0.23
SS-7	1.09	1.00	0.80	0.42	0.63	9.48	1.90	0.07	0.47	0.77	0.19

The primary cause for the increased influx of REEs into soils of anthropized areas is attributed to the removal of soil and vegetation cover in development sites, as well as the construction of embankments for new transit infrastructure. Despite being constructed from the same material as the soil-forming rocks, this embankment material has undergone heavy crushing and thus has been exposed to significant weathering.

The high Cc values for Ca may be linked to the use of quarried material from carbonate rock zones as fill in construction. The high concentrations of elements such as Cr, Ni, and Fe suggest that the construction rocks utilized did not contain material from ore mineralization zones. The close correlation between the elemental composition of the soils in the anthropized areas with that of the construction rocks lends support to this perspective.

The rank correlation coefficients between the Cc values of alluvial soils and artificial embankments downstream of SS-4 were determined to be between 0.78 and 0.96, with a critical value of 0.271. However, no correlation was identified between the soils and construction rocks above SS-4, as reported in Table 3. Before the Olympic construction, ecologists had already classified the Mzymta estuary and the lower and middle reaches as an area with challenging ecological conditions [10]. Despite this, elevated pollution in the area was primarily observed in the fluvial water, consistently exceeding the maximum permissible concentration (MPC) limits for Fe, Cu, Mn, and Zn by 2-4 times. The concentrations of As, Cd, Pb, and Hg in the valley soils did not exceed the MPC limits at that time.

In this study, exceedances of the MPC and TPC (in parenthesis) limits were observed for As (1.9-6.1), Mn (1.3-2.2), Pb (1.1-1.6) and V (1.1), as reported in Table 4. For As, the MPC limit for near-neutral clay soils (10 mg/kg) was used, as we believed the official MPC limit for this element (2 mg/kg) to be underestimated, given its clarke number of 6 mg/kg [14]. None of the listed elements were found to be present in higher concentrations in the anthropized zone as compared to the background. However, it should be noted that arsenic is known to be the most abundant contaminant in floodplain soils in other regions with similar climates [27].

The Cc values of these elements for all the sites were found to be greater than one as per Table 3. The high contents of V, Mn, As, and Pb may be considered as a natural regional characteristic of the soils.

5. Conclusions

The data obtained in this study enabled us to identify the primary factors influencing the elemental composition of soils in the Mzymta River valley. Our overall conclusion is that the elemental composition of the soils is the result of the combined effects of natural and human-induced forces active in the area. The primary influence is due to natural forces represented by the parent rocks. The effects of human-induced forces were associated with various infrastructure construction projects, such as the highways and railways built for the 2014 Winter Olympics. Although the anthropized embankments, which were devoid of soil and vegetation cover, were constructed from the same material as the soil-forming rocks, the material was heavily crushed and thus exposed to intense weathering.

The examination of rare earth total concentrations and fractionation patterns in soils has been proven to be a reliable means of determining the sedimentary or igneous origin of soil-forming rocks. The Ca/Mg ratio was identified as a diagnostic geochemical feature to differentiate between soils formed over clayey or carbonate rocks. The geochemical parameters identified through the study of soils formed on different types of parent rocks suggest potential avenues for further research. Investigating soils formed at the boundaries between different rock sequences, in order to identify the specific geochemical parameters that arise from contrasts between the soil-forming rocks, appears to be a promising direction in the field of soil geochemistry.

