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Soil Science

Soil Contamination with Heavy Metals in Imereti Region (Georgia)

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ABSTRACT. Soil contamination with heavy metals – Cd, Cu, Mn, Ni, Pb and Zn was studied in the main soil types of Imerti region. An attention was paid to diffusion pollution and metal distribution along the river valleys representing the major flow paths for transporting different pollutants including heavy metals. The results of the laboratory analyses were compared to maximum permissible concentrations and guide values defined by Georgian legislation. An attempt was made to establish background concentration for heavy metals in studied soils and to use them as reference values in assessment of soil pollution. The comparison shows that the concentrations of Cd, Cu, Mn, Ni, Pb and Zn exceed their background contents in some soil samples. *© 2007 Bull. Georg. Natl. Acad. Sci.*

Key words: *soil contamination, heavy metals, maximum permissible concentration, background content.*

Heavy metals continue to receive increasing attention due to the better understanding of their toxicological relevance in ecosystems and human health [1]. Pollution of soils belongs to the most important ecological problems today [2]. Anthropogenic emission of heavy metal ions in the environment during the last century has led to increasing accumulation of metal ions in soils and natural waters in both urban and rural areas. Accumulation of some heavy metal ions in soils indicates their relative immobility in the environment and that geochemical dispersion is not efficient [3].

With the increasing demand for metals in industries and rapid urbanisation in many parts of the world, contamination by metals in the terrestrial environment has become widespread in a global context. Increasing metal pollution has severely disturbed the natural geochemical cycling of the ecosystem. Heavy metals from vehicular emissions, incinerators, industrial waste, the atmospheric deposition of dust and aerosols, and other activities have continuously added to the pool of contaminants in the environment [4].

Soil degradation by chemicals has become a major concern because of the soil’s finite capacity to act as a sink for pollutants. Due to the soil’s limited resilience with regard to binding and containing chemicals, these substances can accumulate in soils and become mobile and bioavailable to plants, animals and humans [5]. Past studies have revealed that human exposure to high concentrations of heavy metals will lead to their accumulation in the fatty tissues of the human body and affect the central nervous system, or the heavy metals may be deposited in the circulatory system and disrupt the normal functioning of the internal organs [4].

There are different sources of heavy metals in the environment. These sources can be both of natural or anthropogenic origin [6]. They occur naturally in rocks and soils, but mainly in forms that are not available to biota, such as constituents in rocks and soil minerals. Igneous and metamorphic rocks are the most common natural sources of heavy metals in soil. They account for 95% of the earth's crust, with sedimentary rocks making up the remaining 5%. However, sedimentary rocks are a more important soil parent material since they overlie most igneous formations, and account for 75% of the outcrops at the earth's surface [7]. When the metals are derived from anthropogenic sources, this can strongly influence their speciation and hence bioavailability [8-9].

The study of heavy metal content in soil is of a great importance due to the fact that soils effectively act as a reservoir which, after temporary storage of metals, can act as a source and a sink for metal contamination.

Current research was aimed to study heavy metals content in soils of Imereti region. Study area is located in the central part of Georgia and administratively belongs to the districts of Kharagauli, Zestaponi and Terjola. The economy of the region as in other parts of the country is mainly based on agricultural production, and the study of soil contamination with heavy metals has a great importance for producing qualitative and safe products.

The content of six heavy metals (Cd, Cu, Mn, Ni, Pb, Zn) was studied, which are commonly widespread in different environmental media and can be accumulated in soils having negative impacts on soil organisms, plants and finally have an adverse effect on human and animal health.

The study region represents hypsometrically one of the most developed intermountain areas. Its highest peacks reach about 1500 m (a.s.l.), which define the creation of bridge-like connection between Small and Greater Caucasus and therefore divides the country into two geographical parts. Climate characters of the region are governed by the modern morphology of the relief. The influence of sea is somewhat weakened here, while of continent increased. Consequently the climate is more dry and the winter is noticeably cold than on the Kolkheti Valley. The average annual air temperature is +12.5-13.5^{0}C, the atmospheric precipitations vary in the range of 900-1800 mm. The main soil types in the region are brown forest - dystric cambisols, yellow brown forest - chromic cambisols and stagnic alisols, raw-humus calcareous - rendzic leptosols and alluvial – fluvisols.

The soil sampling was performed by taking into account the geomorphologic peculiarities of the district, due to that 15 soil profiles were made along the river valleys, which are proposed to be the main flow directions for potential pollutants. From each profile 3-4 samples were taken in fixed depths, under natural pastures and forests at 0-10, 10-20, 20-40 and 40-60 cm, and on arable lands at 0-15, 15-30 and 30-60 cm.

