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Trace Element Deficiencies in Hungarian Soils: Realization and Treatment Options

DANIELLA TOLMÁCS, BARBARA KERÉK, UBUL FÜGEDI, TAMÁS MÜLLER

Geological and Geophysical Institute of Hungary,
H-1143 Budapest, Stefánia Str. 14,
tolmacs.daniella@mfgi.hu, kerek.barbara@mfgi.hu, fugedi.ubul@mfgi.hu, muller.tamas@mfgi.hu

Abstract

By the low-density geochemical mapping of Europe and Hungary, we got acquainted with the geochemical properties of the soil-forming sediments.
We found, that the most important environmental problem of geological origin is not toxic element contamination, but nutrient element deficiency. The sediments, which fill up the Carpathian Basin, undergo soil formation between the re-depositional phases; the concentration of nutrient elements decreases further away from the source area. More than half of the area of Hungary is characterised by two little iodine, fluorine, molybdenum and selenium — whereas the calcareous sandy soils of Hungary by too little copper and zinc.

Significant problems in relation with element excess arise only in two regions: (1) the southern and eastern areas of the country, where arsenic accumulates in the young sediments and in the groundwaters; and (2) the "eastern" geochemical region, where too much cadmium is accumulated on the floodplains of large rivers used for agriculture. EU (and Hungarian) legislation treats element excesses as environmental problems, whereas element deficiencies are not counted with: the required minimum concentration levels are not specified by law. The "remediation" of soils that contain elements above the pollution limit value may be harmful for species (indicator plants like *Polycarpaea spirostylis*, *Elsholtzia haichowensis* etc.) living in the refugia of natural anomalies. The original habitats of these species have been destroyed by the mining of superficial ore deposits, and now their survival depends on the presence of tailings and other "contaminated" areas. The remediation of these sites would deprive them from their last habitats.

A treatment option of dealing with element deficiencies would be utilizing such materials (for example ore mining tailings, wastes of ore processing and slags with non-ferrous metals), that are regularly treated as hazardous waste and thus, stored expensively.

Keywords

minor elements, pollutants, soil quality, waste management, refugia

Introduction

One purpose of regional geochemistry is to determine the "natural concentrations" (with other words: baseline values) of toxic and nutrient elements. These concentrations are those, above which EU and Hungarian legislations consider soil-forming sediments contaminated — unless we prove that these concentrations are "natural".

The background is not homogenous; depending on the sampling density and the applied methodology, different heterogeneities can be outlined. Different scales show different levels of the inhomogeneities. In continental scale, the distribution of elements in the surface formations of Europe (FOREGS – Geochemical Atlas of Europe) show a specific pattern: there is a narrow zone stretching from the northern foreland of the Carpathians till Middle England, south of which surface formations have higher element content than those north of it. This zone can be identified with the southern boundary line of the last glacial period (Salminen et al., 2005). In this scale, the whole area of Hungary belongs to the „nutrient-rich", southern province. However, national-scale mappings (Geochemical Atlas of Hungary) showed, that the actual situation is far from it.

One of the most important results of our research was that contrary to popular belief, the most important natural geological environmental problems of Hungary are not element excesses — which are regulated in environmental legislations with priority — but element deficiencies.

The consequences of exaggerating element excesses do not only oppress the problems of element deficiencies, but also threaten rational judgement.

The current system of the Hungarian legislation is deficient from several aspects:

(1) it does not take into account the actual natural concentrations when determining the pollution limit values;
(2) it sanctions only exceedance of the upper limit of the background; whereas it does not deal with the lower limits, under which deficiency diseases could develop;
(3) the remediation of "contaminated" areas would lead to the termination of special, precious habitats;
(4) the limit values are set by political boundaries (by countries), not by geochemical regions (that show the actual differences);
(5) materials, which are regularly treated as hazardous waste and thus are stored expensively (ore mining tailings, wastes of ore processing and slags with non-ferrous metals) could be utilized in treating element deficiencies.

