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Pre-monitoring geochemical research of the river sediments in the area of Ada Tepe gold mining site (Eastern Rhodopes)

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Abstract
The article depicts the geochemical properties of the landscapes in the Ada Tepe gold mine area before its launching. The research is conducted by examining the heavy metals (Cu, Pb, Zn, Co, Cr, Mn and Ni) content in samples of river sediments in the local landscapes. The research aims to analyse the concentration of heavy metals before the launch of gold mining. The study implements the coefficient of Clarke concentration. The deviation from the background concentrations is a ratio between the element concentration in the collected environmental samples and the Clarke value of the element. The coefficient has a scale from 0 to a particular positive value, corresponding to the level of enrichment of the sample in comparison to the background Clarke value. The values corresponding to the Clarke concentration are equal to 1, the lower values are between 0 and 1 (dispersion) and any value higher than 1 is a case of concentration (enrichment). The obtained results display the researched territory as a natural background area. The content of heavy metals in the river sediments of the researched area (mg/kg, median value) by chemical elements is Cu (15), Zn (72), Pb (17), Mn (461), Ni (35), Co (8) and Cr (60). That is the reason it could be defined as not impacted by human activities and it is not influenced by natural geochemical anomalies. Heavy metals do not pollute the researched landscapes before mining. This outcome is obtained by the geochemical content of the investigated heavy metals in the river sediments.

Keywords
Ecogeochemistry, environmental impact, gold mining, landscape assessment, pollution

Introduction

In 2016, the current research was conducted as an environmental pre-monitoring activity in the area of the Ada Tepe gold mining site (Eastern Rhodopes, Bulgaria). The mine itself started exploitation in 2018 after years of delay due to obstructions by local authorities and non-governmental organisations. The non-supporters of the project outlined possible environmental damage, such as contamination of rivers with heavy metals, loss of habitats, air pollution etc., that might be caused by the mine. As a result, the company Dundee Precious Metals Inc. reshaped its initial business plans to satisfy the demands of the local community for better environmental security.

In ancient times, the area of Ada Tepe was a well-known place for its metal deposits. People used to mine gold thousands of years ago. This activity caused local environmental changes such as deforestation, soil erosion and topographical transformations (Popov et al. 2015; Nikov 2017; Nikov et al. 2018). Probably, at that time, people impacted the geochemistry of the area as well.

The study is focused on the concentration of heavy metals (Cu, Pb, Co, Zn, Mn, Ni and Cr) in the river sediments of particular catchments as a geochemical indicator for the environmental status of the territory. The obtained results are a baseline for future monitoring and assessment of contamination with heavy metals and human impact.

Methods

The methodological base of this investigation was the system approach (Perelman 1975; Avesalomova 1987; Kabata-Pendias 2010; Kasimov 2013). We conducted a study through an analysis of the chemical elements'content in the river sediments. The sediments naturally absorb the substances transported by rivers and that is why any anomaly of chemical concentration could be easily detected. This approach allows the tracking of anomalies, either human activities or natural factors.

The chemical elements'content in the various rocks and soils does not match the Clarke value of the element (the average chemical element's content in the lithosphere). That is why the coefficient of Clarke concentration outlines the abundance or the lack of particular elements in rocks, soils and river sediments. It is a quantitative proportion between the chemical element's content in a natural component such as a rock, soil, water, plants and the Clarke value of the element.

In the current study, the deviation from the background concentrations is a ratio between the element concentration in the collected environmental samples of river sediments and the Clarke value of the element. The coefficient has a scale from 0 to a particular positive value, corresponding to the level of enrichment of the sample in comparison to the background Clarke value. The values corresponding to the Clarke concentration are equal to 1, the lower values are between 0 and 1 (a case of dispersion) and any value higher than 1 is a case of concentration (a case of enrichment).

The coefficient allows the implementation of a comparative analysis between particular areas. The current study compares the area of Ada Tepe to technogenic and natural territories in Europe and Bulgaria.

This study analysed 12 samples of river sediments for particular chemical elements (Cu, Pb, Zn, Ni, Co, Cr and Mn). The samples were collected by a standardised methodology. Every sample (500 g, grain size < 0.5 mm) was collected from the upper layer (0–5 cm) of the river-dried thalwegs during the summer when all intermittent rivers in the area dry out. We selected the locations by an analysis of spatial perspective and topographic accessibility. The locations allow interpreting the geochemical influence of the Ada Tepe itself and the influence of the tributaries that confluence the main river in that area.

