CHAPTER 3

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TRACE ELEMENTS IN THE ENVIRONMENT OF MOLDOVA

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The purpose of this chapter is to analyze the content and ratio of trace elements in the components of the environment of Moldova: soil forming rocks, soils, waters, sediments, plants. It is established that the nature of the distribution of trace elements in soil-forming rocks, soils, waters and plants has its own characteristics. The ratio of trace elements in the ecosystems of Moldova is mostly optimal, since there are no noticed antagonistic reactions between the elements. Biogeochemical provinces of I, Co, Zn, Cu, Mn, F have been identified on the territory of Moldova, but this aspect requires clarification. Modern research shows the complex nature of migration and distribution of trace elements in ecosystems. Therefore, further studies of trace elements should cover all components of the environment and trace the migration of chemical elements in the system: soil forming rock – water – soil – plants – fungi – animals – the human body.

Keywords: *Trace elements, Soil forming rocks, Soils, Waters, Sediments, Plants, Ecosystem, Migration.*

INTRODUCTION

Modern biogeochemistry studies the elemental composition of living matter, geochemical processes involving organisms, the interaction of biota with the geochemical environment and the geochemical functions of the biosphere (Ermakov et al., 2018, p.11). It is important in biogeochemistry to understand the interrelation of biogeochemical and geochemical processes and the very close interrelation of all environmental components (Kapitalchuk M. 2021). Of course biogeochemical processes are very complex since they are not limited to the exchange with the environment of chemical elements of an individual organism or species. The study of the processes of mass transfer of chemical elements is important both at the global level and at the regional level, because each ecosystem has its own regional distinctive features (Kapitalchuk & Kochurov, 2022). Biogeochemical studies in Moldova had their beginning in 1938 and they began from the study of the influence of copper on plant growth. During the Soviet period of development in Moldova, much attention was paid to trace elements in agriculture (Toma, 1973; Toma et al., 1980). Biogeochemical and medico-geographical zoning was carried out (Bumbu, 1981; Feldman, 1977). The study of chemical elements gradually covered all the diverse aspects of modern biogeochemistry (Microelementele, 2016).

In the XXI century, studies of trace elements in Moldova began to be conducted on the basis of a systematic approach, covering all components of the environment: soil-forming rocks, soils, waters, sediments, plants, animals, humans (Kapitalchuk M., 2018; Kapitalchuk I. et al., 2020). Much attention was paid to the vital element – Se, about which very little information was available during the Soviet period (Kapitalchuk M. et al., 2020). Much attention has been paid to both natural and anthropogenic ecosystems (Izmailova et al., 2005; Kapitalchuk I. et al., 2012; Kapitalchuk I. et al., 2013). The object of the study was not only domestic, but also wild animals (Kapitalchuk M. et al., 2019). The role of insects in the biogenic cycle of Se was also investigated (Golubkina et al., 2014).

The studies covered not only water, soil, plants, but also food and the human body (Golubkina et al., 2009; Kapitalchuk M. et al., 2011; Kapitalchuk M. et al., 2014a). Migration of selenium in aquatic and terrestrial ecosystems was studied (Kapitalchuk I. & Kapitalchuk M., 2009; Kapitalchuk I. et al., 2011; Golubkina et al., 2012; Kapitalchuk M. et al., 2013; Kapitalchuk I. et al., 2018). Within the framework of one chapter, it is impossible to make a detailed analysis of the results in all areas of biogeochemical research accumulated over more than 80 years. The purpose of this work was to analyze the accumulated material on the research of trace elements in Moldova. The main task of the author was to analyze the content and ratio of trace elements in the components of the environment: soil forming rocks – soils – waters – sediments – plants of Moldova.

GEOCHEMICAL FEATURES OF MOLDOVA

The migration and concentration of chemical elements in ecosystems are significantly influenced by the geochemical conditions of the territory. Located on the border of forest-steppe and steppe in Moldova, the range of variation from balanced to deficient atmospheric humidification caused the formation of a wide range of ecosystems, differe in nature and intensity of all types of migration of chemical elements (Kapitalchuk M. & Kapitalchuk I., 2010).