Geochemical Atlas of Hungary

The Geochemical Atlas of Hungary is a still-running project at the Geological and Geophysical Institute of Hungary and has a 25 years-old history. Its methodology has been elaborated parallel with that of the FOREGS - Geochemical Atlas of Europe. The results of both the Geochemical Atlas of Europe and the Geochemical Atlas of Hungary proved that with stream sediments, the expected values in the soils can be well estimated — however, the variability of the element content of soils is much larger than those of the stream sediments.

The database of the integrated Geochemical Atlas of Hungary combines data of different geochemical surveys:

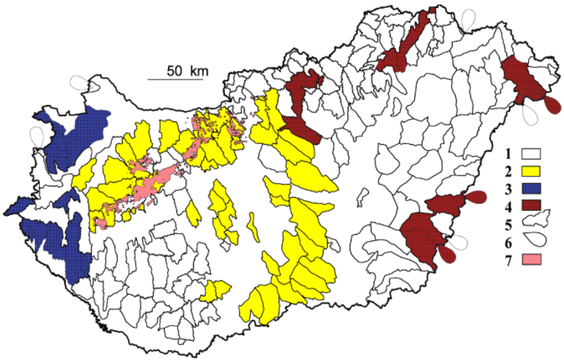
(1) Low-density geochemical survey (1991–1995)
- scale: 1:500 000
- sampled medium: floodplain sediment (196 catchment basins)
- sampled depths: 0–10 cm and 50–60 cm
- number of elements analysed: 25 (Ódor et al., 1997);

(2) Geochemical survey in mountainous and hilly regions (1992-1998)
- scale: 1:50 000
- sampled medium: stream sediment
- number of elements: 32 (Fügedi et al., 2007);

(3) FOREGS geochemical survey (Geochemical Atlas of Europe) (1998-2004)
- scale: 1:5 000.000
- sampled media: floodplain sediment (large drainage basins), stream sediment (small drainage basins), surface water, soil, humus,
- number of elements: 62 (Salminen et al., 2005).

The database has currently 2055 records (the number is increasing year by year). Some of the records represent the average of several samples and analytical data. The new, here presented monoelement maps of the Atlas are based on 314 records.
An important result of the project was to show, that the background is not homogenous. Four geochemical regions (Fig. 1) have been recognized in Hungary, each of them showing different characteristics. The bulk of the country (the "main" region) does not show a characteristic association of elements; the dominant part of variability results from processes of accumulation and leaching. In the middle part of Hungary (the "middle" or "calcareous" region) the association of Ca–Mg–Sr–CO_3^{2-}–PO_4^{3-}–SO_4^{2-} reflects the presence of calcareous soils. Near the western borderline (the "western" or "ferrous" region) the iron and its accompanying elements (Co, Cr, Ni) are accumulated in the surface formations. These elements originate from the basic and ultrabasic rocks of the Alpine Belt. In the floodplain sediments of rivers originating from the mining areas and some industrial centres of Transylvanian (the "eastern" or "industrial" region) we can find characteristic Ag–Au–Cd–Pb–(Cu–Zn) anomalies in the floodplain sediments in the lower sections of water courses; here also the Hg content of the samples were higher. Mercury probably originates from the low-to-medium–temperature hydrothermal ore deposits.

The „main" and the „western" regions fit into the above outlined image of the continent. Heavy metal contamination primarily occurs in the eastern geochemical region, on the floodplains of larger rivers. In the „middle" region intensive soil calcification occurs; carbonate minerals precipitated in the intergranular pores displace all mobile nutrient elements; the soils of the region (representing one quarter of the area of Hungary) can be characterised by extreme nutrient deficiency.



