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ECO-MONITORING OF GEORGIA'S CONTAMINATED SOIL AND WATER WITH HEAVY METALS

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Abstract: Mining and related industrial activities facilitate development and modernization in many countries but have also resulted in serious ecological impacts. This research focuses on environmental monitoring of major gold, copper and manganese mining regions in the country of Georgia. Mineral extraction processes have caused several environmental problems, including metal contamination in nearby agricultural areas. The study is located at a major confluence of the Mashavera (Bolnisi district) and Kvirila Rivers in the Chiatura and Zestaponi districts in Georgia, respectively. In the Bolnisi region the existing mineral deposits are sulfide ores. Open-pit mining results in deposition of metal-loaded dust up to 25 km away. Ore extraction is conducted via controlled explosions that cause the discharge of metal-containing dust, which ultimately is deposited on the soil via wet and dry processes. Monitoring commenced in 2010 and this is the first study of environmental impacts in this region. Soil samples from ten villages in the area, water samples from the Mashavera River and tributaries were collected and analyzed. Additional samples were collected in 2012, 2013, and 2014. The results show that soil and water samples have elevated levels of Cd, Zn and Cu, which vary depending on the geographic proximity of the samples to the primary mining activities. The Mashavera River also has elevated levels of metals, likely due to mining waste. River water is heavily used for irrigation and thus further impacts on the population in the region through consumption of agricultural food products.

Key words: eco-monitoring, water and soil, heavy metals, contamination, Georgia.

1. INTRODUCTION

Modernization of the contemporary world, global development, extraction of valuable minerals and ruthless treatment of the environment by the humans caused a number of ecological problems in many countries, including Georgia (Hanauer et al., 2011; Noble et al., 2010; Imperatoa et al., 2003). Intensive extraction of valuable minerals pollutes the environment to such a degree that the food products grown on soils in many cases are very harmful to human health (Mtunzi1 et al., 2015; Mwegoha et al., 2010). The most dangerous chemical pollutants are the heavy metals and radionuclides (Palapaa In references list Palapaa & Maramisa et al., 2015; Hong et al., 2007; Galan et al., 2003).

Kazreti RMG (the former "Madneuli") Gold and Copper deposit, located in Bolnisi region in south east part of Georgia, on the right bank of Mashavera river is the most important of the existing ores (Avkopashvili et al., 2015). Base metals and copper sulfide ore deposit has been extracted with open-cast method causing intensive environmental pollution with respect to toxic metals (Kavtaradze et al., 2012).

Unfortunately, Bolnisi region is not the only one polluted area in the country; there are a number of other contaminated lands in Georgia, among which: Chiatura region, where manganese extraction is produced; Zestafoni region, where due to manganese ferroalloy production the Kvirila river and the soils of Zestafoni and Chiatura regions are very polluted (Matchavariani et al., 2012, 2014). Local population in the above-mentioned regions is involved in agriculture (crops are grown and used for human consumption) and they raise livestock. Most of the inhabitants can't even imagine how dangerous heavy metals and radionuclides are for their health (Henningsen et al., 2010, 2007).

Soil and water pollution by heavy metals is an important global problem (Mantaa et al., 2002; Rodrıguez et al., 2009). Polluted soils are dangerous for human health, heavily impact ecosystem, and require a variety of cleaning operations (Suciu et al., 2008). When compare with water and air, the environmental pollution by different toxic metals mostly affect soils. This is because water and air have the ability to recover themselves, but soil needs sometimes several centuries to self-remediate (Jimeneza et al., 2009; Zornoza et al., 2012; Cos et al., 2006).

Mining activities are among the most important contributor to soil contamination by heavy metals. Therefore, all companies have to be very careful with this problem, because soil clean-up requires large amount of money and it is also time consuming (Kalandaze et al., 2009; Khasitashvili et al., 2015).

2. STUDY AREA & METHODS

Our research aim is to examine both historical and current areas that are impacted by heavy metal contamination resulting from mining and related industrial activities. The study areas are located in the central west and south east part of the country of Georgia (Fig. 1).

2.1. South east Georgia

Historical mining of gold in east Georgia has been documented more than five thousand years ago (Stöllner In refernces list is Stöllner & Gambashidze et al., 2011). Current mining activities in this region include Madneuli gold and copper mine and processing facility that has operated since 1975. In 2009 the Sakdrisi gold mine has opened. This site is located in the Bolnisi district, in particular, in the borough of Kazreti, which is located approximately 80 km southwest of Tbilisi, on the bank of Mashavera and Kazretula rivers. Copper content is rich in sulfide and mined as open quarry pit. This is a very important source of metals pollution in the environment.