The change of geochemical conditions and types of zonal ecosystems occurs here in both directions from north to south, and under the influence of the relief, the absolute marks of which cover the interval from 0 to 430 meters above the sea level. A variety of soil forming rocks, which are clays, loams and loess-like loams of various mechanical composition, as well as sandy loams, alluvial and alluvial-deluvial sediments, limestones and pebbles, also contribute to the differentiation of geochemical conditions of Moldova. The dominant role in this case belongs to light clays and heavy loams in the northern part of the country, and heavy loess-like loams in the southern part.

As a result of the interaction of climatic factors, lithogenic basis and living organisms in conditions of rugged terrain on the territory of Moldova, which has a length from north to south just 350 km and from west to east – 150 km, an inhomogeneous soil cover was formed here, which reflects the specific features of the biogeochemical processes that took place here. The composition of the soil cover of this country includes several zonal types of soils and their subtypes (Atlas of soils of Moldova, 1988): Cambisols, Humic Luvisols, Luvic Chernozems, Haplic Chernozems, Xeric Chernozems, Humic Gleysols. Azonal soils in Moldova are represented by deluvial soils formed under forest or meadow-forest vegetation, deluvial meadow-chernozem soils, meadow soils that were not formed in the floodplain of the river, alluvial soils, salt marshes (steppe, meadow and meadow-marsh). Despite of such a significant soil diversity, chernozems have become the most widespread in Moldova, which contain about 70% of its territory.

The criteria for the allocation of geochemical landscapes are well defined today, and the biogenic migration of chemical elements largely depends on geochemical conditions. Therefore, when conducting systematic biogeochemical studies, it is necessary to distinguish ecosystems within the boundaries of geochemical landscapes. According to the geochemical classification presented by A.I. Perelman (1975) cultural geochemical landscapes predominate in Moldova, and indigenous biogenic landscapes have been preserved only in fragments. Of total destruction conditions of natural vegetation, the boundaries of the distribution areas of soil types often serve as a reference point for determining the spatial boundaries of biogenic geochemical landscapes (ecosystems) that existed in this territory before their transformation into a cultural landscape.

According to the ratio of biomass and annual production, the geochemical landscapes of Moldova belong to two groups – forest (I), steppes and meadows (II). The division of landscapes on the territory of this country into lower taxa was performed by E.S. Feldman (Atlas of the Moldavian SSR, 1978, pp. 77-80; Feldman, 1977). Within Moldova, E.S. Feldman identified five types of geochemical landscapes: 1) European forest type, including two families – forest on Camsoils with hornbeam-oak forests with beech and forest on Humic Luvisoils with hornbeam-oak forests; 2) forest–steppe type consisting of one family - meadow chernozem steppe on Luvic Chernozems and Haplic chernozems; 3) steppe type, also represented by one family – grass chernozem steppe on Xeric chernozems; 4) meadow type with a family of floodplain meadows of the steppe zone and 5) swamp type with a family of southern grassy marshes.

On the territory of Moldova, the main limiting factor in the spread of various zonal types of landscapes is moisture availability (Kapitalchuk M. & Kapitalchuk I., 2010; Kapitalchuk I. & Kochurov, 2022). In particular, territories with balanced atmospheric humidification correlate with forest landscapes, forest-steppe landscapes are formed in conditions of weakly deficient atmospheric humidification, areas with deficient humidification are occupied by grass-grass steppes, the extreme low values of this humidification range approach the conditions of dry steppes.

According to E.S. Feldman (Atlas of the Moldavian SSR, 1978, pp. 77-80; Feldman, 1977) geochemical landscapes of Moldova are divided into the following classes: 1) transitional from acidic to calcium (H^+–Ca^{2+}), 2) carbonate (Ca^{2+}), 3) carbonate-gley (Ca^{2+}–Fe^{2+}), 4) calcium-sodium (Ca^{2+}–Na^+), 5) salt-gley (Ca^{2+}–Na^+–SO_4^{2-}–Cl^-–Fe^{2+}). The landscapes of the calcium and transition from acid to calcium class have become widespread here. The remaining classes have limited local distribution.