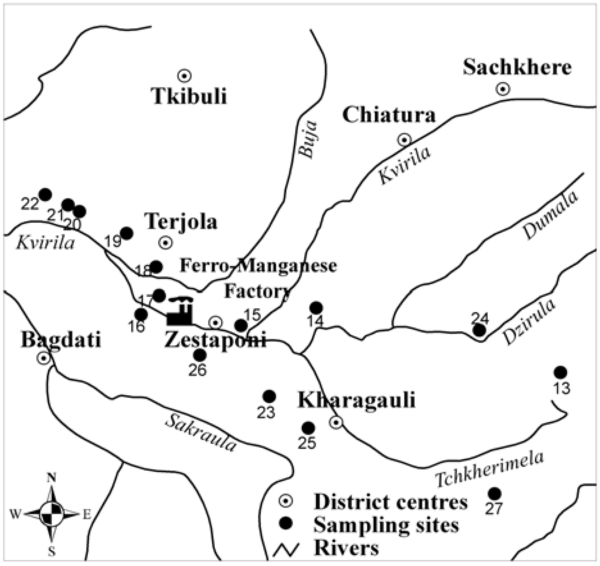


Fig. 1. Map of study area.

The sampling sites were chosen carefully to avoid a direct influence from roads or any other known sources, the most important of which is a Ferro-Manganese factory located in city Zestaponi. The geographic location of soil profiles was measured during field works using GPS-receiver and obtained coordinates were added to topographic basis in ArcView GIS environment, which was used to create a map of the study area (Figure 1).

Samples were air dried, cleaned from stones, plant roots, then crushed and passed through a 2-mm sieve. The samples were digested using *aqua regia* extraction according to Austrian standard method [10]. The extracts for total metal contents were measured by atomic absorption spectroscopic method, using flame (Perkin Elmer) and graphite furnace spectrometer. In total 55 samples were analysed; all analyses were done in two replications.

Besides heavy metals some soil parameters, such as organic matter, pH, carbonates, etc., were measured as well.

The results of laboratory analysis have shown that the soils in the study area are more or less polluted with heavy metals (Table 1). However, their contents vary due to sampling depth, distance from pollution source, soil properties, vegetation type and other factors.

The influence of Zestaponi Ferro-manganese factory on the pollution of the region is considerable. The concentrations of total forms of studied heavy metals (Cd, Cu, Mn, Ni, Pb, Zn) in soils are gradually decreasing in samples taken to the east direction from the pollution source up to mountain chain Likhi (Table 1). Though, the diminution in concentrations has different nature in case of certain elements.

In some cases the concentrations of metals in samples taken to the east and south-east end part of

Table 1

Contents of heavy metals in studied soils (mg/kg)

