

NO UNIQUE BACKGROUND IN GEOCHEMISTRY

Ubul FÜGEDI¹, László KUTI¹, József VATAI¹, Tamás MÜLLER¹, Ildikó SELMECZI¹ & Barbara KERÉK¹

Geological and Geophysical Institute of Hungary, 1143 Budapest, Stefánia út 14., fugedi.ubul@mfgi.hu

Abstract: Background and anomalies always need to be viewed together: the background is the non-anomalous range of concentrations. All geochemical regions have their own background for all elements. In Hungary we have separated four geochemical regions with different characteristics of young, unconsolidated sediments. The first of them has no specific element association: the concentrations in it depend on weathering factors and on the element concentrator phases (clay and ferrous minerals). The second (Central) region is characterised by regular lime accumulation; all the other components are crowded out. As a result of the weathering of the basic-ultrabasic rocks of the Eastern Alps in the third (Western) region relatively high Fe, Co, Cr and Ni contents are found. The fourth (Eastern) region is not a unique area: it consists of the floodplains of the rivers arriving from the Transylvanian ore mining areas and the northern heavy industrial centres. These floodplains are contaminated by basic, ferrous and precious metals. In countries having more characteristic metallogenic provinces more and more different geochemical regions must be distinguished. The background ranges could be determined only for the geochemical regions one by one, not for the entire countries.

Keywords: geochemical anomalies, background, erosion, deflation, carbonate accumulation, mineral exploration

1. BACKGROUND AND ANOMALIES

Neither the term background nor the term anomaly is well defined. According to Reimann & Garrett (2005) more than 10 quite different definitions are in use in the scientific literature. The Hungarian rule of law (10/2000, 219/2004, 6/2009) and most of the EU documents (for example EU, 2008) define the background of some components, such as its “natural” concentration (s) without (any) anthropogenic influence in various forms. According to the above mentioned, they:

- give a great chance to the subjectivity,
- can qualify only positive anomalies.
- cannot use for the characterisation of geological media forming by anthropogenic influence (ie. the soil), so the background of them is not even tried to be specified by certain authors (Szilassi et al., 2010).

Directly opposite to this conception in our opinion there is no reason to estimate where geochemical cycles of individual atoms have been influenced by some human activities and where activities could be considered as “natural” and where as “anthropogenic” influences. The atoms have not

any “labels” of origin and their environmental role is independent from their origin. Our (purely technical, i.e. formal) conception is that background and anomalies need to be viewed together and they can only be defined on the base of statistical distribution patterns, but always regarding the possible heterogeneity of the background (geological-geographical setting).

The background could never be a distinct value, but — in every case — a range (in case of heterogenic backgrounds: some ranges) of concentrations characterised by the so-called “background distribution(s)”. Anomalies are beyond the background, and it means both the positive and negative anomalies. This is very important for us because most of the positive geochemical anomalies (except the arsenic content of the groundwater) have only a local importance in Hungary, whereas (as it will be shown) the negative ones play regional environmental roles.

Some anomalous and background distributions could be detached with monoelement methods. For example (Fig. 1) in the Zemplén Mts. — which is affected by low-temperature hydrothermal processes — we have a group of weak and a second group of

strong anomalous samples separated from the background by frequency minimums.

Of course, this method could be affected by subjective elements, too. The role of subjectivity can be decreased by multielement methods.

2. HETEROGENEITY OF THE BACKGROUND

We have to take the following four basic types of background heterogeneity into account:

- lithological heterogeneity,
- heterogeneity generated by secondary processes,
- analytical heterogeneity,
- heterogeneity resulted by the different scales of investigation.

Lithological heterogeneity: if the territory is covered with geochemically different rocks, in the moderately representative samples we can probe either one or the other but practically never the “mean composition” of them. For example, if the sampling area is covered with limestone and sand, in some lithogeochemical samples we have more than 95% CaCO_3 and less than 5% SiO_2 , but in others we will have more than 95% SiO_2 and less than 5% CaCO_3 . The soil-forming processes moderate these differences; nevertheless, they can be detected for a long time (Fig. 2).

The secondary processes (soil forming, lime accumulation etc.) may considerably influence the composition of the geological formations, and their intensity is strongly variable.