According to the classification of geochemical landscapes according to the genera of A.I. Perelman (1975) landscapes of the second kind prevail in Moldova, since the territory belongs to the crossed erosion-denudation plains. Geochemical landscapes of the third kind are common in the conditions of the low-mountain and highly hilly relief of the Moldavian woods (Codru). Some areas in the extreme South and South-East of Moldova with poorly dissected relief can be correlated with landscapes of the first kind. The signs for distinguishing the types of geochemical landscapes are numerous. Nevertheless, today it is clear that these signs are associated with the soil forming rocks of soils. The problem lies mainly in the geochemical classification of the soil forming rock (Perelman & Kasimov, 1999). E.S. Feldman based the selection of landscape species on the type of the parent rock and then combined the selected species into groups depending on their age and position in the relief. Thus, 12 groups of types of geochemical landscapes were identified on the territory of Moldova (Feldman, 1977, pp. 83-85).

Natural waters are an important indicator of geochemical conditions and the ecological status of chemical elements in landscapes. Despite the small size of the territory, the chemical composition of the surface waters of Moldova is diverse. Sulfate-calcium-sodium waters with a mineralization of 1000-2000 mg/l are common in the main part of the Dniester-Prut interfluve. Bicarbonate-magnesium-sodium waters with a mineralization of 500-1000 mg/l are characteristic of the woods of Codru and the northern regions of Moldova. In the Dniester valley, bicarbonate-calcium waters with a mineralization of 200-500 mg/l prevail, and in the left-bank Transnistria, the same waters with a mineralization of 500-1000 mg/l. In the south of the country, in the basin of small rivers, where sulfate-sodium-calcium and sulfate-chloride-sodium waters are common, mineralization can reach up to 2000-5000 mg/l (Atlas of the Moldavian SSR, 1978). Thus, the territory of Moldova is characterized by a significant variety of geochemical conditions that determine the features of the migration of chemical elements in the ecosystem formed here.

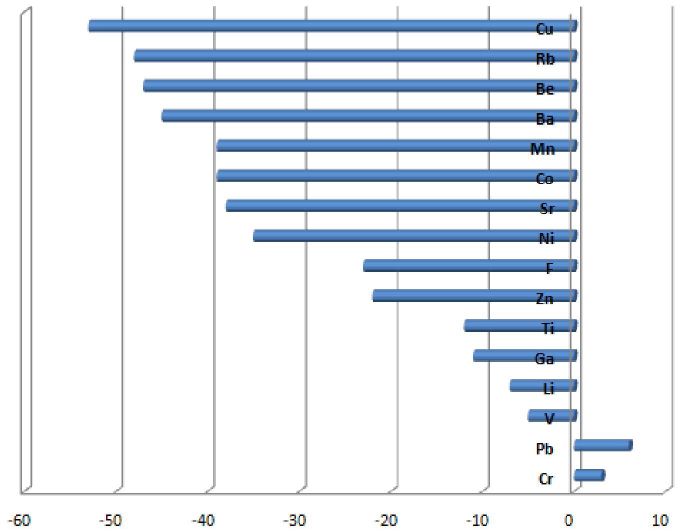
FEATURES OF THE DISTRIBUTION OF TRACE ELEMENTS IN SOIL FORMING ROCKS AND SOILS

The initial link in the biological cycle of trace elements in the ecosystem is the soil. The content of chemical elements in the soil is initially determined by their quantity and ratio in the soil forming rock. Despite the diversity of the soil-forming rocks of Moldova, it turned out that these lithological and genetic groups differ little in the content of trace elements. The greatest amount of trace elements is contained in clays and organogenic sediments, and their lowest content is inherented in sands, sandstones and limestones. At the same time, in Moldova, the well-known dependence of the content of elements on the granulometric composition of soil forming rocks is clearly manifested.