Soil samples were collected from ten villages in this region, located at different distance from the gold mine. The villages of Dmanisi (N1) and Gantiadi (N2), act as controllers since they have significantly less contamination. The other eight village sites showing contamination are: Sakdrisi (N3), Balichi (N4), Kazreti (N5), Qveshi (N6), Ratevani (N7), Mtskneti (N8), Naxiduri (N9), and Tsugrugasheni (N10). Table 1 shows the distance between the ten souths east Georgia villages from the active gold and copper mine (See fig. 1)

Water samples were collected near the gold and copper mines from both Mashavera and Kazretula rivers. Water samples were taken at eight sites, three from the Kazretula River and five from Mashavera River. N1 sample was used as a control and it was collected from Mashavera river ~500 m upstream the confluence with Kazretula river. Samples N6 and N7 come from Kazretula River. N 6 ~0.3 km upstream the confluence with the Dam water, N7~0.3 km downstream of the confluence of Dam water and Kazretula River. Sample N2 Dam water from the waste water reservoir ~0.3 km above the confluence between the Kazretula River and waste water reservoir.

N3 samples is 0.3 km downstream of the confluence of the Mashavera and Kazretula rivers. N4, N8 and N5 samples is of the villages Ratevani, Mtskneti and Naxiduri irrigation water from Mashavera river~17 km, 25 km and 29 km downstream of the confluence of Mashavera and Kazretula rivers. Figure 2 shows the water samples collected from Mashavera and Kazretula rivers.

Figure 1. The study sites (red dots) on the map of Georgia

Table 1. Soil samples location area and their linear and transport distance from the factory, south east Georgia

Villages Name		Distance from Mine Sakdrisi, (km)		Distance from Mine Madneuli, (km)	
		Linear distance	Transport distance	Linear distance	Transport distance
1	Dmanisi	15	19	20	27
2	Gantiadi	10.5	15.5	16	22.5
3	Sakdrisi	0.2	0.3	6	8
4	Balichi	0.8	1.5	3.8	6
5	Kazreti	2.5	4.5	3	3.4
6	Qveshi	8	9	7	10
7	Ratevani	13	15	12	17
8	Mtskneti	24	27	18	23
9	Naxiduri	28	31	22.5	28
10	Tsugrugasheni	13	30	5	33

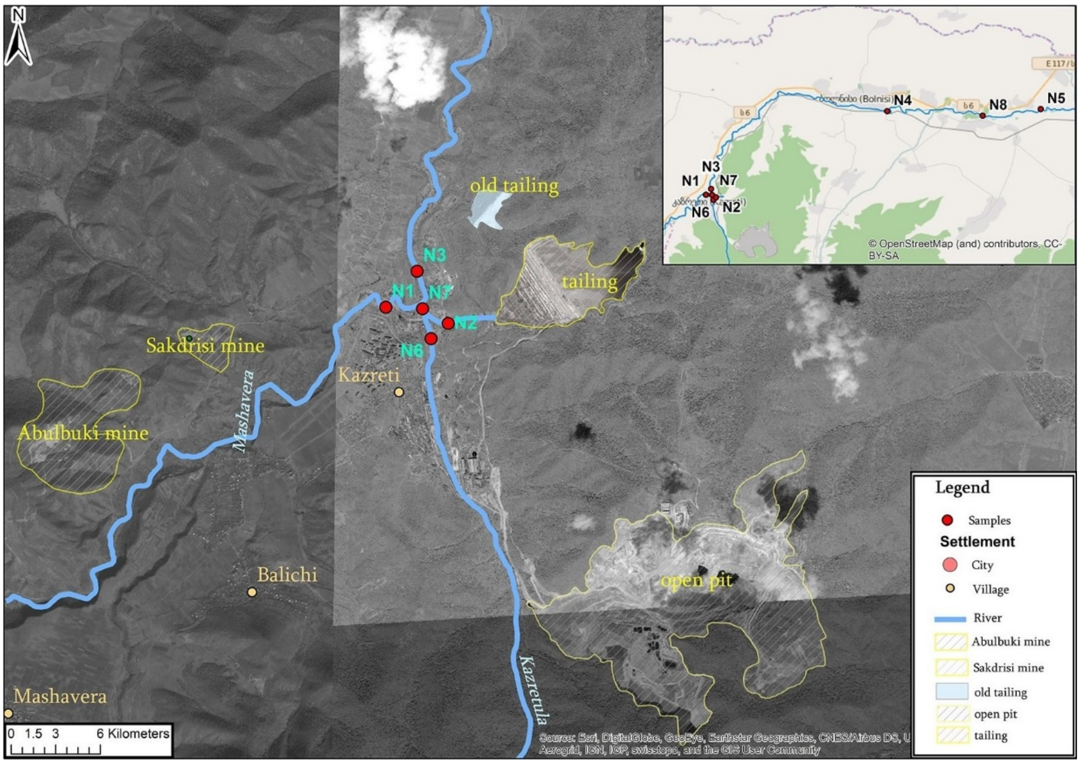


Figure 2. Location of water samples from Mashavera and Kazretula rivers

2.2. Central west Georgia

The manganese mine operations started in 1879. The manganese deposit is located near the Kvirila Valley in the city of Chiatura. There are numerous underground mine shafts and open-pit mines. The current manganese ferro-alloy factory which receives manganese-enriched ore from Chiatura region is in the Zestafoni region. The Kvirila river flows to the Zestafoni region and eventually discharges in the Black Sea (Fig. 6).