1 – “main” geochemical region;
2 – “middle” geochemical region;
3 – “western” geochemical region;
4 – “eastern” geochemical region;
5 – boundary of drainage basins;
6 – drainage areas beyond the country's border;
7 – distribution of friable carbonate sediments on the surface

Figure 1. Geochemical regions of Hungary (after Ódor et al., 1997, corrected)

In Hungary, contrary to popular belief, the most important natural geological environmental problem is not toxic element contamination, but nutrient element deficiency. Significant problems in relation with minor element excess arise only in two regions: (1) the southern and eastern areas of the country, where arsenic accumulates in the young sediments and in the groundwaters; and (2) the "eastern" geochemical region, where too much cadmium is accumulated on the floodplains of large rivers used for agriculture.

There are a lot more regional problems related to nutrient element deficiencies: in the drinking waters mostly there is too little iodine and fluorine, in the calcareous soils of the middle region, copper and zinc, while in the other parts of the country, molybdenum and selenium. An essential mistake of the Hungarian legislation is that element excesses are treated as environmental problems, whereas element deficiencies are not counted with: the required minimum concentration levels — in contrast with the upper limit values — are not specified by law (Table 1.).

Table 1. Background element concentrations of several elements along with necessary amounts for plants

Element (mg/kg)	**necessary for plants**	**„main” region**		**„middle” region**		**„western” region**		**„eastern” region**	
		from	**to**	**from**	**to**	**from**	**to**	**from**	**to**
As	—	< 2.5	19	< 2.5	(57)	5.8	13	5.4	22
Cd	—	< 0.5	1.5	< 0.5	3.4	< 0.5	< 0.5	< 0.5	10.4
Mo	0.5	< 0.2	2.7	< 0.2	2.8	< 0.2	1.2	< 0.2	< 1
Cu	8	8.5	42	5.5	33	18	32	21	103
Zn	40	32	150	14	180	69	96	100	600

Problems of the pollution limit values are discussed in details in our other article (Fügedi et al., 2015).

Toxic element contaminations and essential element deficiencies in Hungary

Toxic element contaminations: As, Cd

Arsenic-contaminated drinking water is the most known natural geological environmental problem of Hungary (Fig. 2 and 3), thus the behaviour of arsenic in natural media is well-studied. Csalagovits (1999) showed, that in the more arid parts of the Carpathian Basin the arsenic binds to the iron hydroxides (bog iron, limonite patches) of superficial formations.

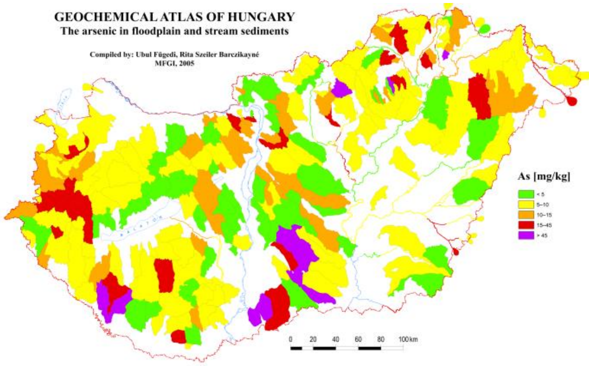


Figure 2. The arsenic in floodplain and stream sediments. (FOREGS – Geochemical Atlas of Europe)

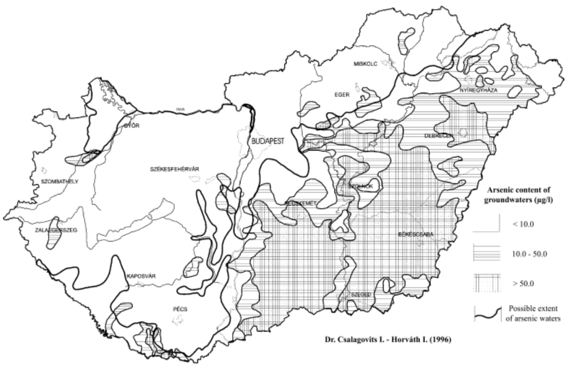


Figure 3. Arsenic in drinking waters (after Csalagovits, 1999)

As these sediments are buried and get below the water level, the Fe^{3+} is reduced to Fe^{2+}; the limonite and the arsenic redissolves. Arsenic accumulation began in the ice age and it is still occurring.Similar processes are responsible for the mass arsenic poisoning in Bangladesh.