The collected samples were analysed in the Geochemistry Laboratory of Sofia University. The sediments were dried, quartered, levigated in a porcelain cup, sifted through a 63 μm sieve, burned at 500 °C and dissolved by a mixture of acids ($HClO_4$, HF and HCl). Heavy metals content in the chemical solution was obtained by the method of atomic-absorption spectrometry (Perkin-Elmer 3030).

Results

River sediments are a geochemical indicator for the environmental status within a catchment. In recent years, many scientists have applied the basin approach in evaluating the natural processes and human impact on the environment (Kasimov and Penin 1991; Perelman and Kasimov 1999; Kotsev 2003; Kasimov 2013; Zhelev 2016; Nikolova 2020).

The bedrock, the topography, the vegetation and the climate determine the properties of the river sediments in the area of Ada Tepe. The impact of ancient people is still visible in the features of the landscapes with some rock niches and ancient mining topography changes. The precipitation rates (760 mm per year) directly affect the river sediments'accumulation, transportation and deposition. The precipitations are at a maximum in autumn and winter. They affect the slope of the streams and the formation of sediments in the riverbeds of Krumovitsa and its tributaries. Deforested landscapes in the area enable active bedrock weathering and enforce lateral erosion, a triggering factor for increasing the solid outflow in the rivers. The numerous gullies and ravines in the local topography enable the easy accumulation of sediments alongside the river banks. The local lithology is the primary natural factor that determines the geochemical content of the river sediments. Different types of rocks specifically predetermine the variation in the mechanical and chemical structure of the river sediments.

The results from the investigated locations (Fig. 1) are shown in Table 1. Four elements significantly vary in different locations: Mn, Ni, Cr and Zn. The obtained results allow a comparative spatial analysis between particular locations alongside the river course (absolute values) and the comparison with other areas and norms outside the catchment (median values).

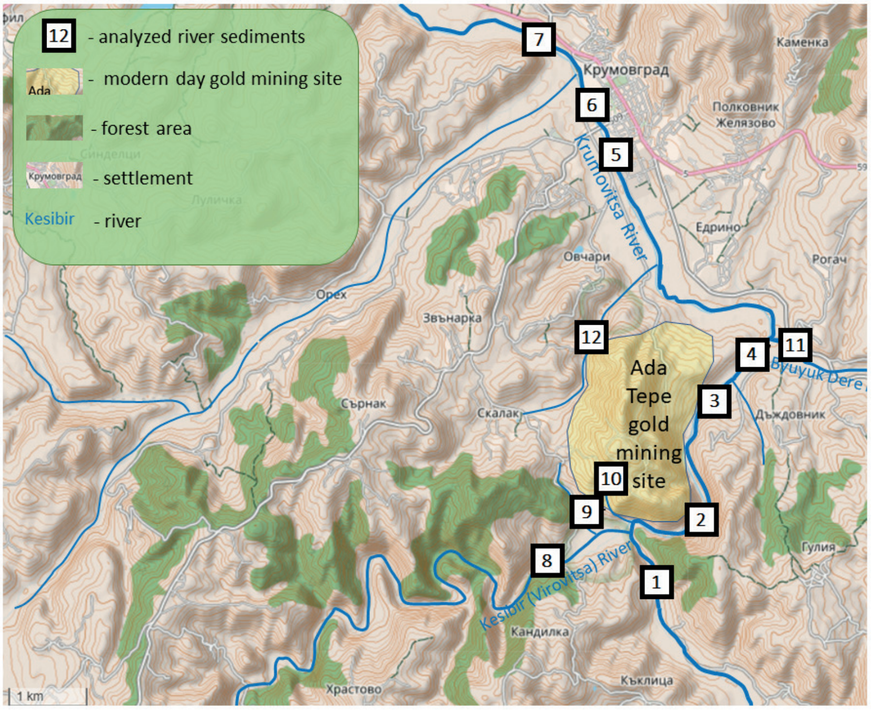

Figure 1. Locations of collecting samples of river sediments around Ada Tepe.

Table 1. Content of heavy metals in river sediments in the Ada Tepe Mining Site area (mg/kg).