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Appendix

Table A1. Coordinates of extreme survey sites of the geochemical profiles

Number on the map	Latitude	Longitude	Number on the map	Latitude	Longitude
SS-1/1	$43^0 57^I 09.04^{II}$	$40^0 62^I 57.14^{II}$	SS-1/10	$43^0 57^I 23.92^{II}$	$40^0 62^I 50.91^{II}$
SS-2/1	$43^0 60^I 43.25^{II}$	$40^0 49^I 41.48^{II}$	SS-2/10	$43^0 60^I 86.4^{II}$	$40^0 49^I 64.44^{II}$
SS-3/1	$43^0 66^I 02.62^{II}$	$40^0 33^I 98.84^{II}$	SS-3/10	$43^0 6613.86^{II}$	$40^0 34^I 05.63^{II}$
SS-4/1	$43^0 65^I 73.32^{II}$	$40^0 17^I 07.00^{II}$	SS-4/10	$43^0 65^I 87.95^{II}$	$40^0 16^I 92.83^{II}$
SS-5/1	$43^0 61^I 08.4^{II}$	$40^0 05^I 04.24^{II}$	SS-5/10	$43^0 61^I 41.12^{II}$	$40^0 04^I 65.94^{II}$
SS-6/1	$43^0 53^I 20.79^{II}$	$40^0 00^I 02.07^{II}$	SS-6/10	$43^0 53^I 32.03^{II}$	$39^0 99^I 51.49^{II}$
SS-7/1	$43^0 44^I 55.99^{II}$	$39^0 96^I 00.3^{II}$	SS-7/10	$43^0 44^I 90.59^{II}$	$39^0 95^I 52.14^{II}$

Table A2. Chemical properties of soils

Point	pH		Humus	Ca^{2+}	Mg^{2+}	Hydrolytic acidity	Base saturation
	water	KCl	%	cmol(equiv.) kg-1			%
SS-1	5.26	4.46	5.67	11.06	4.23	18.03	45.90
SS-2	5.86	5.16	5.42	10.89	4.32	9.32	61.99
SS-3	6.41	6.01	4.74	17.12	3.49	2.97	87.42
SS-4	7.33	6.96	3.33	18.00	2.87	0.58	97.31
SS-5	6.68	6.30	3.71	16.38	2.95	2.34	89.19
SS-7	7.23	7.12	3.72	13.86	2.84	0.52	96.98

Table A3. Concentrations of chemical elements in alluvial soils of the Mzymta river valley (SS 1 to 7), in man-made embankments, and their clarke numbers in continental soils (C according to [16]) in mg/kg