There are six villages in the study area; three are in the Chiatura region, where as the other three are in the Zestafoni region. Soil samples were collected at all these six sites. The Chiatura region samples are N11 taken in the Beretisa village. N12 is from the village of Shukruti and N13 was collected in the village of Merevi. In the Zestafoni region, samples N15, N16, and N17 were taken from the villages Saqara, Sviri and the city of Zestaponi. Table 2 shows the distance between the six villages of west Georgia from the active manganese mine and the manganese ferro-alloy factory.

2.3. Soil sampling

Each sample represents a surface soil aliquot taken at 0-5 cm from the surface and a deeper sample from 30-35 cm. Soil samples were taken with scoop samplers, which were washed between each sampling collection. The study area was divided in regular grids of 1000 x 1000 m, where sample was collected at five point, mechanically mixed and a composite sample was prepared.

Table 2. Soil samples location area and their linear and transport distance from the factory, central west Georgia

Villages Name		Distance from manganese mine (km)		Distance from manganese ferro-alloy factory (km)	
		Linear distance	Transport distance	Linear distance	Transport distance
11	Beretisa	25	30	32	55
12	Shukruti	3	5	30	38
13	Merevi	7	10	28	43
14	Saqara	26	30	4	5
15	Sviri	34	42	9	11
16	Zestaponi	29	34	0.3	0.5

The composite soil sample was transferred into a polyethylene bag, labelled, and transported into the laboratory.

The soil samples were oven dried at 105°C for 24 h, followed by grinding and sieving using a 0.18 mm sieve. In order to determine the concentrations of metals, 5 ml of 65% HNO_3 (trace metal grade) were added to 1.000 g of soil in a 50 ml volumetric flask. The flask was heated in a water bath ($100^{\circ}C$) for 2 hours, after cooled down at room temperature for 15 minutes and then filtering with a Whatman 0.45 µm paper filter in to a 50 ml volumetric flask, the volume was made up to 50 ml with distilled water. These solutions were analyzed for Cd, Cu, and Zn by Atomic Absorption Spectrophotometers (AAS) in 2010, 2012, 2013. In 2014, solutions were analyzed for heavy metals by ICP-MS in the University of Georgia Laboratory for Environmental Analysis, GA, USA.

2.4. Water sampling

Water samples were collected in 1000 ml (HDPE) plastic bottles, which were washed and rinsed 3 times with distilled water prior of using them. Preservation of water samples was done by adding 2 drops of concentrated HNO_3 *(trace metal grade)* to each sample. Each bottle was labeled according to the sampling location and time. The samples were then put in an insulated box and taken to the laboratory for further processing. Water samples were filtered with Whatman 0.45 µm filter paper in a Buchner funnel and heated at $100^{\circ}C$ until the volume was reduced to 50 ml, in a normal volumetric flask 100 ml. The volume was made up to 100ml with acidified water (3 ml concentrated HNO_3 + 1 L distilled water). Samples were analyzed by AAS in the chemistry laboratory of the Tbilisi State University, country of Georgia.

3. RESULTS

The aim of our research was to monitor the contaminated soil and river water in certain areas of central west and south east Georgia. Processing of data obtained from chemical survey and with using GIS systems create the maps showing the contaminated areas of south east and central west Georgia. According to the map (Fig. 3), we can see the contaminated areas of the south east Georgia.

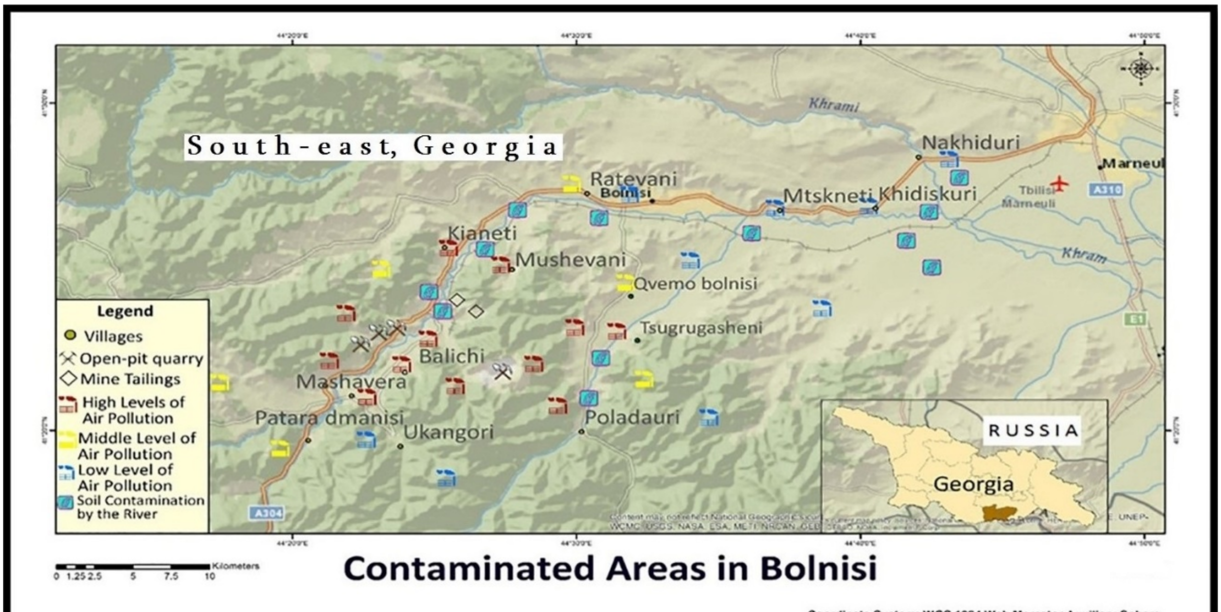


Figure 3. Contaminated area in Bolnisi region, south east Georgia

The map clearly shows the areas of the atmospheric air and river water contaminated soils. According to our research, in the villages near the mining area, contamination by heavy metals is quite higher, by the reason of using the river for irrigation, which contains heavy metals (Table 3, 4).