No.	Location	Coordinates	Cu	Zn	Pb	Mn	Ni	Co	Cr
1	Krumovitsa River before the confluence of Kesibir River	41°25'18"N, 25°39'21"E	5	61	29	459	4	7	5
2	Krumovitsa River (a large meander south east of Ada Tepe)	41°25'30"N, 25°39'55"E	5	130	19	206	6	5	11
3	Krumovitsa River east of Ada Tepe (before the confluence of Kalach)	41°26'12"N, 25°39'56"E	24	46	10	553	55	16	95
4	Krumovitsa River before the confluence of Byuyuk Dere	41°26'34"N, 25°40'24"E	50	76	13	766	124	25	195
5	Krumovitsa River near the bridge between Ada Tepe and Krumovgrad	41°28'06"N, 25°39'03"E	42	80	10	609	94	21	149
6	Krumovitsa River in Krumovgrad	41°28'21"N, 25°38'54"E	45	68	15	92	53	7	88
7	Krumovitsa River north of Krumovgrad	41°28'47"N, 25°38'30"E	13	43	13	438	40	13	102
8	Kesibir River before the confluence in Krumovitsa River	41°25'14"N, 25°38'50"E	8	147	39	2000	12	4	16
9	A nameless left tributary of Kesibir River	41°25'27"N, 25°38'55"E	28	62	16	89	63	10	89
10	An intermittent stream – a small left tributary to Krumovitsa River	41°25'39"N, 25°39'09"E	6	141	21	250	4	3	7
11	Byuyuk Dere (Golemi Dol) – a right tributary of Krumovitsa River	41°26'39"N, 25°40'44"E	10	54	30	464	30	5	11
12	Kese Dere – a left tributary of Krumovitsa in Ada Tepe	41°26'29"N, 25°38'54"E	18	155	28	490	13	8	31
	Average		21	89	20	535	41	10	67
	Median		15	72	17	461	35	8	60
	Minimum value		5	43	10	89	4	3	5
	Maximum value		50	155	39	2000	124	25	195

Discussion

At first, the content of heavy metals of all sediments in the researched area (median value) is compared to other territories (Europe, Bulgaria), to lithological data (lithosphere, acidic metamorphic rocks in Bulgaria) and to adopted threshold environmental concentrations and predicted environmental concentrations (Table 2).

The data outline the similarities and differences between the Ada Tepe area and the compared references. A geochemical spectrum (Fig. 2) visualises the associations of chemical elements within the river sediments of the Ada Tepe area, Europe, natural background territories in Bulgaria and technogenic areas in Bulgaria. Several peculiarities are visible on the spectrum. Most of the investigated chemical elements are with a lower concentration in comparison to the river sediments of Europe. Only nickel has a higher value than Europe's: 35 mg/kg in the Ada Tepe area compared to 11 mg/kg in Europe. Comparing the research area to the natural background territories in Bulgaria (protected areas with minor human impact) outlines a similar situation. Only nickel has higher concentrations: 35 mg/kg in the Ada Tepe area and 28 mg/kg as a reference for a natural background territory in Bulgaria. The scale of this excess is relatively

Table 2. Comparative data for content of heavy metals (mg/kg) in the river sediments.

Area	Cu	Zn	Pb	Mn	Ni	Co	Cr
Lithosphere (Vinogradov 1962)	47	83	16	1000	58	18	83
River sediments in Europe (Salminen et al. 2005)	22	120	39	1120	11	35	93
River sediments in Bulgaria – natural background territories (Penin 2003)	45	94	25	777	28	17	64
River sediments in Bulgaria – industrial (technogenic) territories (Penin 2003)	217	155	102	972	35	37	74
River sediments in Ada Tepe Area (Median)	15	72	17	461	35	8	60
Soils in Ada Tepe Area (Median)	18	77	19	597	41	10	34
Acidic metamorphic rocks in Bulgaria – predominant in the Ada Tepe Area (Kuykin et al. 2001)	20	50	20	287	10	11	8
Threshold environmental concentrations (TEC) (MacDonald and Ingersoll 2002)	32	121	36	460	23	-	43
Predicted environmental concentrations (PEC) (MacDonald and Ingersoll 2002)	149	459	128	1100	49	-	111