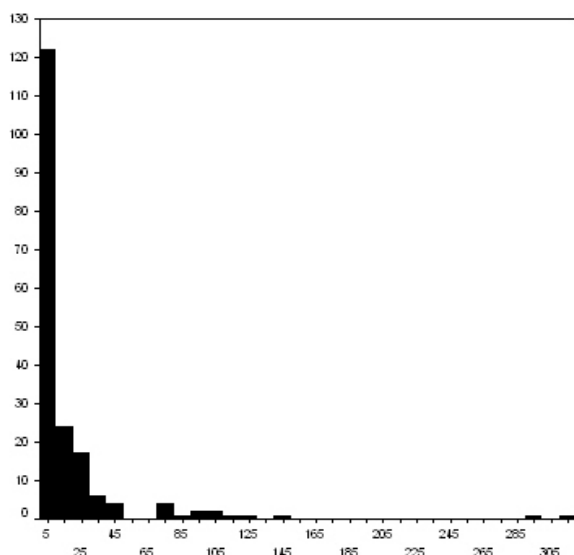


Figure 1. Distribution of arsenic (mg/kg) in the stream sediments of the Zemplén Mts. (N=187)

According to the Hungarian law the pollution limits are defined as “total” concentrations of toxic

elements. Practically, the great majority of users consider them as concentrations which can be dissolved in some concentrated acids (nitric acid, aqua regia etc.). Plant nutrition is modelled usually on the base of leaching with some complex-forming extractants (NH_4Ac , Lakanen-Erviö etc.) or distilled water. These digestions produce significantly lower concentrations than those of the concentrated acids and these types of data cannot be processed together.

The range of the background depends on the type of the samples. The type of the samples and the scale of investigation are in close connection with each other: overbank sediments represent larger catchment basins (with lower variability) than stream sediments, whereas stream sediment samples represent a larger area than a soil sample. These relations will be presented in the next chapter. Effects of the scale enhancement will be illustrated by the arsenic maps, since this element is the most problematic one in Hungary in an environmental point of view.

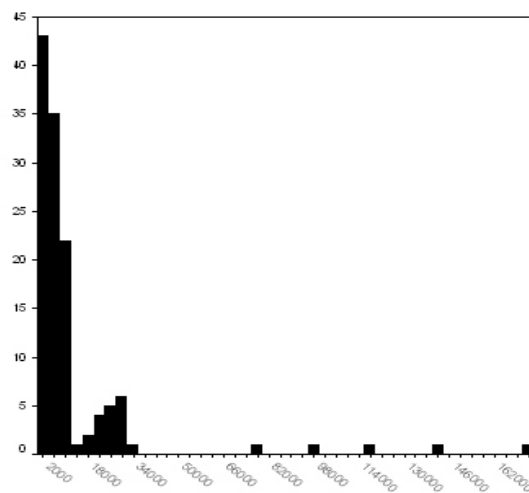


Figure 2. Distribution of calcium (mg/kg) in the soils of the Northern Bükk Mts. N=115 with 98 eluvial and proluvial soils formed on shales (Ca 500–13500), 18 on basic volcanics (Ca 15500–32000) and 5 eluvial soils formed on limestones (Ca>65000).

3. REGIONAL GEOCHEMICAL INVESTIGATIONS IN HUNGARY

The Hungarian Geological Institute participated in the ‘Geochemical Atlas of Europe’ project (Salminen et al., 2005). 14 overbank sediment samples and 14 stream sediment samples were collected — overbank sediments for the characterisation of large (1000–6000km²) basins and stream sediments for the moderate (<100km²) catchment basins. According to the FOREGS (Forum of European Geological Surveys) map of overbank sediments arsenic concentrations (Fig. 3) that are

depicted on the map, three of the highest values can be found in the inner Carpathian Basin. As Csalogovits (1999) has proved, the regional arsenic anomaly characterising the environmental geological facies of central and eastern Hungary has developed in the time of glaciations, under oxidative surficial conditions.

Similar to the FOREGS sampling method, the big catchment areas ($>100 \text{ km}^2$) were characterised by overbank sediment samples and the small ones ($<10 \text{ km}^2$) by stream sediment samples in Hungary too. The two sample types were compared by Peh and Miko (2001) in the Žumberak Region, Croatia.