Prof. №	Sampling location	Depth (cm)	pH	Cd	Cu	Mn	Ni	Pb	Zn
13	Rikoti cross, district of Kharagauli	0-10	4.60	0.11	9.99	1034.48	22.45	27.11	52.96
		10-20	5.10	0.07	9.99	948.01	24.98	23.24	54.46
		20-40	5.15	0.05	14.97	872.01	27.44	23.47	56.63
		40-60	5.10	0.05	17.49	616.23	32.47	23.61	65.45
14	vil. Shrosha, district of Zestaponi	0-10	7.55	0.09	24.94	1240.53	22.44	12.28	78.83
		10-20	8.00	0.07	29.95	1202.75	24.96	13.88	69.88
		20-40	7.75	0.06	24.98	995.21	24.97	13.47	76.17
		40-60	7.70	0.05	19.92	921.57	24.90	14.75	70.72
15	vil. Upper Sakara, district of Zestaponi	0-10	5.85	0.09	49.94	1993.81	22.47	29.79	88.14
		10-20	5.80	0.05	47.43	1443.25	24.96	17.49	93.10
		20-40	5.70	0.04	39.88	1153.13	22.43	16.42	77.52
		40-60	5.75	0.05	37.46	904.78	19.98	15.81	71.68
16	vil. Second Sviri, district of Zestaponi	0-10	4.30	0.09	122.34	561.23	22.47	18.95	54.18
		10-20	4.50	0.08	119.69	309.49	19.94	23.98	53.62
		20-40	4.40	0.10	122.04	340.98	19.92	21.93	50.06
		40-60	4.30	0.09	122.19	517.03	29.93	18.96	52.37
17	vil. Argveta, district of Zestaponi	0-10	7.70	0.09	34.91	1683.33	34.92	10.93	64.09
		10-20	7.90	0.07	29.93	755.55	32.43	9.06	59.62
		20-40	8.00	0.07	32.46	783.80	34.94	9.71	57.91
		40-60	7.90	0.06	29.97	775.45	32.47	9.08	55.44
18	vil. Ghvankiti, district of Terjola	0-10	5.90	0.05	24.95	2191.33	27.44	22.78	49.65
		10-20	5.90	0.04	24.93	2616.54	27.43	23.16	49.36
		20-40	6.05	0.05	24.96	2660.62	27.46	22.38	51.68
		40-60	6.50	0.05	24.95	2768.01	24.95	22.05	48.90
19	vil. Etseri, district of Terjola	0-15	6.50	0.06	22.46	1384.55	19.96	26.73	63.64
		15-30	6.55	0.05	22.46	1550.05	24.95	25.96	63.13
		30-60	6.75	0.01	22.46	1248.28	22.46	27.16	48.40
20	vil. Lower Simoneti, district of Terjola	0-15	6.80	0.10	39.89	3065.64	37.39	29.72	52.86
		15-30	6.90	0.11	39.95	3676.96	42.44	31.24	52.69
		30-60	7.10	0.13	27.42	2845.42	57.33	29.97	54.84
21	vil. Lower Simoneti,district of Terjola	0-10	7.65	0.34	34.91	5163.67	49.88	43.47	76.79
		10-20	7.60	0.18	32.47	3465.35	49.96	43.07	64.20
		20-40	7.55	0.30	34.47	4398.81	54.95	52.29	63.69
		40-60	7.20	0.39	29.97	4273.43	52.45	41.03	67.68
22	vil. Nakhshirghele, district of Terjola	0-10	7.55	0.06	39.91	1988.13	54.88	24.52	57.87
		10-20	7.85	0.04	37.40	1880.37	52.35	23.82	54.35
		20-40	7.80	0.03	37.43	1401.73	57.38	19.72	53.14
		40-60	8.10	0.04	34.96	1079.64	57.43	13.08	47.94
23	vil. Kitskhi, district of Kharagauli	0-10	8.10	0.13	127.37	979.44	52.45	13.14	77.43
		10-20	8.00	0.12	59.93	895.01	54.93	11.66	67.42
		20-40	7.65	0.11	49.93	840.41	57.40	9.89	69.88
24	vil. Khevi, district of Kharagauli	0-15	6.10	0.17	49.91	911.22	24.99	7.60	77.46
		15-30	5.70	0.11	59.97	844.01	24.95	10.01	72.35
		30-60	5.60	0.10	74.85	749.75	22.47	26.83	67.35
25	vil. Partskhnali, district of Kharagauli	0-10	7.85	0.46	62.43	1397.56	32.41	21.03	62.35
		10-20	8.05	0.45	29.97	1442.44	34.97	21.24	52.45
		20-40	8.20	0.49	29.93	1515.19	37.41	21.50	57.38
26	vil. Tskhratskaro, district of Zestaponi	0-10	6.90	0.21	114.83	1023.99	57.41	24.93	92.37
		10-20	7.40	0.19	104.79	899.99	59.88	18.89	87.33
		20-40	7.95	0.14	54.92	875.04	49.92	12.32	57.42
		40-60	8.10	0.06	44.97	765.34	49.96	12.85	57.46
27	vil. Nunisi, district of Kharagauli	0-10	6.45	0.07	64.84	1295.76	47.38	14.53	72.32
		10-20	6.10	0.07	69.86	1092.14	42.41	7.02	69.86
		20-40	6.50	0.08	69.97	1077.68	34.98	6.10	69.97
		40-60	6.40	0.08	74.85	1071.50	42.41	6.18	76.58

study area, at 40th and 41st km, were relatively high in comparison to those taken nearer to the pollution source. Such rising in concentrations can be caused by taking samples under forests, which usually defines comparably high contents of metals than under meadows and arable lands [11-12].

The distribution of heavy metals to the west direction from the Ferro-manganese factory is not characterized by such regularity. Especially in case of manganese, the concentration of which is marked out by the highest values to the eastern part of the study area and in upper humic horizon of 21st profile reaches 5163.67 mg/kg (Table 1). In 21st and also 20th profile, located near to 21st, along the whole profile manganese content is quite high, which varies between 3000-4000 mg/kg, and can be explained by its naturally high concentration in parent rock, which enriched in manganese and the percentage of atmospheric deposition is low.

In order to estimate whether the high concentrations of metals have an anthropogenic origin or are due to the chemical composition of parent rocks graphs showing metal distribution within the soil profiles were created (Figure 2-7). The graphs show that the metal concentrations in top horizons (15-20 cm) are mainly higher than in lower layers, but the contents do not decrease gradually by increasing profile depth. That was proved