Regional geochemical features of the territory can be represented by correlating the average content of chemical elements in its soil forming rocks with their clark in the lithosphere according to A.P. Vinogradov (1957). Thus the soil forming rocks of Moldova contains trace elements (average values): Ba (360 mg/kg), Be (2.0 mg/kg), Co (11 mg/kg), Cu (22 mg/kg), F (510 mg/kg), Mn (610), Li (30 mg/kg), Ni (38 mg/kg), Rb (78 mg/kg), Sr (210 mg/kg), Ti (4000 mg/kg), V (86 mg/kg), Zn (65 mg/kg). The content of these trace elements in the soil forming rocks of Moldova is less than the clark of these elements in the lithosphere. The content of trace elements (average values) is also observed in the soil forming rocks of Moldova: Ag (0.35 mg/kg), B (65), Cr (86 mg/kg), I (3.1), Mo (3.1 mg/kg), Pb (17 mg/kg), Sn (5.4 mg/kgkg), Zr (440 mg/kg). The content of these trace elements in the soil forming rocks of Moldova is greater than the clark of these elements in the lithosphere (Kirilyuk, 2006; Toma et al., 1980; Kapitalchuk I. & Kapitalchuk M., 2020).

In the soil forming rocks of Moldova the average values of Cu, Rb, Be, Ba, Mn, Co, Sr, Ni are more than 30% less than the clark of these elements in the lithosphere. The average values of Li, V, Pb, Cr are close to the clark of these elements in the lithosphere (Figure 1).

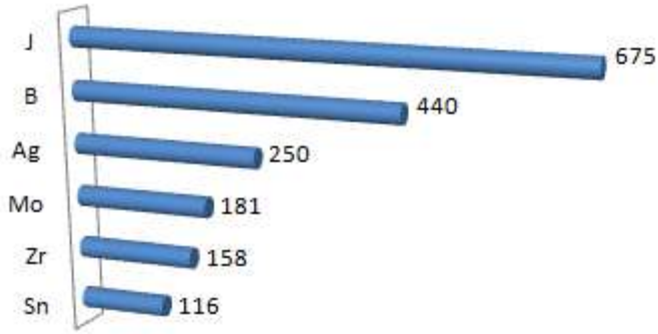
Figure 1. The ratio of the average values of trace elements in the soil forming rocks of Moldova with the clark of these elements in the lithosphere according to A.P. Vinogradov



	Cr	Pb	V	Li	Ga	Ti	Zn	F	Ni	Sr	Co	Mn	Ba	Be	Rb	Cu
%	3	6	-5	-7	-11	-12	-22	-23	-35	-38	-39	-39	-45	-47	-48	-53

However against the background of the low content of Cu, Rb, Be, Ba, Mn, Co, Sr, Ni in the soil-forming rocks of Moldova, there are significant exceedances of the average values of I, B, Ag, Mo, Zr, Sn relative to their clarks in the lithosphere (Figure 2).

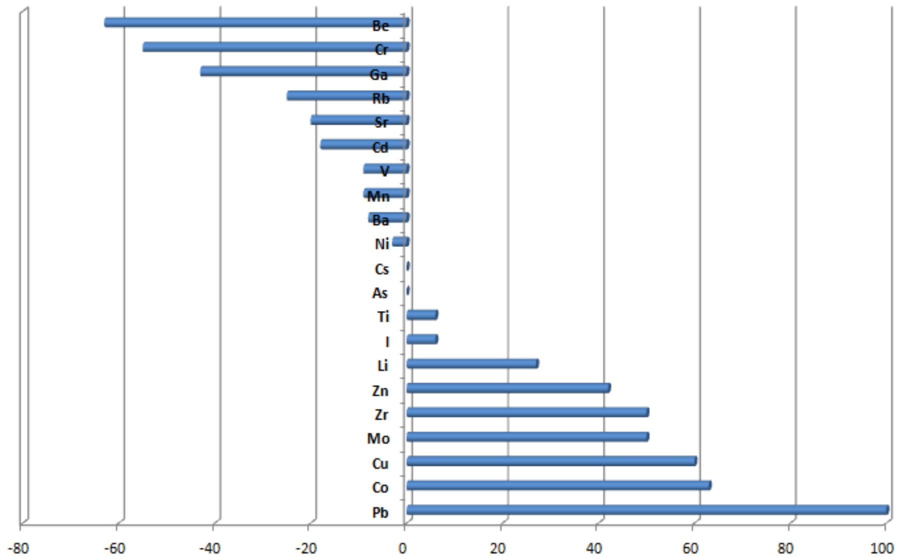
Figure 2. Excess (%) of the average values of trace elements in the soil forming rocks of Moldova with the clark of these elements in the lithosphere according to A.P. Vinogradov