The given data clearly shows that the Kazretula River is highly polluted with waste water from the factory which contains large amounts of heavy metals, such as cadmium and zinc. Industrial waste water have low pH, ranging between 2 and 3.

Our research results show that the water in the dam (which undergoes cleaning by cementation method) is not fully free of heavy metals.

We also studied in the study region, the pollution caused by irrigation water. Water samples were taken in the villages Ratevani, Naxiduri, and Mtskneti. The study results showed that in the samples of heavy metals (Cu, Zn, Cd) concentration exceeds the environmental limit. However, it should be noted that in this case the samples were taken just one time. River water and industrial waste waters were monitored during 2010-2011 and according to this data, we can conclude that the mining companies pose a great impact to the hydrographic system and soils in this region. The concentration of pollutants is not always same in the river, because of the volume of waste water is always different. Therefore, this process is uncontrollable and it is difficult to determine the connection of correlation. This process is also characterized by seasonality (in the spring and autumn period a large volume of water flows into the Kazretula river) and it is impossible to accurately calculate the flow of water, because during the rainy season a resulting of washing down with rain and snow water of the slopes and contaminated water mix in the Mashavera and Kazertula rivers.

Also, we have opportunity to discuss the soil monitoring data. Bolnisi Villages soil monitoring was conducted in 2010 (Table 5, 6, and 7). If we discuss according to the date of 2010 we will see that in all three villages the pollution exceed the maximum allowable concentration. In the Ratevani Village, copper content is higher than the admissible limit with an average of 1300%, zinc 979% and cadmium 3760%.

Table 3. Heavy metals content in the waste water and Mashavera and Kazretula rivers (2010)

Number of samples and name		Cu, mg/l	Zn, mg/l	Cd, mg/l	Fe, mg/l
Georgian environmental limit		1.0	1.0	0.001	0.3
N1	Mashavera river 0.5 km upstream the confluence with the Kazretula river	0.01	0.04	0.004	0.12
N6	Kazretula river 0.3 km upstream the confluence with the Dam water	1.4	510.2	13.2	1.1
N2	Dam water 0.3 km above the confluence between the Kazretula river and waste water reservoir	1.6	3.5	0.2	17.3
N7	Kazretula river 0.3 km downstream of the confluence of Dam water and Kazretula river	1.1	324.4	9.8	9.0
N4	Mashavera river 17 km downstream of the confluence of Mashavera and Kazretula rivers	1.6	26.6	0.3	18.2
N8	Mashavera river 25 km downstream of the confluence of Mashavera and Kazretula rivers	0.3	1.7	0.05	0.6
N5	Mashavera river 29 km downstream of the confluence of Mashavera and Kazretula rivers	0.04	0.2	0.01	0.4

Table 4. Heavy metals content in the waste water and Mashavera and Kazretula rivers (2011)

Rivers name and location area	Cu mg/l	Zn mg/l	Cd mg/l
Contaminated waste water	537.3	5010.0	23.65
Cleaned waste water	165.3	4460.8	2.0
Kazretula river 0.3 km downstream of the confluence of Dam water and Kazretula river	1.04	15.18	1.49
Mashavera river 0.5 km upstream the confluence with the Kazretula river	0.006	0.19	0.11
Mashavera river 0.5 km downstream of the confluence of Mashavera and Kazretula rivers	0.65	6.54	0.47

Table 5. The heavy metals content of soil in Ratevani Village (2010)

Sample	pH	date	Cu mg/kg	Zn mg/kg	Cd mg/kg
Maximum admissible limit			132	220	2
Soil depth 0-5 cm	7.85	19.07.10	1840	5610.0	121.5
Soil depth 30-35 cm	7.81	19.07.10	806.0	224.7	12.1
Soil depth 0-5 cm	7.90	19.10.10	511.3	5420.0	68.7
Soil depth 30-35 cm	7.81	19.10.10	2050.0	499.0	100.3

Table 6. The heavy metals content of soil in Naxiduri Village (2010)

Sample	pH	Date	Cu mg/kg	Zn mg/kg	Cd mg/kg
Soil depth 0-5 cm	5.46	19.05.10	231.8	3770.0	34.6
Soil depth 30-35 cm	6.00	19.05.10	285.4	404.0	41.5
Soil depth 0-5 cm	5.29	19.10.10	46.3	165.9	-
Soil depth 30-35 cm	6.40	19.10.10	72.0	217.0	-

Table 7. The heavy metals content of soil in Balichi Village (2010)