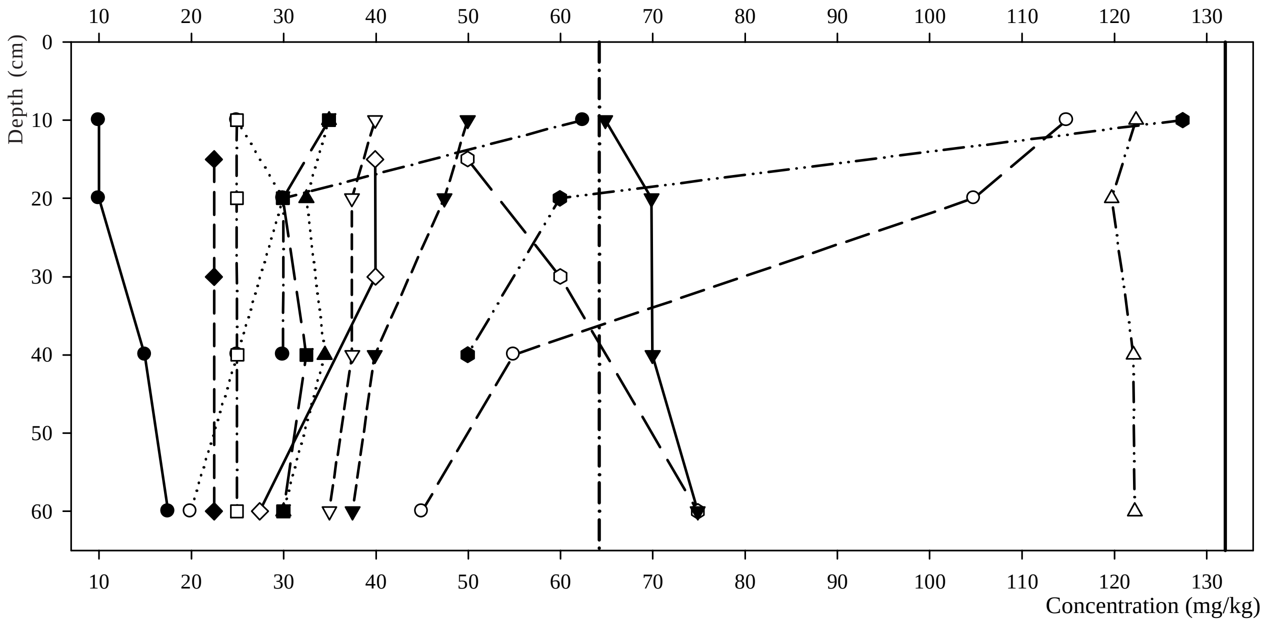


Fig. 2. Distribution of cadmium within soil profiles.

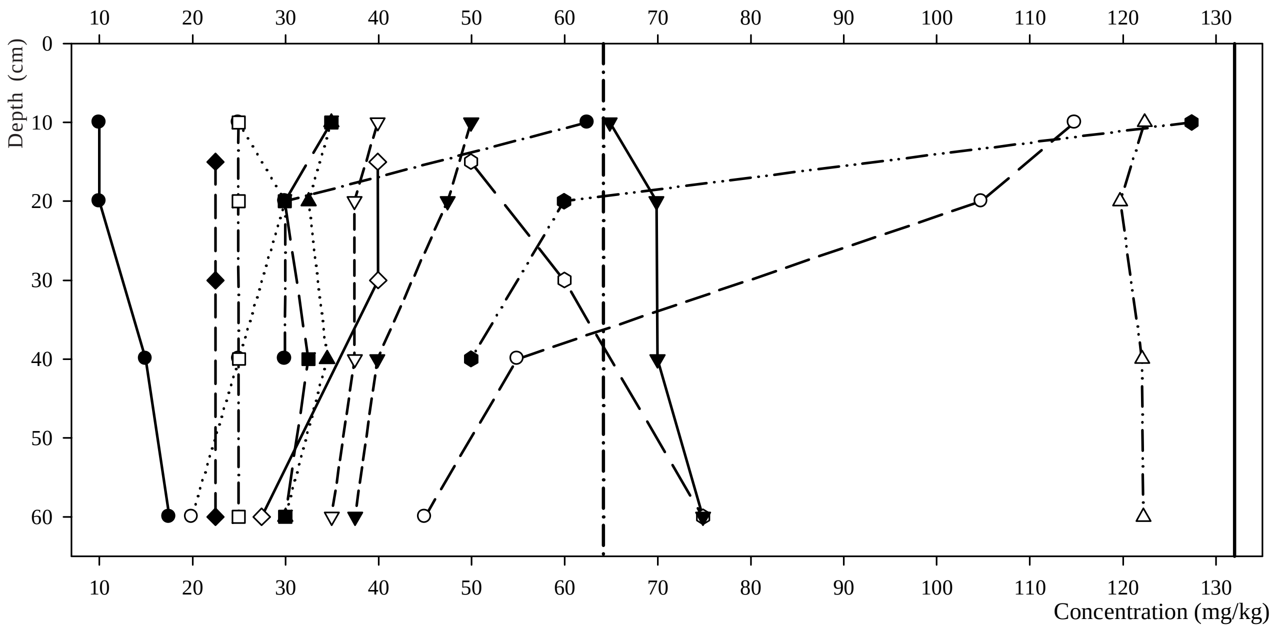


Fig. 3. Distribution of copper within soil profiles.