A similar comparison of the average content of trace elements in the soil cover of Moldova with their clark in soils according to A.P. Vinogradov (1957) showed that in the soils of this country, the average values of some trace elements are higher than the clark set for soils. These are the following trace elements: Ag (0.5 mg/kg), B (70 mg/kg), Co (13 mg/kg), Cu (32 mg/kg), F (485 mg/kg), Hg (0.19 mg/kg), I (5.3 mg/kg), Li (38 mg/kg), Mo (3.0 mg/kg), Pb (20 mg/kg), Sb (2.0 mg/kg), Ti (4900 mg/kg), Zn (71 mg/kg), Zr (450 mg/kg). At the same time there is a reduced content of the following trace elements in the soils of Moldova (average values): Ba (460 mg/kg), Be (2.2 mg/kg), Cd (0.41 mg/kg), Cr (91 mg/kg), Ga (17 mg/kg), Mn (790 mg/kg), Ni (39 mg/kg), Rb (75 mg/kg), Sr (240 mg/kg), V (91 mg/kg), which is lower than the clarks established for soils of the corresponding trace elements (Kirilyuk, 2006; Toma et al., 1980; Leah, 2013; Kapitalchuk I. & Kapitalchuk M., 2020).

The average values of Be, Cr, Ga, Rb, Sr, Cd in soils are noticeably less than clark for soils, but these elements are not vital for biota. It is important to note that the average values of biogenic trace elements in the soils of Moldova exceed the clarks (according to A.P. Vinogradov) of these elements for soils. Mn is a vital element for plants and animals, however, the average value of this element in soils is not significantly lower than clark (Figure 3).

Figure 3. The ratio of the average values of trace elements in the soils of Moldova with the clark of these elements in soils according to A.P. Vinogradov

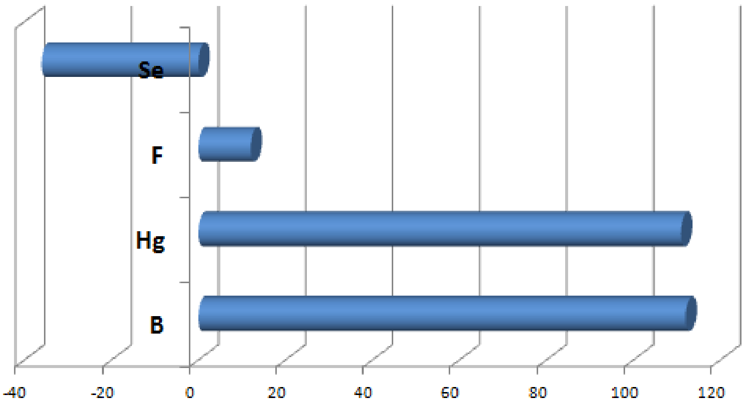


	Pb	Co	Cu	Mo	Zr	Zn	Li	I	Ti	As	Cs	Ni	Ba	Mn	V	Cd	Sr	Rb	Ga	Cr	Be
%	100	63	60	50	50	42	27	6	6	0	0	-3	-8	-9	-9	-18	-20	-25	-43	-55	-63

Figure 3 does not show elements for which there is an excess of average values relative to clarks for soils by several times. The average values in the soils of Moldova are F 2.5 times, Ag 5 times, B 7 times, Hg 19 times, and Se 25 times more clarks of these elements for soils according to A.P. Vinogradov (1957). But if the average values of these elements are compared with the average values of the authors H.T. Shacklette & J.G. Boerngen (1984), then this ratio looks quite different (Figure 4). The average value of F is comparable, the excess of B and Hg has significantly decreased, and the content of Se is even less than the average values according to H.T. Shacklett & J.G. Boerngen (1984).