Sample	pH	Date	Cu mg/kg	Zn mg/kg	Cd mg/kg
Soil depth 0-5 cm	6.29	19.05.10	970	159.1	43.8
Soil depth 30-35 cm	7.23	19.05.10	49.5	140.3	20.0

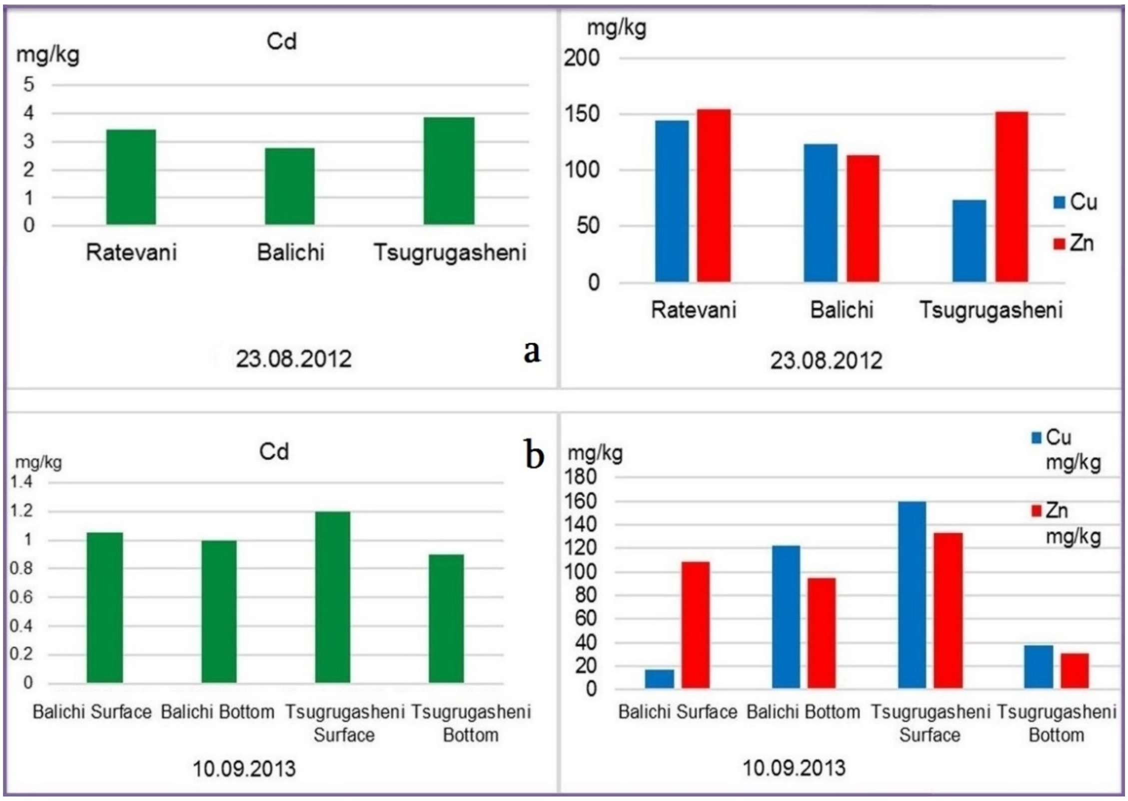


Figure 4. a). The Cd, Cu and Zn content of soil in Ratevani, Balichi and Tsugrugasheni Villages (average data of surface and bottom, 2012), b). The Cd, Cu and Zn content of soil in Ratevani, Balichi, and Tsugrugasheni Villages (2013)

In the Naxiduri Village copper increased with 143 %, zinc 379% and cadmium 1875%. In Balichi, only cadmium concentration is increased with 1575%. In these villages the great pollution is caused by the fact that agricultural soils are extensively irrigated with highly polluted water from Mashavera river.

Due to the fact that population of the Balichi Village uses clean river water for irrigation, we assume soil pollution was not caused by the river. Thus, industrial dust, which is absorbed in the soil, causes soil contamination in this village.

In 2012-2013 we conducted a contamination soils monitoring program in the three villages of Bolnisi region. Researches studies were carried out in summer and autumn (Fig. 4). According to the 2012-2013 dataset collected in these villages, Cd exceed the maximum permissible concentration, but compared to 2010, it was significantly lower. As for copper and zinc, their content does not exceed the limit value.

At the end of 2014, the enterprise resumed its intensive activity and furthermore, they even launched a new open-pit mine (Sakdrisi), which caused many environmental problems to emerge. The concentration of heavy metals increased due to the intensive mining processes (Fig. 5). The plot in figure 5 illustrates the heavy metals distribution in soils of some villages. The data reveals that in Sakdrisi, Ratevani, Mtskneti, and Naxiduri villages, soils are contaminated with such elements as Cd, As, Pb, Zn, Cu, Sr, and Ni.

In 2014, we collected samples and monitored 7 villages of 3 municipalities from central west part of Georgia. It is worth noting that this was the first full monitoring of heavy metals distribution in soil in the above mentioned area (Fig. 6).