In natural systems cadmium occurs with zinc. That is the base of its toxicity: it takes the place of the enzyme-activator zinc — which is essential in all organisms —, but mostly does not perform its function (Takács, 2001). From out 2049 Cd analyses 75 (less, than 4%) exceed 1 mg/kg — they mainly occur in the eastern geochemical region, where, according to the cadastre of fertile soils, the best arable lands are situated. However, the trace elements

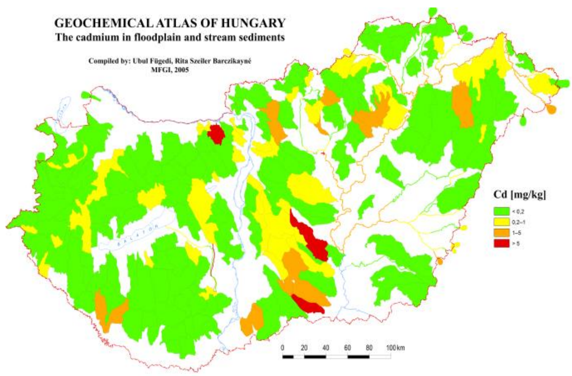


Figure 4. The cadmium in floodplain and stream sediments

were not counted with during the compilation of the cadastre. On the floodplains of the Körös Rivers, the Berettyó, the Szamos, the Kraszna, the Upper Tisza, the Túr and the Hernád (as well as on the Sajó under Kazincbarcika and on that of the Zagyva under the outfall of the Gyöngyös Stream) mining waste and smelting slag are mixed in the natural sediments. Ore mineral exploitation was initiated by the Romans in Transylvania; that of Upper Hungary, by the Árpád Dynasty. The upper 60 cm of the floodplain sediment series of the rivers is characterised by high content of Ag, As, Au, Cd, Cu, Pb and Zn. Crops cultivated on these lands are occasionally sent back due to their large cadmium content (the other toxic heavy metal of the group, the lead, is less mobile) (Fig. 4).
In the southern part of the Danube-Tisza Interfluve arsenic, cadmium and silver anomalies occur together. This interesting phenomenon still needs to be clarified.

Element deficiencies in the drinking waters: I, F

In the drinking waters of Hungary not only arsenic causes problems, but the fluorine and iodine as well. Their distribution is extremely fluctuating; mostly too low concentrations occur, but locally very high concentrations can be measured.

Government Decree No. 201/2001 on the quality control of drinking waters does not give limit values for the iodine; for the fluorine, it is 1.5 mg/kg.Fluorine is essential in the calcium-metabolism, for strengthening bones and preventing tooth decay (Olivares & Uauy, 2004). On most parts of the country the water has lower concentration than the optimal (about 1 mg/l).

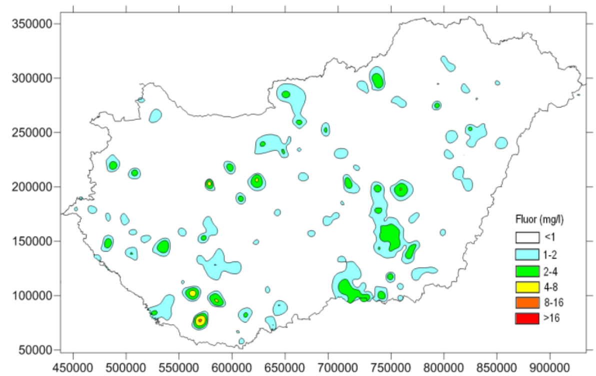


Figure 5. Fluorine content of Hungarian drinking waters (mg/l)

Around 98 % of the population does not get enough fluorine for the prevention of tooth decay. On the fluorine concentration map of the drinking waters of Hungary (Fig. 5) it is striking, that on most parts of the country the fluorine is critically low; locally (mainly in the southern part of the Transdanubian Region), however, it greatly exceeds the pollution limit value.