Low-density geochemical mapping of Hungary (Ódor et al., 1997) has been developed in 1991–1995 on the base of sampling overbank sediments of relatively large (approx 400 km^2) catchment basins. Two samples were collected in 196 sites; one from a depth of 0 to 10 cm — in order to represent the present environment — and one from 50 to 60 cm to provide the natural background characteristics of prehistoric flood-plain sedimentation. A close correlation is observed between the concentration values of the two sampling levels. However, the

concentrations of certain elements like P, Pb and S are 15–40% higher than those in the upper layer.

The first Geochemical Atlas of Hungary comprises the concentration interval mosaic maps (Fig. 4) of 25 elements. Some of them (Fügedi et al., 2009) were shown in the series of conferences organised by the Committee of Environmental Geochemistry of the Hungarian Academy of Sciences.

The middle-scale geochemical mapping of the uplands (Fügedi et al., 2007) was completed in 1989–1998 on the base of sampling stream sediments of small (approx 4 km^2) catchment basins. On karst plateaus, where no recent alluvial deposits were found, the stream sediment samples were replaced by composite sinkhole samples.

As a result of this work we could contour the sub-regional-scale pollutions beneath the “historical” mining areas; find some new gold deposits; and determine the geochemical background ranges in the individual geographical units of the Transdanubian and Northern Hungarian Ranges. The scale of investigation is reflected on the concentration distribution patterns.

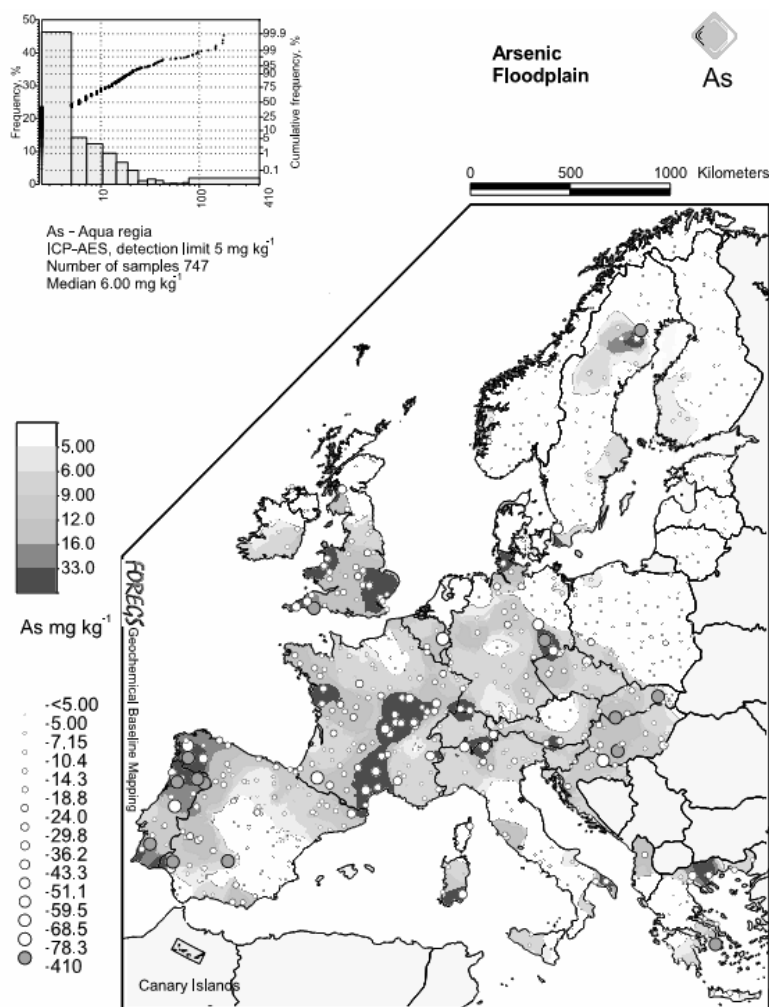


Figure 3. Arsenic concentrations of the European overbank sediments. (Salminen et al., 2005)