Element	C	SS-1	SS-2	SS-3	SS-4	SS-5	SS-6	SS-7	Embank-ments	LOD
Li	30.00	12.92 ± 0.26	61.38 ± 1.84	88.96 ± 0.89	61.54 ± 3.08	60.68 ± 2.43	61.59 ± 1.85	64.80 ± 1.94	64.33 ± 2.57	0.01
Be	1.50	2.70 ± 0.05	2.36 ± 0.12	2.83 ± 0.11	2.13 ± 0.04	2.09 ± 0.06	2.15 ± 0.11	2.11 ± 0.04	2.23 ± 0.09	0.03
Na	63000	24400 ± 1200	12000 ± 500	11400 ± 500	13300 ± 700	12100 ± 400	12300 ± 500	16000 ± 200	13000 ± 700	70
Mg	63000	11700 ± 100	11800 ± 100	11500 ± 100	14800 ± 600	14200 ± 100	130 00± 700	16100 ± 300	14700 ± 400	40
Al	71300	66000 ± 1300	92000 ± 3700	102500 ± 3100	89800 ± 900	88100 ± 1800	90100 ± 3600	102600 ± 3100	91100 ± 1800	70
P	8000	1100 ± 10	1700 ± 70	1400 ± 40	900 ± 10	800 ± 20	900 ± 30	900 ± 10	900 ± 10	40
S	8500	700 ± 10	800 ± 40	500 ± 30	700 ± 30	400 ± 10	400 ± 10	400 ± 20	500 ± 10	50
K	13600	13300 ± 100	23000 ± 200	26500 ± 300	22000 ± 1100	21600 ± 200	21900 ± 400	25400 ± 300	22300 ± 700	30
Ca	13700	10400 ± 300	6400 ± 200	6400 ± 100	13600 ± 300	23300 ± 700	14300 ± 600	30500 ± 1200	17400 ± 200	50
Sc	8	11.52 ± 0.35	14.80 ± 0.15	16.26 ± 0.81	15.18 ± 0.15	15.09 ± 0.75	14.97 ± 0.60	14.27 ± 0.57	15.53 ± 0.47	0.1
V	90	93.1 ± 3.72	140.7 ± 5.36	163.5 ± 4.91	147.7 ± 4.43	140.7 ± 2.81	141.6 ± 7.08	163.5 ± 1.64	149.0 ± 2.98	0.7
Cr	60	41.8 ± 1.25	86.9 ± 0.87	100.3 ± 1.00	121.4 ± 6.07	105.5 ± 2.11	94.9 ± 1.90	127.6 ± 3.83	112.6 ± 5.63	0.6
Mn	500	900 ± 1	1900 ± 100	3300 ± 30	1400 ± 10	1400 ± 60	1400 ± 60	1500 ± 60	1500 ± 20	10
Fe	38000	37000 ± 1100	49100 ± 1000	54000 ± 2700	51000 ± 1700	51500 ± 2600	50600 ± 1500	54600 ± 2700	53100 ± 2700	70
Co	9	11.64 ± 0.35	22.17 ± 0.22	27.85 ± 1.39	18.66 ± 0.93	19.58 ± 0.59	19.56 ± 0.59	16.47 ± 0.66	19.65 ± 0.59	0.1
Ni	20	21.44 ± 0.64	58.98 ± 0.59	75.35 ± 3.77	67.05 ± 2.68	68.67 ± 2.75	67.66 ± 2.71	64.13 ± 1.92	69.83 ± 3.49	0.5
Cu	23	13.24 ± 0.40	55.89 ± 1.68	92.25 ± 3.69	50.81 ± 0.51	54.13 ± 2.71	57.34 ± 0.57	56.03 ± 0.56	55.72 ± 0.56	0.7
Zn	60	93.9 ± 0.94	165.1 ± 1.65	150.2 ± 3.00	164.6 ± 1.65	124.4 ± 3.73	147.0 ± 4.41	138.1 ± 4.14	151.1 ± 3.02	0.3
Ga	20	16.88 ± 0.17	18.2 ± 0.73	20.7 ± 0.21	18.0 ± 0.18	18.24 ± 0.18	18.18 ± 0.91	18.23 ± 0.36	19.03 ± 0.57	0.02
As	6	5.51 ± 0.28	27.79 ± 1.39	60.89 ± 1.22	24.91 ± 0.75	24.55 ± 0.74	21.83 ± 0.87	18.97 ± 0.57	24.48 ± 1.22	0.06
Rb	70	55.3 ± 2.77	120.8 ± 4.83	142.4 ± 4.27	119.6 ± 4.78	115.0 ± 5.75	116.9 ± 1.17	127.1 ± 6.36	120.6 ± 3.62	0.08
Sr	220	106.1 ± 3.18	90.2 ± 1.80	114.1 ± 5.71	125.1 ±6.26	139.9 ± 4.20	123.1 ± 2.46	162.9 ± 8.15	133.2 ± 5.33	0.07
Y	25	22.55 ± 0.68	10.23 ± 0.41	9.89 ± 0.20	10.51 ± 0.42	14.21 ± 0.43	14.52 ± 0.29	12.80 ± 0.26	13.34 ± 0.40	0.03
Zr	300	63.62 ± 1.27	40.27 ± 0.40	26.17 ± 0.26	30.76 ± 0.31	47.73 ± 1.91	54.16 ± 2.71	54.16 ± 1.08	45.10 ± 1.35	0.04