Comparative analysis shows that for some elements an increased (Ag, B, I, Mo, Pb, Zr) or a reduced (Ba, Be, Mn, Ni, Rb, Sr, V) average content relative to the corresponding clarks is observed both in the soil forming rock and in the soil. There is no such match for other elements. For example the amount of Cr in the soil forming rocks of Moldova is on average higher than clark in the lithosphere, and in the soil cover it is less than clark for soils. Conversely, the content of Co, Cu, F, Li, Ti, Zn in the soil forming rocks is less than clark in the lithosphere, and the content of these trace elements in soils is more than clark for soils.

Figure 4. The ratio of the average values of trace elements in the soils of Moldova with the average values of these elements in soils according to H.T. Shacklette & J.G. Boerngen



	B	Hg	F	Se
%	112	111	12	-36

At the same time the content of trace elements in soils is generally higher than in soil forming rocks. In the soils of Moldova, on average, the greatest excesses relative to the soil forming rocks are observed for I (71%), Cu (45%), Ag (43%), Mn (30%), Ba (28%), Ti (22%), less significant – for Co (18%), Pb (18%), Sr (14%), Be (10%), minor – for Zn (9%), B (8%), V (6%), Ni (3%), Zr (2 %). A decrease in the average content in the soil relative to the soil forming rocks was found for the elements: F (10%), Rb (4%) and Mo (3%).

On the territory of Moldova, geochemical conditions typical of the steppes are fully manifested (Dobrovolsky, 2003; Perelman, 1975; Perelman, Kasimov, 1999): slightly acidic, neutral and slightly alkaline environment, the presence of poorly soluble humic acids, a significant amount of organic colloids, high absorbing capacity of chernozems, non-washing water regime, which cause a low intensity of migration of many metals and other chemical elements. Thus, a high concentration (10-100 times higher than in soil) of Ag, Co, Cu, Mo, Ni, Pb, V, Zn was found in the ash of humic acids (Kirilyuk, 2006).

Due to the low mobility of many chemical elements, the content of their gross forms in soils gives only an approximate idea of the availability of trace elements available to plants. To determine the mobile forms of metals in the soil, an acetate-ammonium buffer pH = 4.8 and an aqueous extract for F and I have been used in Moldova for about 50 years. It considers that mainly water-soluble compounds and easily exchangeable ions pass into these extracts.

According with the norms adopted in Moldova for the provision of agricultural plants with mobile forms of elements, the following trace elements get into the category of low security: B (1.4 mg/kg), Mn (24 mg/kg), Cr (0.91 mg/kg), Pb (0.40 mg/kg) and in the category of medium security – Cu (1.6 mg/kg), F (7.4 mg/kg), I (0.53), Mo (0.15 mg/kg), Co (1.3 mg/kg), Ni (0.80 mg/kg), Zn (4.4 mg/kg). Significant areas of land may also belong to the category with a very low content of mobile forms of Mn, Zn and Cu (Kirilyuk, 2006). Thus the content of mobile forms of many trace elements in the soils of Moldova is not able to fully contain the needs of plants, which is confirmed by many years of experience in the use of micronutrients, which give a positive effect in the form of increasing the yield and quality of crops (Toma, 1973; Toma et al., 1980; Microelementele, 2016).