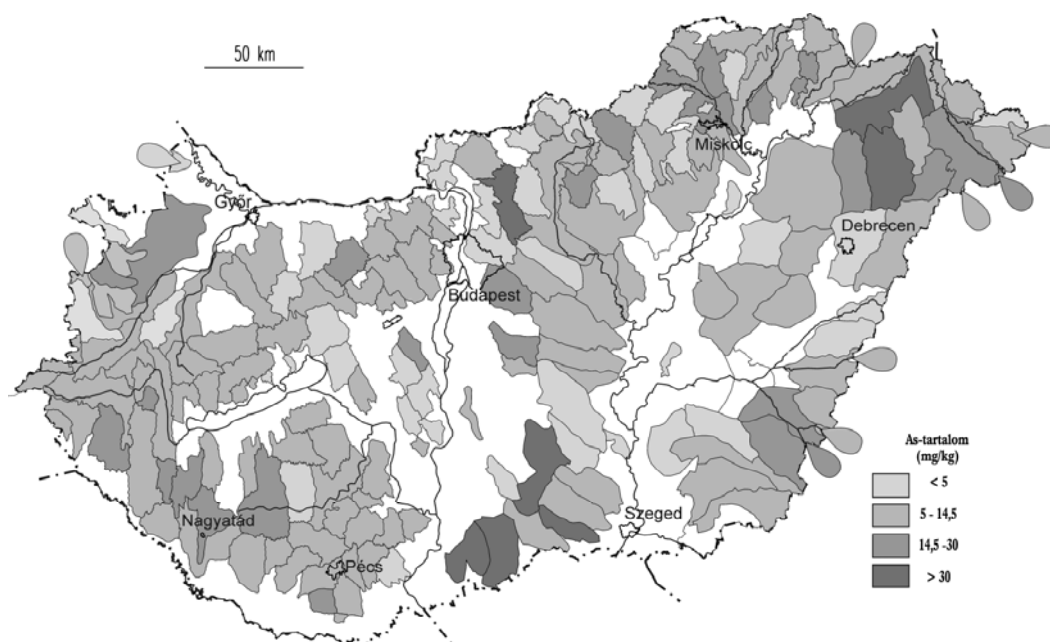


Figure 4. Arsenic content (mg/kg) of the Hungarian overbank sediments (50–60 cm depth) (after Ódor et al., 1997, corrected)

For example, in the Zemplén Mts. where we can find approximately average arsenic concentrations in the Geochemical Atlas, the upland mapping revealed a complicate system of anomalies (Fig. 5), and as a result of a much more detailed soil sampling (Fig. 6) a post-volcanic, low temperature gold deposit was found.

The predominant part of the primarily detected anomalies and outlying values were controlled by a more compact re-sampling of the environs (for example, Fügedi et al., 2010 — most of the results can be found in the Hungarian Geological Archive, in unpublished reports). Based on the results of these investigations the Geochemical Atlas of Hungary has been renewed and corrected several times.

3.1. Field works

1. In low-density geochemical mapping of Hungary (Ódor et al., 1997) the sampling method was adapted from the FOREGS Field manual (Salminen et al., 1998). In the course of the middle-scale geochemical mapping we collected our samples from the active stream sediments from small, mainly first-order drainage basins (<6 km²). We preferred sites above the confluence points of streams with the main and second-order channel of the larger drainage basin.

2. In order to get additional samples and do re-sampling for the anomalies of the Hungarian Geochemical Atlas we sampled the overbank sediments. A small part of these samples was collected from shallow boreholes. The re-sampling of the middle-scale geochemical mapping has been completed on the basis of stream sediment samples.

3.2. Laboratory procedures

Sample preparation was carried out according to the WEGS proposal (Bolviken et al., 1990). Drying under 40°C, sieving <0.025 mm (using nylon sieves), splitting (storage of approx. 300 g), grinding (agate grinding). The archived materials are available for future analyses.

The basic 392 sample were analysed in two laboratories, whereas the following samples were analysed only in the Geological Institute of Hungary. Samples were analysed by ICP-OES and AAS techniques after leaching with hot aqua regia. Until 1994 Hg was leached in teflon bombs, later it was detected by AMA 254 mercury analyser in powdered solid samples. FOREGS samples were analysed (Sandström et al., 2005) for total concentrations and for those that are leachable with aqua regia. The total concentration of elements in baryte and minerals such as titanomagnetite is significantly higher than their soluble element content. This is the reason why — contrary to the Geochemical Atlas of Europe — in our Atlas we use leachable concentrations which can be compared to our other data.