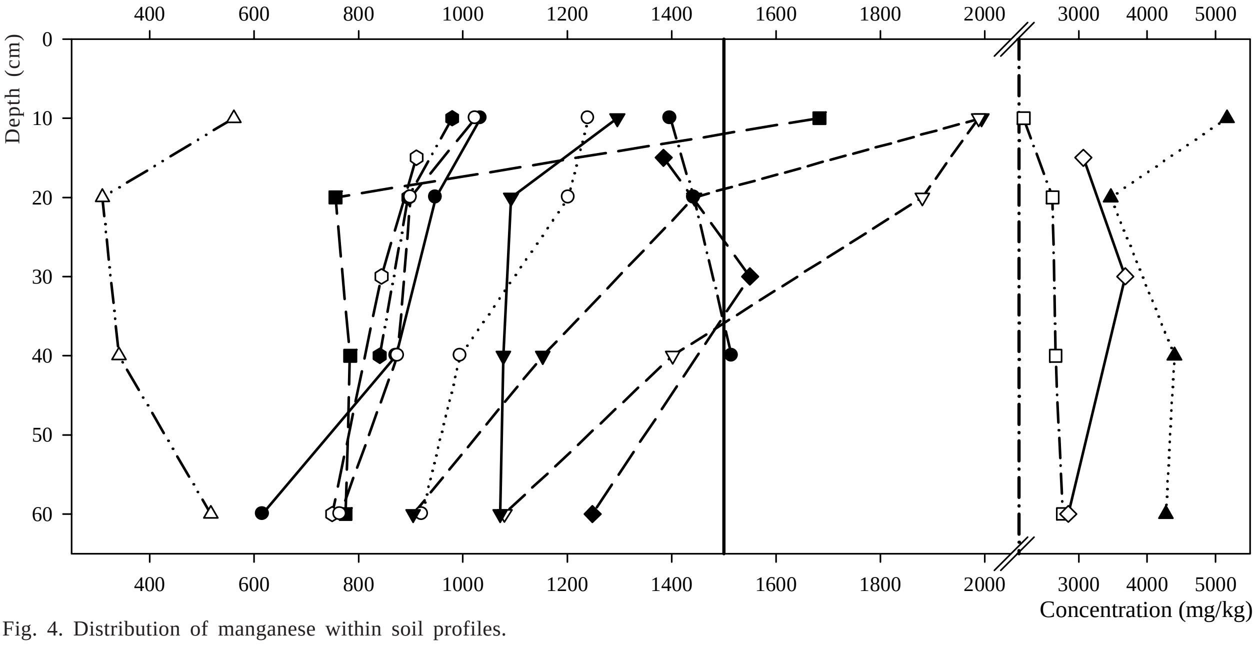


Fig. 4. Distribution of manganese within soil profiles.

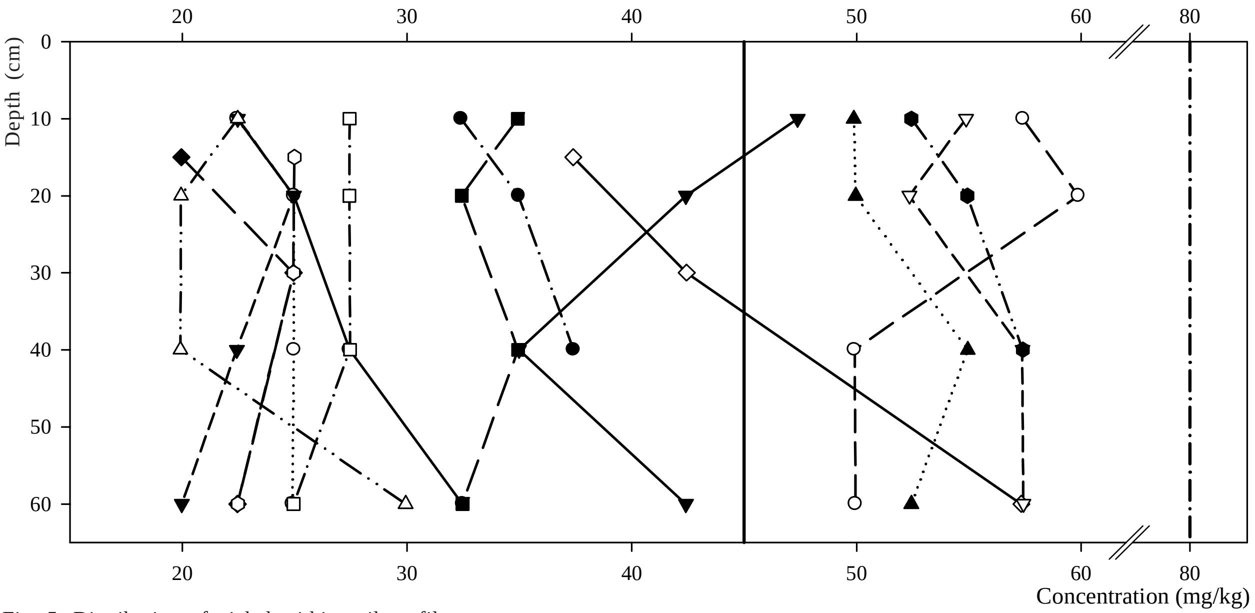


Fig. 5. Distribution of nickel within soil profiles.

statistically where correlation between the metal concentration and profile depth was calculated. The correlation coefficients for five metals – Cd, Cu, Mn, Pb and Zn were negative but not significant. In case of Ni the correlation is positive, but statistically negligible.