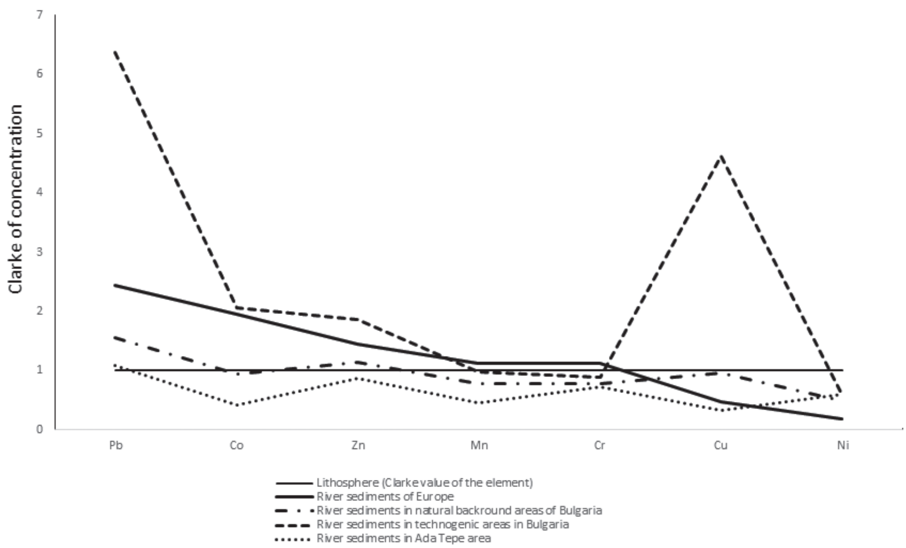

Figure 2. Heavy metals in river sediments in Europe, Bulgaria and Ada Tepe area, based on the Clarke concentration.

tiny and it demonstrates no anomaly. Nickel has coefficient values of Clarke concentration varying between 0.5 and 0.6 in the three comparable territories in Bulgaria. In the rivers of Europe, it is more dispersed and has smaller coefficient values (0.2). The obtained data certify no geochemical anomalies for this territory, either caused by natural factors or human impact. We published results based on investigated plant tissues about geochemical anomalies in the area (Penin and Zhelev 2020), with the same outcomes. The investigated heavy metals did not contaminate the catchments in the Ada Tepe area by 2016.

Another analysis compares the geochemical properties of the local rock formations of acidic metamorphic rocks in the area (Kuykin et al. 2001) and the investigated river sediments. The chemical elements, Zn, Mn and Cr, have higher concentrations in the river sediments than the rocks. The difference is relatively small and it correlates to local geochemical variants within the landscape.

We compared the river sediments of the Krumovitsa River (the main river in the catchment) in different sections of its course to clarify the spatial differentiation of chemical elements in the area (Fig. 3). The spectrum displays an association of chemical elements (Co, Cu, Ni and Cr) from the analysed sample, collected before the Ada Tepe area (Location 1, Fig. 1). Only lead has higher concentration (a Clarke concentration of 1.8) in this sample. The other chemical elements are dispersed in the sediments. Four of them (Co, Cu, Ni and Cr) have significantly lower concentrations than the results of the area where the Krumovitsa River passes near the foothill of Ada Tepe (Location 4, Fig. 1) and the downstream area after the river passes through the town of Krumovgrad (Location 7, Fig. 1). The results outline the local geochemical influence of Ada Tepe's metallogenic rock formations for chemical elements (Co, Cu, Ni and

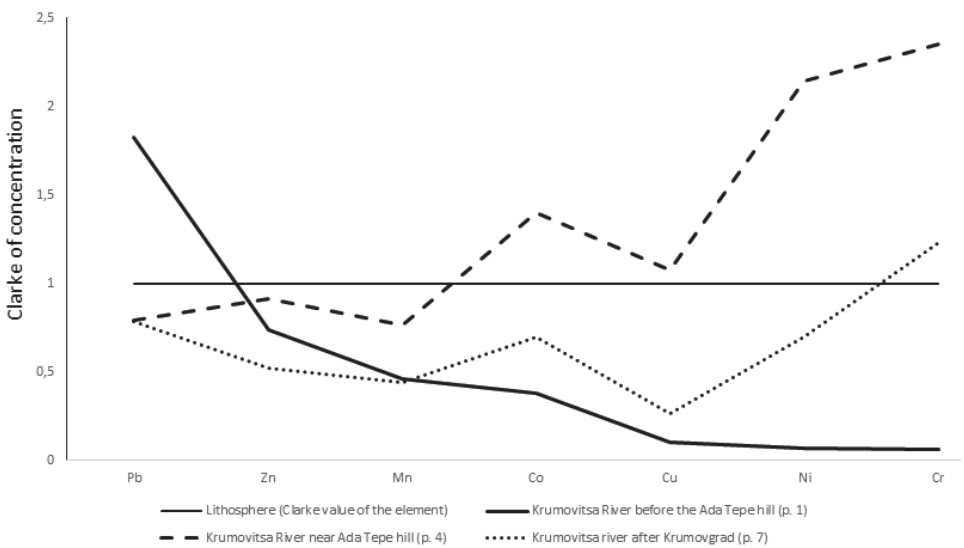

Figure 3. Heavy metals in the sediments of the Krumovitsa River, based on the Clarke concentration.

Cr). Six elements (Zn, Mn, Co, Cu, Ni and Cr) are with lower concentrations in the downstream area after the river passes through the town of Krumovgrad, compared to the area where the Krumovitsa River passes near the foothill of Ada Tepe. This circumstance proves that there is no technogenic geochemical anomaly in the river sediments caused by industrial or urban infrastructure.