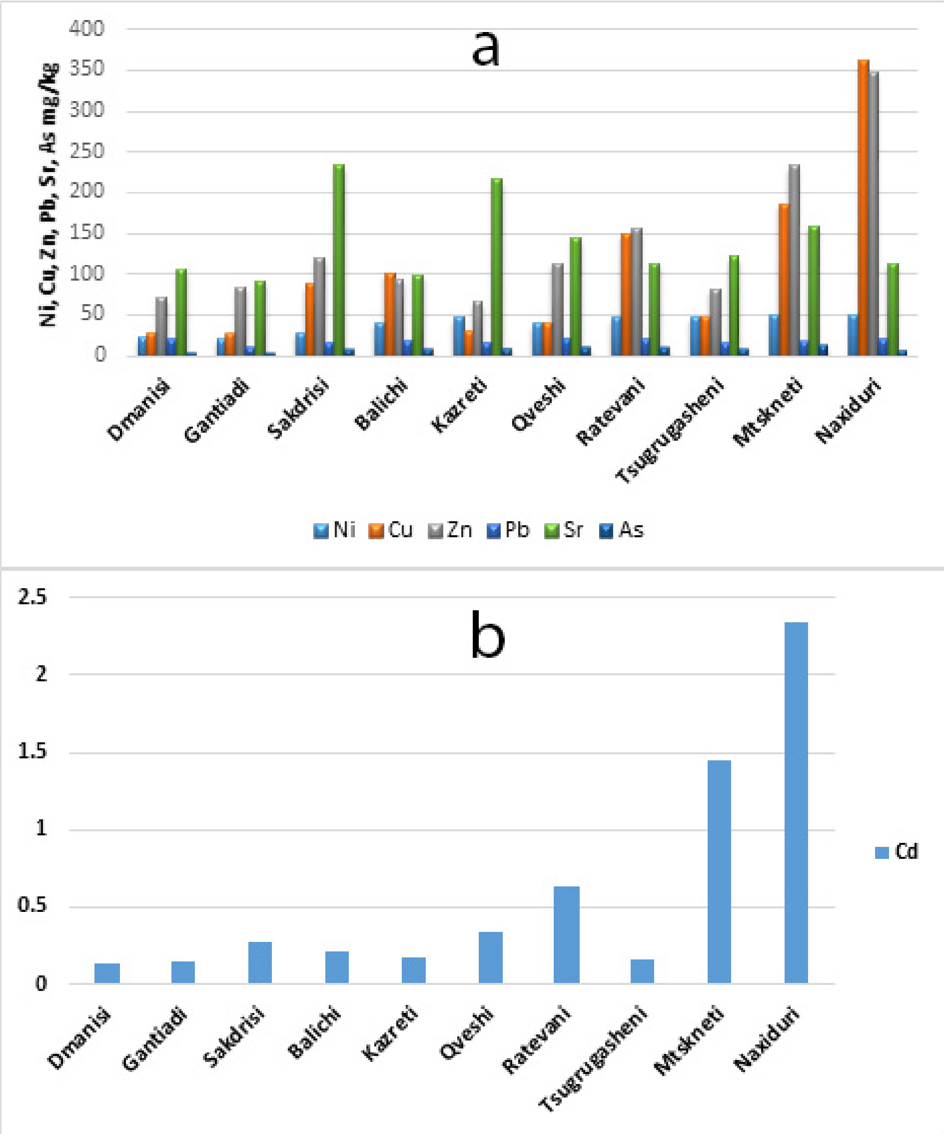


Figure 5. a) Ni, Cu, Zn, Pb, Sr, As metals content in villages from the Bolnisi region, b) Cd content in villages from the Bolnisi region (2014)

Our results clearly indicate that in villages of Chiatura municipality, contamination by heavy metals is accomplished via atmospheric processes. This is because manganese processing does not take place in closed Manufacturing. There are also many small open-pit quarries which do not follow any environmental regulations for processing the ore. In this area, east wind blows most of the year and the mining dust spread long distances (Figs. 7, 8).

In Shukhruti, soil contamination is less, although the factory is located 3 km from the village. Our research documents that the further the distance is between the village and the polluting industry center, heavy metals concentration is increasing in proportion in the soil there. The villages in the Chiatura region (Shukruti, Merevi, and Beretisa) have a high content of Mg, As, Pb, Sr, and Ni (Figs. 7, 8).

In Chiatura, open-pit mines and ore extraction shafts are situated on the bank of Kvirila river, as the company uses its water for washing the ore; consequently, the river is very polluted by heavy metals. The water of Kvirila river is used intensively for irrigation purposes over the agricultural fields.

Manganese factory uses very old devices for processing the ore, fact that promotes harmful gases and dust containing ore released into the atmosphere. Industrial dust accumulates in the soils of the surrounding villages and causes soil pollution by heavy metals. In the village Kveda Sakara and Sviri soil pollution originates from both atmosphere and Kvirila river water, which is used for irrigation.