3.3. Data processing

At the moment the results of the 3 geochemical settings (Atlas of Europe, Atlas of Hungary and Atlas of Uplands) are interpreted independently. The unique database concerning the sampling of all the stream and overbank sediments should be constructed in 2011. In this paper we try to show the regional tendencies, i.e. follow the interpretation of the Geochemical Atlas of Hungary (Ódor et al., 1997).

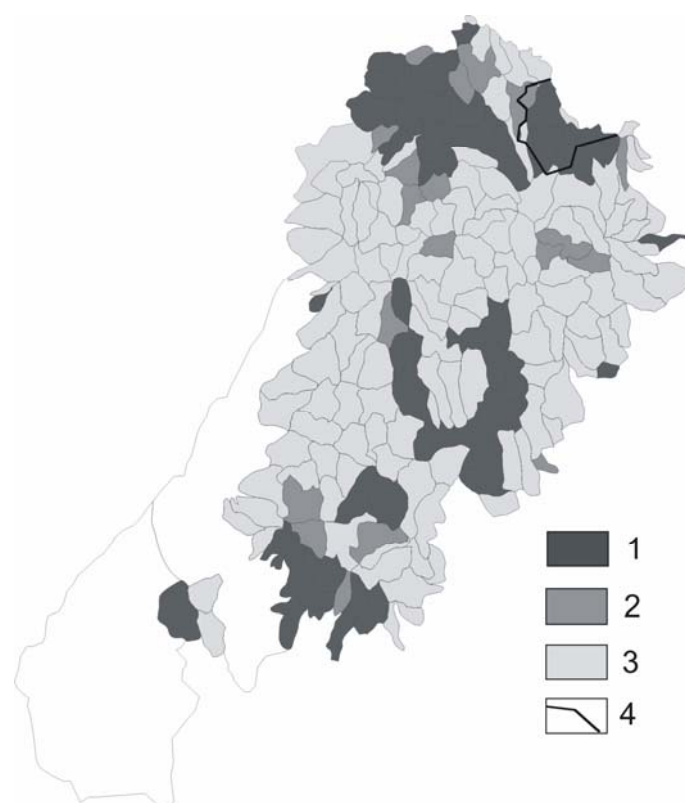


Figure 5. Arsenic content in the stream sediments of the Zemplén Mts. 1. <7.5 mg/kg; 2. 7.5–15 mg/kg; 3. >15 mg/kg; 4. catchment basins. (after Hartikainen et al., 1993)

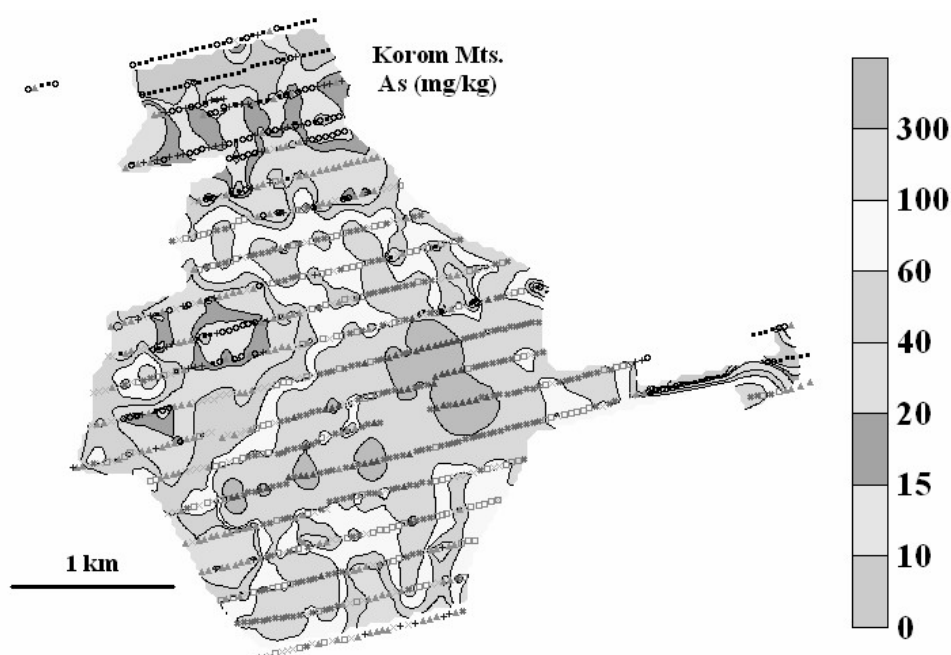


Figure 6. Arsenic content (mg/kg) in the soil samples of the Korom Hill area, NE Zemplén Mts. (after Horváth et al., 1999)