Another more detailed analysis of the distribution of heavy metals in the river sediments alongside the Krumovitsa River focuses on seven locations (Fig. 4). The absolute values of chemical content in the sediments vary and there is one more specific sample (Location 4, Fig. 1) where there are increased concentrations of four chemical elements (Cu, Zn, Ni and Cr). This local anomaly is probably naturally determined and reflects the local geochemical influence of the ore-rich hill of Ada Tepe. The influence of Buyuyk Dere (one of the significant tributaries) explains the decrease of concentrations downstream. The values with a lower concentration of chemical elements in the tributary sediments (Location 11, Fig. 1) prove its impact as a natural disperser.

There are no legally adopted norms for recommended environmental concentrations in the river sediments of metals and metalloids in the European Union, although there are such norms in the United States of America. The Environmental Protection Agency (US EPA) institutionalises them. The norms adopted by the US EPA consider two levels of quality for the river sediments (MacDonald and Ingersoll 2002). The first is the threshold environmental concentration (TEC) and the second is the predicted environmental concentration (PEC). The threshold environmental concentration highlights the acceptable levels of metals and metalloids, while the predicted environmental concentration raises awareness for possible negative effects on the wildlife in the ecosystems where the river sediments are. There is a similar approach in

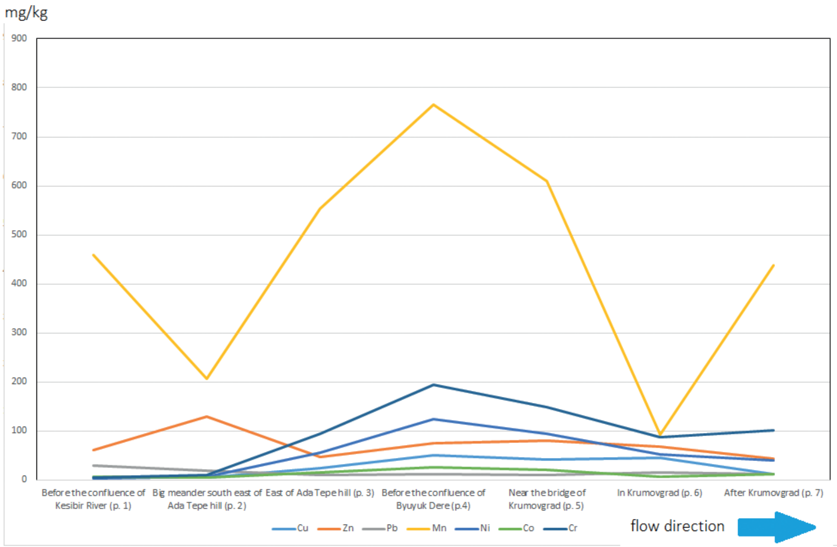

Figure 4. Quantity of microelements in the river sediments of the Krumovitsa River.

the Canadian Province of Ontario, where manganese and iron are chemical elements used for monitoring (Guidelines for Identifying, Assessing and Managing Contaminated Sediments in Ontario: An Integrated Approach 2008). Table 2 applies the norms for Mn from Ontario, Canada. The concentration of cobalt in river sediments does not have a standard value neither in the USA nor in Canada. Similar studies use the application of threshold environmental concentration and predicted environmental concentrations as a reference for a comparative analysis (Cholakova and Penin 2016). The obtained results from the Ada Tepe area are analysed under the perspective of threshold and predicted environmental concentrations for metals and metalloids. The results show that five of the investigated chemical elements (Cu, Zn, Mn, Co and Pb) do not exceed the threshold environmental concentrations. Nickel (35 mg/kg) and chromium (60 mg/kg) exceed the threshold environmental concentrations (23 mg/kg for Ni; 43 mg/kg for Cr). None of the investigated chemical elements exceeds the predicted environmental concentration.

Conclusion

The performed study highlights the environmental status of the Ada Tepe area before the start of the mining activity. There was no contamination with heavy metals of the investigated river sediments in the Krumovitsa River catchment up to 2016. The geochemical properties of the seven examined chemical elements (Cu, Zn, Pb, Mn, Cr, Co and Ni) within the local landscapes resemble a natural background territory with no traces for human impact. Local lithological specifics, but not anthropogenic activity, determine the geochemical properties of the river sediments in the catchment.

The study is a baseline for future research on the mining impact on landscapes and ecosystems. An extension of the list of investigated chemical elements is recommended to encompass the geochemical picture of the area. The effect of the ongoing mining activity in Ada Tepe must be a subject of regular independent environmental monitoring.

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