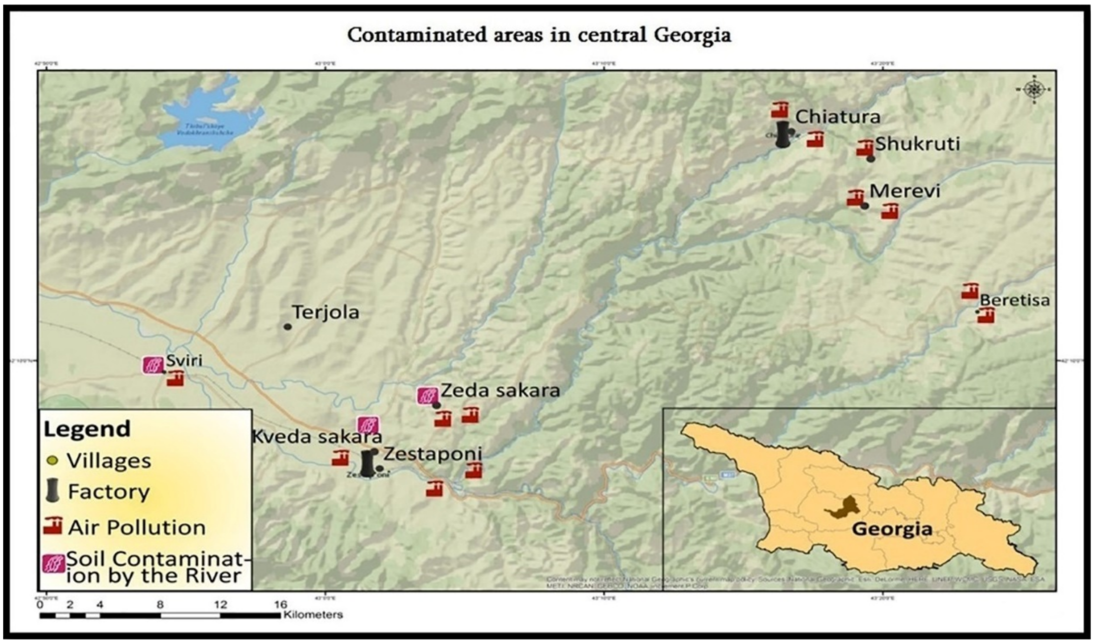


Figure 6. Contaminated areas in Chiatura and Zestaponi regions, central Georgia

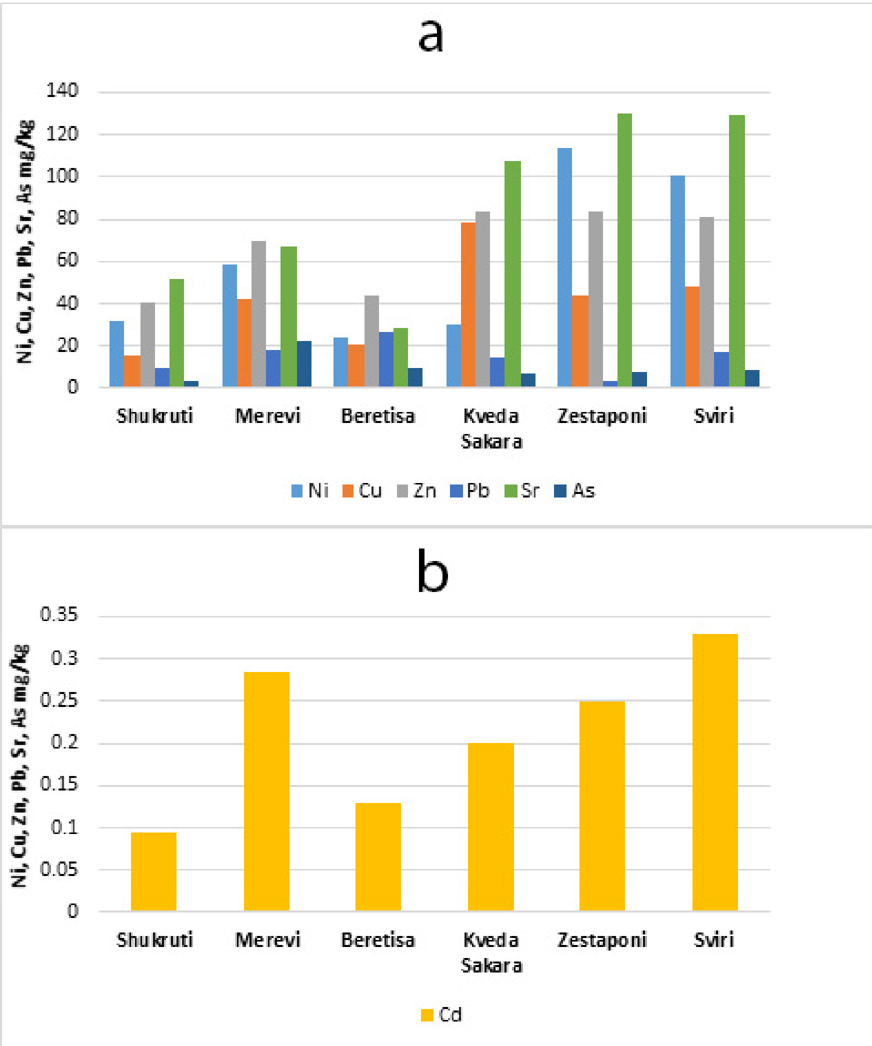
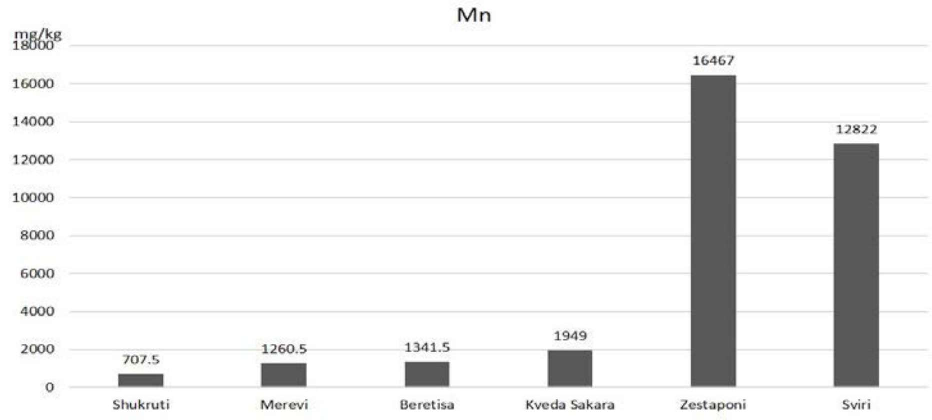