The iodine concentration map is structurally similar (Fig. 6) - with the only difference, that high values occur along the southwestern country border and in the southern part of the Great Plain. Based on urinary iodine concentrations, Hungary belongs to those countries where mild iodine deficiency occurs (50-99 μg/l, instead of the optimal 100-199 μg/l) (de Benoist et al., 2004).

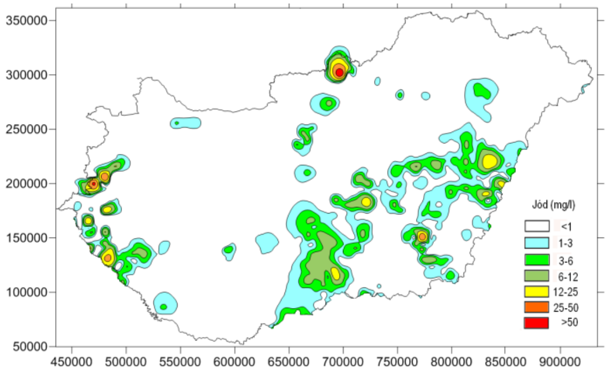


Figure 6. Iodine content of Hungarian drinking waters

The main factor responsible for iodine deficiency is a low dietary supply of iodine. It occurs especially on such areas, where the soils have low iodine concentrations. Crops grown in such soils, therefore, do not provide adequate amounts of iodine.

Essential element deficiencies in alkaline soils: Cu, Zn

Both the copper and zinc are well-known bioessential elements: every group of organisms require them as basic enzyme-activators; moreover, they are essential in many other processes as well.

Deficiency diseases primarily occur in plants; their increase is the main task of soil fertilizing. For most arable crops the necessary amount of copper is 8 mg/kg, that of the zinc is 40 mg/kg. These values were determined at the end of the 1980s (Szabó S. A. et al., 1987). Despite all of this, in the environmental legislations lower limit values are not determined, neither for these two elements, nor for other bioessential elements.

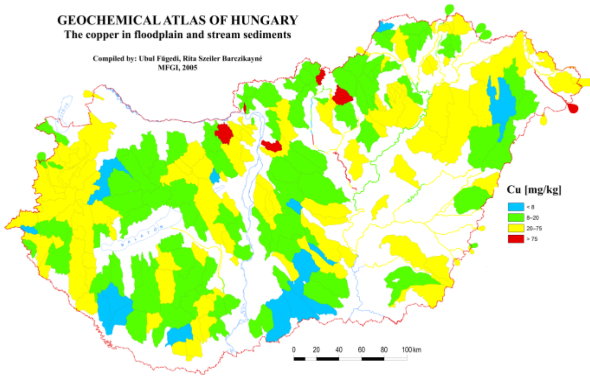


Figure 7. The copper (mg/ kg) in floodplain and stream sediments

However, upper limit values are set as 75 and 200 mg/kg (6/2009), even though no data is known from Hungary on toxic copper and zinc contamination of soils.In our samples the distribution of copper is near-lognormal. The concentrations (Fig. 7) are lower in the middle geochemical region than in the other parts of the country. From 2050 analytical record 911(!) does not reach 8 mg/kg — nearly half of the area of the country can be characterised by copper deficiency.

The western geochemical region seems to be well supplied by copper, while in the eastern geochemical region its concentration values regularly exceed the “B” limit values. Other anomalies occur under non-ferrous ore mines (Recsk–Parád, Gyöngyösoroszi) and around heavy industry centres (Budapest, Salgótarján). Some of the higher concentrations indicate Miocene post-volcanic processes. The lowest measured concentration of the copper was less than 0.2 mg (in stream sediments), 1–2% of the necessary amount. The large, uninterrupted areas of the main and middle geochemical regions, mainly the sandy soils of the Danube-Tisza Interfluve Ridge, can be characterised by definite copper deficiency.