To assess whether high concentration of metals are induced by the Ferro-Manganese factory correlation coefficients were computed using Pearson correlation (Table 2). The analysis have shown that Mn content in soils, which can be taken as a good indicator of the influence from the factory due to highest percentile of Mn in factory exhausts, is correlated with Cd (r=0.370, p=0.01), Pb (r=0.754, p=0.01) and Ni (r=313, p=0.05). Mn is negatively correlated with Cu (r=-0.351, p=0.01). The correlation of Mn with Zn is negligible. The conducted statistical analysis indicates that the Ferro-Manganese factory seems to be more associated with contamination with Cd, Mn. Ni and Pb and less or not connected with the Cu and Zn content in soils of the study area. However, combustion of petroleum products (especially by

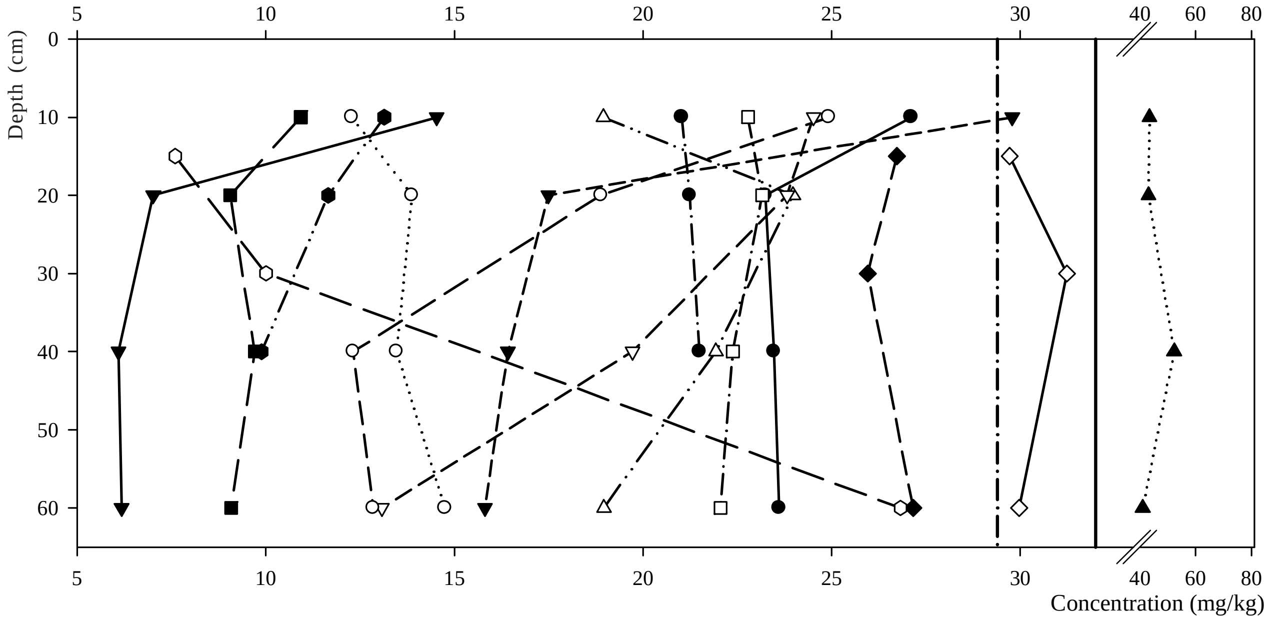


Fig. 6. Distribution of lead within soil profiles.