Figure 7. a) Ni, Cu, Zn, Pb, Sr, As metals content in villages from the Bolnisi region, b) Cd content of soil in the Chiatura and Zestaponi regions villages



(2014)

Figure 8. The manganese content of soil in the Chiatura and Zestaponi regions villages (2014)

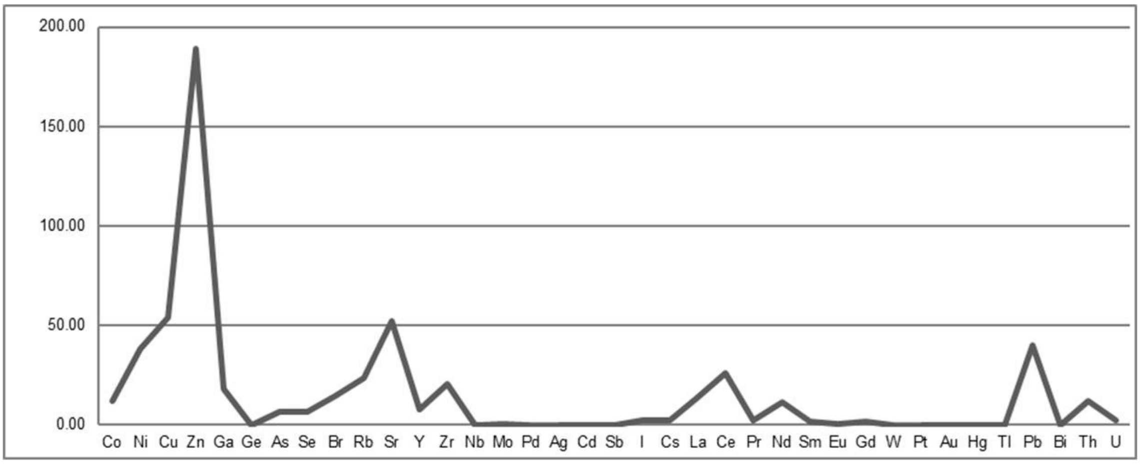


Figure 9. Soil spectrum of heavy metals in Anaseuli Village. Note the high levels of Zn, Sr, Pb, and Cs

Monitoring the soil irrigated with water from Kvirila river, revealed that the soil in the villages of Kveda Sakara, Zestaponi, and Sviri is rich in Mg, Pb, Zn, Cu, and As. People intensively use this soil for the agriculture, which has bad impact on their health and on the living habitats.

We also measured heavy metals contentment in the soil of Anaseuli, situated in Ozurgeti municipality of west Georgia (Fig. 9). The most important problem is that the population of this village does not know anything about the pollution existing there, so they use the soil for the agricultural purposes.

4. CONCLUSION

Our research evidence that, in Bolnisi district (South east Georgia), environmental pollution is caused by gold and copper mining. Uncontrolled industrial waste water discharging into the Kazretula river leads to the death of living organisms. Likewise, Mashavera river is very contaminated with heavy metals, but ~60% of the population in this region uses its water for agriculture.

Our research documented that in 2010, the heavy metals (Cu, Zn, Cd) contained in soils was higher than in the previous years. In 2012-2013 heavy metals content in soils decreased significantly. This is because during this period the company has temporarily reduced the active production of the ore. Consequently, the heavy metals moved deeper in the soil (below 30 cm) and thus, lower concentration was measured in our samples.

Through our monitoring, conducted in the central west of Georgia, it can be concluded that mining, ore processing and extraction is impact the environment very harmful in Zestaphoni and Chiatura districts.

Industrial air particulate is spreads by wind over large surfaces, then absorbed by the topsoil and may move deeper in the soil or is even mixed sometimes with the groundwater.

It should be noted that in the village Anaseuli (west Georgia), Strontium and Cesium content is quite high, which is cause by the old radiation devices, which are buried in the soil without any norms.

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