There are a number of different techniques for the statistical calculation of the background (Reimann et al., 2005). In our experience the most effective method is the separation of the so-called “uncorrelated background” from the well-correlated anomalies (Ódor et al., 1998, Fügedi, 2004). Unfortunately, this procedure cannot be used in case of heterogenic

backgrounds, so this is why we followed the method of frequency minimums in this paper. The neighbourhood of the highest peak of the histogram with the majority of the values was counted as background. The positive and negative anomalies are placed outside of this range. If the distribution is unimodal, all samples may be considered as

background. Due to the irregular character of our distributions (Figs. 1, 2.) at first we had to use robust statistics (median for the predictable value, middle absolute deviance and interquartile range or detected concentration range for the variability). Relations are characterised by Kendall's τ rank correlations.

In a regional scale heterogeneity (geological setting) could effectively be exposed by factor analysis. Originally the factor analysis was used for variables with normal distribution. The significance levels are invalid if the variables do not have a normal distribution, and they give false results if the distributions are different or asymmetric. Distribution of all the variables should be transformed into form of the same type for eliminating a part of these failures. The best method is to replace the original concentrations with their ranks. In this case all the derived variables will have discrete uniform distribution and we can follow our processing on rank correlations instead of Pearson's linear correlation method. Unfortunately the test with SPSS PC+ software used by us can be fulfilled only on the base of Spearman's rank correlation coefficients (i. e. linear correlations of ranks). Therefore, though the results of the factor analysis are realistic, the given significance levels are informative. The statistically correct methods were represented by the test based on the Kendall's rank correlation method but the mistake in our method isn't too high (Fügedi et al., 2010).

4. GEOCHEMICAL REGIONS OF HUNGARY

The factor analyses of the Geochemical Atlas of Hungary divided the territory of Hungary into 4 geochemical regions (Fig. 7, Table 1). Region 1 covers more than a half of the country and the others appear as isolated "isles" in it. This region has no characteristic element association: the concentrations vary regarding only the local accumulating and dissolving factors (clay mineral content etc.).

Region 2 in Central Hungary is characterised by the Ca–Mg–Sr–CO₃ (–PO₄–SO₄) association. In the result there is a regular lime accumulation in the upper horizon of the soil. Investigations of the last years showed that the additional carbonate grains, respectively, could be transported here by the wind from the friable dolomites and limestones of the Transdanubian Central Range during the Upper Ice Age (Fügedi et al., 2008a). There are two different types of carbonate accumulation from lacustrine and capillary carbonate muds.

The recently formed carbonate accumulations are different (Ca/Sr ratio etc.) from the corroded, wind-blown carbonate grains mixed into the sand and loess (Fügedi et al., 2008b). Region 3 in Western Hungary is characterised by the Co–Cr–Ni–Fe association. This is the result of the erosion of basic and ultrabasic rocks of the Eastern Alps. Region 4 in some isolated aquifers in Eastern and Northern Hungary is characterised by Ag, As, Au, Cd, Cu, Hg, Pb and Zn contamination — these elements came from the classic mining areas in Transylvania (Damian & Damian, 2006; Nagy-Korodi, 2011) and from the heavy industrial complexes in the north (Gazdag & Sipter, 2008). Examinations of the transport lines were began in a good cooperation with Romanian colleagues.

Similar results are shown in the Geochemical Atlas of Croatia, by soil sampling (Halamić & Miko, 2009) and the territory of the country has been divided into five geochemical regions. We compared the predictable values in the Hungarian stream sediments that were collected from different geological settings in the course of the upland middle-scale geochemical mapping. In contrast to the soil samples, we could not find any significant difference between the samples collected from terrains made up of carbonates and various silicate rocks, but some characteristic differences between the countries belonging to different geochemical regions could be registered (Fügedi et al., 2007).