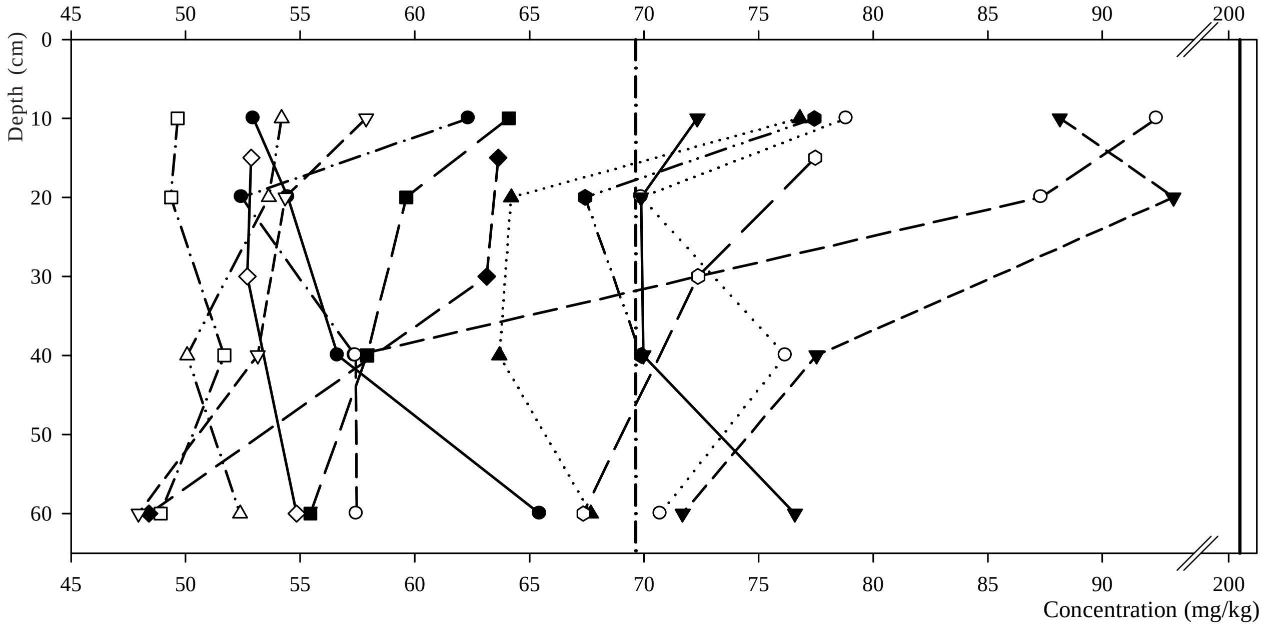
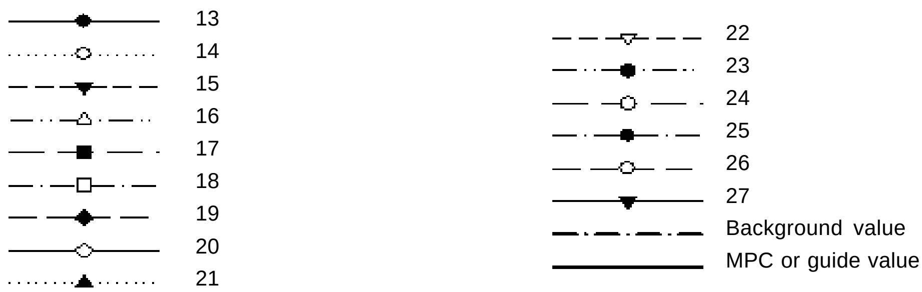


Fig. 7. Distribution of zinc within soil profiles.



Indicated numbers correspond to certain profiles.

Table 2

Correlation between studied heavy metals

	Cd	Cu	Mn	Ni	Pb	Zn
Cd	1	0.010	0.370**	0.274*	0.375**	0.104
Cu	0.010	1	-0.351**	0.135	-0.204	0.250
Mn	0.370**	-0.351**	1	0.313*	0.754**	-0.072
Ni	0.274*	0.135	0.313*	1	0.133	0.086
Pb	0.375**	-0.204	0.754**	0.133	1	-0.148
Zn	0.104	0.250	-0.072	0.086	-0.148	1
Number of samples	55	55	55	55	55	55

** Correlation is significant at the 0.01 level
* Correlation is significant at the 0.05 level

Table 3

MPC and guide values for total forms of heavy metals in soil (mg/kg) [15, 16, 17, 18, 19, 20]

Country	Cd	Cu	Mn	Ni	Pb	Zn
Austria	1	100	-	60	100	300
Czech Republic	1	100		80	140	200
Denmark	0.5	40	-	15	40	100
Finland	0.5	100	-	60	60	150
France	2	100	-	50	100	300
Germany	1.5	60	-	50	100	200
Georgia	0.5 [a]; 1 [b]; 2 [c]	33 [a]; 66 [b]; 132 [c]	1500	20 [a]; 40 [b]; 80 [c]	32	55 [a]; 110 [b]; 220 [c]
Italy	3	100	-	20	100	300
Norway	1	50	-	30	50	150
Spain	1	50	-	30	50	150
Sweden	0.5	40	-	15	40	100
United Kingdom	3	135	-	75	300	200
EU	1–3	50–140	-	30–75	50–300	150–300
Russia	0.5 [a]; 1 [b]; 2 [c]	33 [a]; 66 [b]; 132 [c]	1000	20 [a]; 40 [b]; 80 [c]	32-120	55 [a]; 110 [b]; 220 [c]
United States	20	750	-	210	150	1400

a – Guide values for sandy soils
b – Guide values for loam or clay soils with pH <5.5
c – Guide values for loam or clay soils with pH >5.5

transport facilities) are well-known source of Cd, Mn, Ni and Pb in the environment and should not be excluded during the assessment. The fact that Mn has a negative correlation with Cu can be explained by wide usage of Cu in agriculture as fungicide.