Zinc is the most abundant non-ferrous metal; in natural soils, its regular concentration is 10–300 mg/kg (Takács, 2001). Its distribution, differently from that of other non-ferrous metals, is near-symmetric, though with long "tails", stretching towards positive values. It is the consequence of the heterogeneity of the background. Due to the diverse utilizations large concentration may occur everywhere, but typically they occur in three environments:

- on the eastern geochemical region;
- in water courses under the Mátra;
- around Budapest.

The recommended 40 mg/kg is not reached by 417 samples out of 2045. Ca. one quarter–one third of the area of Hungary can be characterised by zinc deficiency; mainly the middle geochemical region (Fig. 8). There are no such soils in Hungary, in case of which the zinc concentration would be so high, that it would cause environmental problem; toxicosis practically occurs among workers working with hot zinc metal (non-ferrous metallurgists, welders).

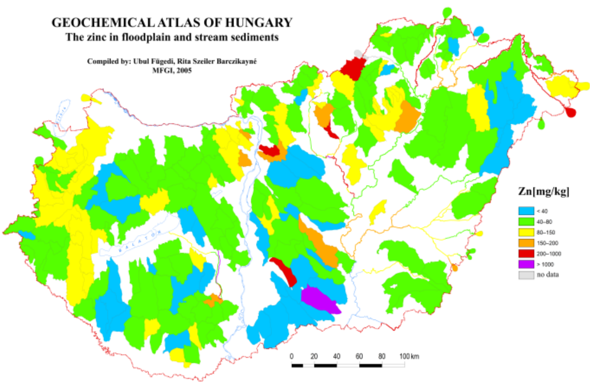


Figure 8. The zinc (mg/kg) in floodplain and stream sediments

Mainly sand-soils are characterised by copper and zinc deficiency; loams are better supplied. It seem reasonable to set lower limit values for the copper and zinc content of soils and promote improvement of soils in which the copper and zinc is lower than the recommended minimum concentrations. Copper and zinc deficiency problems could also be treated with the tailings of ore mining (e.g. Gyöngyösoroszi) and the slags of non-ferrous metallurgy (e.g. Metallochemia). These materials are currently considered to be hazardous waste. Using the tailings of ore mining to improve the sand–soils of Middle Hungary would be optimal all the more, since the sulphuric acid (forming due to the decomposition of the sulphide minerals) would reduce the pH of the soils, and at the same time, the weathering and the fine-grained flotation tailing could improve the grain size as well.

Essential element deficiencies in non-alkaline soils: Mo, Se

Both the molybdenum and the selenium are anion-forming elements; in the different ecological systems they mainly occur in the form of molybdata and selenium. These dissolve well in alkaline environment, but acidic soils bind them — mainly on iron and aluminium oxyhydroxides.

The molybdenum is the metal component of different enzymes in plants; the mechanism of action is based on the MoV-MoVI transition. No spontaneous Mo deficiency has been observed in humans so far. In Hungary the lack of the element affect plants on quite large areas (Fig. 9). Symptoms of molybdenum deficiency in plants include nitrogen shortage, yellowing of older leaves, interveinal chlorosis, leaves, rolling-up of leaf margins, twisted leaves, and stunted plant growth (Hewitt, 1956). Molybdenum causes also yield decline and quality deterioration (Radics (ed.), 1994). Too much molybdenum could cause gout-like symptoms, thus the metal is considered toxic. The molybdenum ion binds on the adsorption complex of the soils; its uptake is facilitated by the carbonate content. On "normal" soils the Mo content ranges between 0.5 and 10 mg/kg. In the examined stream sediment samples the molybdenum concentration exceeded 0.6 mg/kg only in 94 cases; the country can be characterised by molybdenum deficiency. Molybdenum deficiency is not really typical in the middle geochemical region; it mostly occurs in other parts of the country. The outlier, >2 mg/kg concentrations, however, primarily occur in the Zemplén Mountains.