Considering the needs of agriculture the closest attention of Moldovan researchers was attracted primarily by Cu, Zn, Ni, Co, Mo, I. Extensive material has been accumulated for these trace elements and maps of their spatial distribution in soils and soil forming rocks have been compiled (Atlas of the Moldavian SSR, 1978; Bumbu, 1981).

FEATURES OF ACCUMULATION OF TRACE ELEMENTS BY PLANTS

The most important link in the biological cycle of chemical elements are plants, among which some families or specific species selectively concentrate certain trace elements. Thus in the conditions of Moldova, some families show the ability to accumulate trace elements: *Leguminosae* – Mo and V; *Solanaceae* – Li, B, Co, I; *Rosaceae* – Ag, Cu, Mn, Pb, Sr; *Vitaceae* – Co, Cu, Pb. It is also noted that sunflower accumulates Zn well; corn – Ba and F, sugar beet – Ti; cabbage – Mo, and tobacco – Cr, Cu, F, Ni, V, Zn, Zr. Among wild grasses that can be weeds, families and subfamilies can be distinguished that are characterized by an increased content of certain trace elements: *Leguminosae* – Cu, Mo, Ni, Pb, V; *Amaranthaceae* – B, Ba, Co, Cr, Pb, Ti; *Chenopodioideae* – Ba, Pb, Zn; *Umbelliferae* – Fe, Al, Mn, Cu; *Cyperaceae* – Ag, Mn, Ni; *Euphorbiaceae* – Co, Sr; *Lamiaceae* – Ni, Zn; *Brassicaceae* – Co. A comparative analysis of the content of trace elements in agricultural plants of Moldova with the former Soviet republics was carried out. It turned out that agricultural plants grown in geochemical conditions of Moldova contain more Cr, Cu, F, Fe, Li and less content of I, Pb, Sr, V, Zn than plants from the former Soviet republics (Kirilyuk, 2006).

These results are for Cu, F, Li, Pb, Sr, V well correlated with the regional geochemical situation. But for the rest of the elements, the correlation to the geochemical situation is not traced. As it was mentioned above the average gross content of Cu, F, Li in the soil cover of Moldova exceeds the corresponding clarks for the soil. In addition, the soils of Moldova have an average availability of mobile forms of these elements. Thus the increased content of Cu, F, Li in the soil relative to clarks for soils and the normal provision of soils with mobile forms provides a regionally increased concentration of these trace elements in plants.

At the same time an increased regional content of Cr in plants was revealed in conditions of its increased content in soil forming rocks (relative to clark in the lithosphere), but a reduced content in the soil cover (relative to clark for soils to A.P. Vinogradov) and low availability of mobile forms of this trace element in soils. But if the average Cr content in the soils of Moldova is compared with the average content of this element in the soils according to H.T. Shacklette & J.G. Boerngen (1984), then the Cr will be significantly less.

The reduced content of Sr and V in plants are good related with their low content in soil forming rocks and soils (below the corresponding clarks). Low accumulation of Zn and Pb in plants of Moldova occurs under conditions of relatively high their gross content in soils, but low provision of soils with mobile forms. Bioavailable forms of these elements are connected by insoluble humic acids and carbonates.

Weak accumulation of I in plants occurs against the background of its relatively high gross content in soil forming rocks and soils and high provision of soils with its mobile forms. The reasons for this discrepancy have not been clarified yet (Kapitalchuk M. et al., 2014a; Kapitalchuk, M. et al., 2018a). But mushrooms accumulate very well I. *Agaricus bisporus* grown in the Dniester floodplain accumulated 340 µg/kg of iodine, which was 3 times higher than the iodine content (110 µg /kg) in artificially grown *Agaricus bisporus* (Kapitalchuk M. et al., 2014a).

It is necessary to note another trace element, which has its own distribution characteristics in the components of the environment of Moldova. At the present stage of the development of science, special attention in Moldova is attracted by studies of the trace element Se. As a result of the analysis of 139 averaged samples (Kapitalchuk I. et al., 2014), a low and optimal Se content in soils was noted. The range of fluctuations ranged from 100 to 668 µg/kg, the average value was 246 µg/kg. The authors (Tan J. et al., 2002) propose the following gradations of Se in soils: less than 125 μg/kg – selenium deficiency region; 125 – 175 μg/kg – marginal insufficiency; 175 – 3000 μg/kg – optimum region; more than 3000 μg/kg excess area.