Table 1. Concentrations (mg/kg) of some elements of the flood-plain sediments of Hungary

Element	Region 1		Region 2		Region 3		Region 4	
	Background range	Median	Background range	Median	Background range	Median	Background range	Median
As	<2.5–19	7.3	<2.5–57	6.3	5.8–13	8	5.4–22	12
Ba	53–158	95	22–158	68	87–190	135	88–160	113
Cd	<0.5–1.5	<0.5	<0.5–3.4	<0.5	<0.5	<0.5	<0.5–10.4	1.0
Co	4.9–13	9	1.7–10	5.7	10–15	12.8	9.4–14	11.1
Cr	8–39	21	4–32	14.5	25–39	36	27–92	36
Cu	8.5–42	19	5.5–33	15	18–32	24	21–103	40
Hg	0.04–0.2	0.08	0.03–0.37	0.08	0.06–0.12	0.09	0.08–0.75	0.14
Ni	11–36	22	7–30	16	25–37	32	25–41	29
Pb	10–34	17	5.3–23	13	16–26	18	32–90	46
Zn	32–150	65	14–180	46	69–96	82	100–600	132

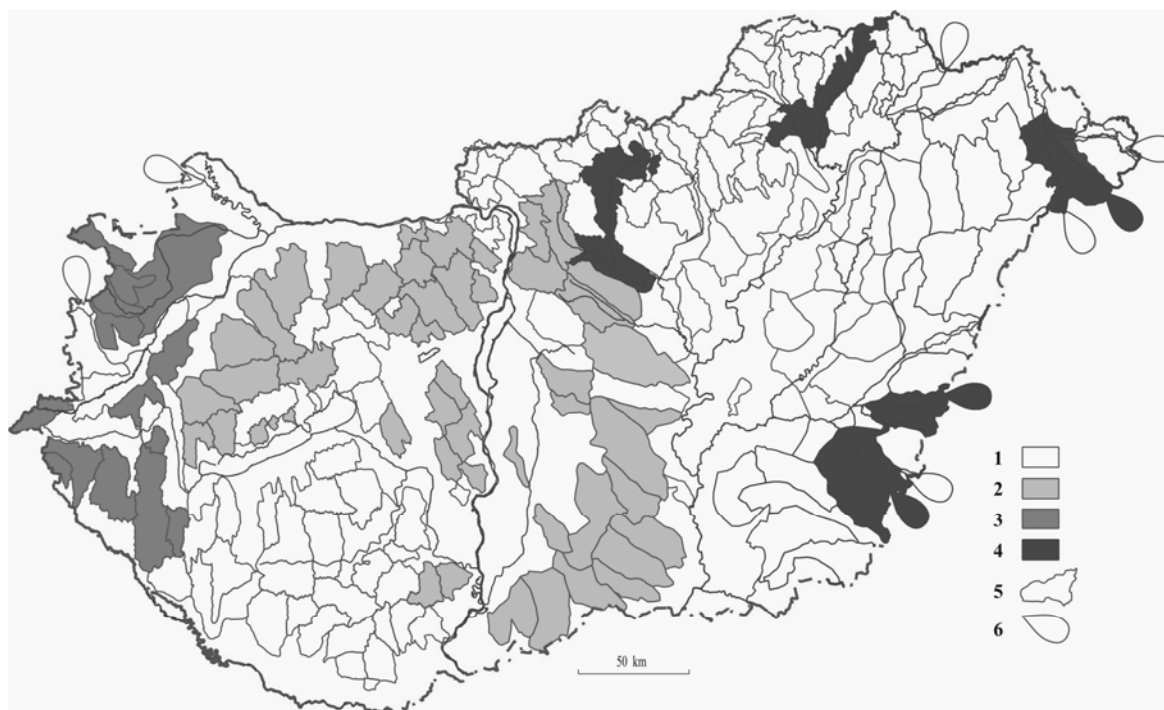


Figure 7. Geochemical regions of Hungary (after Fügedi et al., 2007) 1. 1st geochemical region; 2. 2nd (Central) geochemical region; 3. 3rd (Western) geochemical region; 4. 4th (Eastern) geochemical region; 5. catchment basins; 6. catchment basins out of the border.

5. CONCLUSIONS

The main factor controlling the geochemical patterns in Hungary is the predominance of young (Miocene to Pleistocene) clastic sediments at the surface. Approx. 90% of the surface is covered by these young sediments — and we have four, such different regions in the middle of the accumulating basin. In more mountainous countries with characteristic metallogenic belts there must be more geochemical regions with more different background values.

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