Table A3 Continued

Nb	11	10.22 ± 0.51	12.28 ± 0.25	16.27 ± 0.49	10.54 ± 0.21	13.34 ± 0.53	15.47 ± 0.62	39.79 ± 0.80	13.77 ± 0.14	0.05
Mo	2	1.61 ± 0.02	1.92 ± 0.06	3.46 ± 0.14	1.58 ± 0.02	1.47 ± 0.01	1.59 ± 0.06	6.95 ± 0.14	1.62 ± 0.06	0.05
Ag	0.1	0.01 ± 0.0002	0.06 ± 0.003	0.03 ± 0.0003	0.02 ± 0.0008	0.04 ± 0.0008	0.04 ± 0.002	0.01 ± 0.0004	0.04 ± 0.0012	0.05
Cd	0.16	0.19 ± 0.01	0.18 ± 0.004	0.16 ± 0.008	0.14 ± 0.007	0.14 ± 0.001	0.19 ± 0.006	0.14 ± 0.003	0.16 ± 0.008	0.05
Sn	1.1	2.26 ± 0.07	2.76 ± 0.14	1.37 ± 0.03	1.59 ± 0.02	1.68 ± 0.07	1.67 ± 0.05	0.78 ± 0.01	1.71 ± 0.09	0.04
Sb	0.9	0.36 ± 0.02	2.03 ± 0.04	2.11 ± 0.02	1.82 ± 0.02	1.39 ± 0.06	1.54 ± 0.05	2.12 ± 0.06	1.62 ± 0.05	0.05
Cs	3.0	1.94 ± 0.08	9.12 ± 0.18	10.98 ± 0.55	6.01 ± 0.12	5.48 ± 0.11	5.97 ± 0.12	1.97 ± 0.06	5.94 ± 0.18	0.05
Ba	500.0	192.0 ± 3.84	333.7 ± 10.01	415.0 ± 8.30	361.6 ± 10.85	401.8 ± 12.05	400.3 ± 4.00	168.2 ± 5.05	403.4 ± 12.10	0.05
La	40.0	21.59 ± 0.86	13.30 ± 0.13	15.61 ± 0.16	13.69 ± 0.41	21.27 ± 0.64	22.24 ± 0.44	19.67 ± 0.79	20.02 ± 0.40	0.01
Ce	50.0	46.54 ± 1.40	33.07 ± 0.33	39.30 ± 1.97	32.87 ± 0.66	47.21 ± 1.89	49.67 ± 1.49	43.73 ± 0.87	44.98 ± 0.90	0.01
Pr	7.0	5.27 ± 0.16	3.47 ± 0.07	4.25 ± 0.17	3.42 ± 0.03	5.16 ± 0.21	5.34 ± 0.16	4.29 ± 0.21	4.78 ± 0.14	0.007
Nd	33.0	21.44 ± 0.86	15.71 ± 0.16	19.48 ± 0.19	15.39 ± 0.62	21.30 ± 0.85	22.12 ± 0.88	19.77 ± 0.59	20.38 ± 1.02	0.008
Sm	5.0	4.81 ± 0.14	3.98 ± 0.08	4.82 ± 0.14	3.85 ± 0.04	4.76 ± 0.19	4.96 ± 0.05	4.59 ± 0.23	4.71 ± 0.05	0.01
Eu	1.0	0.96 ± 0.01	0.85 ± 0.04	1.05 ± 0.04	0.89 ± 0.04	1.08 ± 0.03	1.09 ± 0.05	1.01 ± 0.04	1.06 ± 0.03	0.007
Gd	4.0	4.24 ± 0.13	3.09 ± 0.06	3.66 ± 0.11	3.04 ± 0.09	3.76 ± 0.15	3.90 ± 0.12	3.55 ± 0.07	3.64 ± 0.04	0.008
Tb	0.70	0.69 ± 0.01	0.43 ± 0.01	0.48 ± 0.01	0.44 ± 0.02	0.52 ± 0.02	0.55 ± 0.02	0.53 ± 0.03	0.52 ± 0.03	0.005
Dy	5.00	4.08 ± 0.20	2.19 ± 0.04	2.34 ± 0.12	2.30 ± 0.02	2.74 ± 0.05	2.91 ± 0.12	2.76 ± 0.06	2.76 ± 0.08	0.012
Ho	0.60	0.79 ± 0.03	0.38 ± 0.02	0.39 ± 0.02	0.41 ± 0.02	0.50 ± 0.02	0.53 ± 0.03	0.48 ± 0.02	0.50 ± 0.02	0.005
Er	2.00	2.38 ± 0.05	1.04 ± 0.04	1.03 ± 0.01	1.09 ± 0.04	1.42 ± 0.04	1.51 ± 0.02	1.32 ± 0.04	1.38 ± 0.07	0.005
Tm	0.40	0.33 ± 0.01	0.15 ± 0.01	0.15 ± 0.002	0.16 ± 0.006	0.20 ± 0.002	0.21 ± 0.006	0.22 ± 0.011	0.20 ± 0.006	0.005
Yb	3.00	2.34 ± 0.09	0.94 ± 0.02	0.86 ± 0.01	0.97 ± 0.01	1.31 ± 0.04	1.43 ± 0.01	1.16 ± 0.01	1.27 ± 0.03	0.005
Lu	0.35	0.33 ± 0.01	0.13 ± 0.003	0.12 ± 0.002	0.13 ± 0.003	0.19 ± 0.002	0.20 ± 0.006	0.17 ± 0.005	0.18 ± 0.005	0.004
Hf	7.0	1.98 ± 0.10	1.06 ± 0.05	0.72 ± 0.04	0.82 ± 0.02	1.22 ± 0.06	1.39 ± 0.06	1.16 ± 0.01	1.19 ± 0.02	0.02
Ta	1.0	0.83 ± 0.02	0.60 ± 0.02	0.79 ± 0.02	0.61 ± 0.02	0.72 ± 0.01	0.73 ± 0.04	0.61 ± 0.01	0.72 ± 0.02	0.01
W	1.0	1.19 ± 0.06	1.38 ± 0.06	1.57 ± 0.05	1.77 ± 0.04	1.70 ± 0.02	1.60 ± 0.02	1.63 ± 0.07	1.72 ± 0.07	0.02