To evaluate the possible toxicity of heavy metals maximum permissible concentrations (MPC) are established. Maximum permissible concentrations for toxic substances are calculated on the basis of risk considerations, where ‘‘risk’’ usually has the meaning of the extent of an adverse effect, quantified in relevant dimensions [13].

Table 3 shows MPC values for heavy metals in agricultural soils in Europe and in the United States, as well as limits of heavy metals content which are common for member states of the European Union and contents of metals in uncontaminated soils. According to Table 3, MPC values vary greatly from country to country, but are mainly in the same order of magnitude, with some exceptions. Generally it is very difficult to compare maximum permissible concentrations from different countries because of the heterogeneity in geology, soil types, and climatic conditions, as well as in purposes for which limits are set [14]. As it is shown in the Table

Table 4.
The main statistical parameters of heavy metals contents in studied soils and their background values. *[11]

	Cd	Cu	Mn	Ni	Pb	Zn
Average	0.12	47.64	1534.32	36.25	20.40	63.84
Median	0.08	34.97	1092.14	32.47	21.03	63.13
Minimum	0.01	9.99	309.49	19.92	6.10	47.94
Maximum	0.49	127.37	5163.67	59.88	52.29	93.10
Standard deviation	0.11	31.68	1067.66	13.32	9.81	11.80
Contents in clean soils*	0.5	20-40	20-800	5-50	2-20	10-80
Backgound value	0.18	64.16	2119.95	45. 83	29.39	69.63
Above background	9	12	11	17	8	19
Above background (%)	16.4	21.8	20.0	30.9	14.5	34.5
Number of samples	55	55	55	55	55	55

Georgia and Russia have similar MPC and guide values, the reason of such similarity is that these values are taken from sanitary norms of the former Soviet Union and country specific MPCs are not yet defined for Georgia with consideration of local conditions, which creates difficulties for evaluation and monitoring of soil pollution. Furthermore, from presented six metals maximum permissible concentrations only for two elements (Mn and Pb) are derived.

The results of our research were compared to MPC and guide values defined by Georgian legislation. The comparison shows that the concentration of Cu, Mn and Pb exceeds in current MPC and guide values in 4, 17 and 4 samples, respectively. Other metals are in the recommended range.

Background concentrations of trace elements in soils can act as a true reference level for estimating the extent of soil pollution with these elements [21]. Average crustal composition is sometimes used for global reference values but these may differ widely from the regional background values [22] and it is suggested to define background content of elements on regional basis. However, more importantly, knowing them can help in defining areas which need further study because of likely anthropogenic influences [23].

Different approaches have been suggested to obtain natural background concentrations. For the background values of our study area, we have selected the method recommended by Salminen and Tarvainen [24], which is based on the usage of median value in calculations instead of arithmetical mean and is supposed to be nearer to real background content. According to our results the upper soil horizons in the study area are affected by man and due to that these soil layers were excluded from calculations.

The calculated background concentrations were compared to our results, which are given in Table 2 together with the descriptive statistical parameters. The comparison shows that the concentrations of Cd, Cu, Mn, Ni, Pb and Zn exceed their background contents in 9, 12, 11, 17, 8 and 19 samples, respectively.

On the basis of our research carried out in three administrative districts of Imereti region several conclusions can be made: 1) The soils in the study area are slightly polluted with heavy metals and an influence of Ferro-Manganese factory is evident; 2) The MPCs and guide values are not enough for estimating the soil pollution rate and it is necessary to use background concentration too; 3) There is a need for deriving the national maximum permissible concentration with consideration of background content.

ნიადაგმცოდნეობა

ნიადაგის გაჭუჭყიანება მძიმე ლითონებით იმერეთის რეგიონში (საქართველო)

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ნაშრომში განხილულია იმერეთის რეგიონში მძიმე ლითონების შემცველობის შესწავლის შედეგები. მიღებულ ლაბორატორიულ კვლევის შედეგებზე დაყრდნობით გაკეთებულია დასკვნები ნიადაგში ლითონების მოხვედრის შესაძლო წყაროების შესახებ. ამასთან, შეფასებულია საკვლევ ტერიტორიაზე გავრცელებული ნიადაგების გაჭუჭყიანების ხარისხი მოქმედ ზღვრულად დასაშვებ კონცენტრაციებსა და ადგილობრივ ფონურ მაჩვენებლებთან შედარებით, რომელიც გამოთვლილია მიღებული შედეგების საფუძველზე.

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