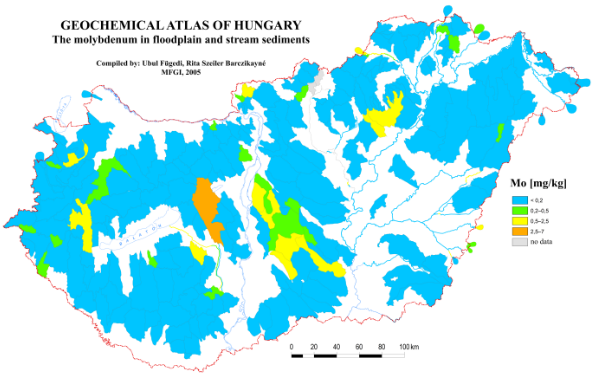


Figure 9. The molybdenum (mg/ kg) in floodplain and stream sediments

Selenium is toxic in large doses, but it is an essential element for humans and animals. It normally acts as an antioxidant. Selenium has been implicated in the protection of body tissues against oxidative stress, maintenance of defences against infection, and modulation of growth and development (McCormick, 2001). Its uptake depends on the pH: alkaline soils are considered selenium-deficient only under a concentration of 0.005 mg/kg. Acidic soils on the other hand, from 2 mg/kg. Hungarian legislation does not take into account this fact; selenium is shown as a toxic element and the pollution limit value is set as 1 mg/kg. Limit values of the selenium is reasonable to be regulated taking into account also the pH of soils.

Due to their anion-forming characteristics, molybdenum and selenium deficiencies are not practical to be treated with tailings and the slags of non-ferrous metal industry (with the exception of extreme alkaline soils), since these materials have acidifying properties. The optimal solution would be using alkaline red mud. As the experiences of other EU countries show, this is the only currently known economic utilization of the material. In Finland, selenium deficiencies have been reduced with sodium selenate (Stranges S. et al., 2011).

Uniforming soils — destroying species

If bioactive element concentrations are limited in every soil, it could cause mass destruction of species; the diversity of habitats is a criterion of the diversity of species. The so-called bioindicator plants are oppressed by more viable species on "normal soils". They prefer soils which are toxic for most plants. Such soils are formed on the secondary dispersion halos of surface ore deposits. Since these all have been exploited, the bioindicator plants moved to the tailings and other contaminated areas — the remediation of these sites would deprive these species from their last habitats. Some species adapted to such special conditions (Hawkes & Webb, 1962):

- copper — Gypsophila patrini, Polycarpea spirostylis, Acrocephalus roberti, Elsholtzia haichowensis;
- iron — Clusia rosea;
- lead — Erianthus giganteus;
- selenium — Astragalus bisulcatus, A. racemosus, A. pectinatus, Aster venustus;
- silver — Eriogonum ovalifolium;
- zinc — Viola calamineria (lutea).

These habitats (for example the flotation tailing at Gyöngyösoroszi) in Hungary are recultivated — in accordance with regulations. The rich, natural flora (Fig. 10) is eliminated and the "hazardous waste" is covered with protection layer.

Figure 10: One-time (before recultivation) grove on the flotation tailing at Gyöngyösoroszi (Lake Alsó)

Conclusion

As our research showed, the most important natural geological environmental problems of Hungary are not element excesses but element deficiencies.

The current system of the Hungarian legislation is deficient from several aspects. It would be rational to take into account the actual natural concentrations and to determine lower limit values since on most parts of the country soils can be characterised with element deficiencies. These deficiencies, on the other hand, could be treated with materials which are currently considered to be "hazardous waste".

Moreover, exaggerating contaminations could hit back: environmental protection should preserve the special habitats of the contaminated areas not destroy them.

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