Table A3 Continued

Hg	0.10	0.03 ± 0.001	0.09 ± 0.002	0.15 ± 0.006	0.07 ± 0.004	0.08 ± 0.002	0.07 ± 0.004	0.07 ± 0.004	0.07 ± 0.002	0.01
Tl	0.3	0.24 ± 0.01	0.50 ± 0.03	0.64 ± 0.02	0.48 ± 0.005	0.47 ± 0.005	0.51 ± 0.005	0.56 ± 0.017	0.51 ± 0.015	0.005
Pb	20.0	15.66 ± 0.47	51.45 ± 2.57	44.63 ± 1.34	34.47 ± 0.34	26.40 ± 1.32	29.35 ± 1.47	24.60 ± 0.25	30.98 ± 0.31	0.06
Bi	0.2	0.27 ± 0.003	0.46 ± 0.023	0.55 ± 0.006	0.45 ± 0.005	0.38 ± 0.008	0.39 ± 0.012	0.41 ± 0.016	0.42 ± 0.004	0.010
Th	6.5	6.63 ± 0.07	5.99 ± 0.12	7.44 ± 0.37	6.06 ± 0.24	7.71 ± 0.39	8.12 ± 0.16	6.57 ± 0.07	7.66 ± 0.23	0.009
U	1.5	2.80 ± 0.08	0.91 ± 0.05	0.85 ± 0.01	0.87 ± 0.03	1.19 ± 0.01	1.34 ± 0.04	1.07 ± 0.04	1.19 ± 0.05	0.003
		Zc			**4.43**	**6.45**	**6.06**	**12.45**		

Note. The contents of Rh, Pd, Ag, Te, Re, Ir, Pt, Au were below the detection limit of the method: < 0.01, 0.01, 0.01, 0.2, 0.0009, 0.01, 0.05, 0.05.

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