Based on the proposed gradations both optimal and deficient concentrations of Se (100 μg/kg) in soils take place on the territory of Moldova. But agricultural plants actively accumulate selenium from the soil in conditions of its low gross content (Kapitalchuk M. & Golubkina, 2008; Sheshnitsan et al., 2016). High concentrations of Se in the biota of Moldova especially in water are associated not so much with the provision of soils with this trace element, but with a high content of selenium in water bodies (Kapitalchuk M. et al., 2013).

A special position in ecosystems is occupied by the Fe, which belongs to the most common elements on Earth and is not a trace element in soils. But in living organisms, Fe is found as a trace element that is necessary for plants, animals and humans. The Fe content in the soils of Moldova varies from 12300 to 37700 mg/kg. According to authors from different regions of the world, the iron content in soils is 38000-40000 mg/kg (Ermakov et al., 2018, pp.64). Based on the global average data, it can be noted that the soils of Moldova have a low content of gross Fe.

In the plants of Moldova, researchers note a very wide range of iron concentrations from deficient to high (Kirilyuk, 2006; Kapitalchuk I. et al., 2020). The iron content in fungi, bee products and in animal and human biomaterials indicate a high availability of Fe in the ecosystems of Moldova (Kapitalchuk M. et al., 2014; Kapitalchuk M. et al., 2022). Thus the availability of biota with high concentrations Fe in the ecosystems of Moldova is not also related to the gross content of this element in soils. Probably the high content of Fe in biota is associated with high concentrations of Fe in surface waters, especially in the main waterway of the Dniester River (Kapitalchuk I. et al., 2012).

THE CONTENT OF TRACE ELEMENTS IN WATERS AND BOTTOM SEDIMENTS

Subaqual landscapes occupy just over 1% of the territory of Moldova. The main volume of runoff falls on the Dniester River (10.7 km^3/year) and the Prut River (2.9 km^3/year). The flow of small rivers is only about 1 km^3/year (Kazak, 2009). During the Soviet period, more than 3.5 thousand artificial reservoirs were built in Moldova on small rivers and temporary watercourses. But by 1990 the 1200 ponds had already disappeared, as the processes of silting up of reservoirs were actively taking place (Soil erosion, 2001).

Researching of a water body in an ecological aspect involves three main components: water mass, bottom sediments and biota. All components of water bodies are considered from the standpoint of hydrochemical hydrophysical and hydrobiological processes. Information about the content of trace elements in the water of the subaqual landscapes of Moldova is presented in numerous articles and generalizing monographs (Feldman, 1977; Bumbu, 1981; Kirilyuk, 2006; Microelementele, 2016). However, using such data, it should be remembered that hydrochemical parameters are very dynamic, their values vary significantly in time and space. Concentrations of trace elements in water also depend largely of the nature and magnitude in anthropogenic impact.

For example the 30-year period of observations of hydrochemical indicators in the Lower Dniester in the area of the town Bendery can be divided into three periods corresponding to different degrees of anthropogenic load on the river (Kapitalchuk I. et al., 2009): 1) 1984-1991. (the economic maximum is the period of steady excess of permissible norms of pollution with petroleum products and occasional excess of MPC – synthetic surfactants and Fe, 2) 1992-2000 (economic depression) – the period of compliance of water quality according to the considered indicators with the established standards, 3) 2001-2008. (recovery from economic depression) – a period of episodic excess of permissible standards of Pb, petroleum products and synthetic surfactants pollution. The Dniester water is characterized by a low metal content. On average, the Fe content in the Dniester for the period under review was 0.3 MPC, Cu – 0.007 MPC, Pb – 0.01 MPC.

Since 2000, there has been a tendency to increase Fe, Cu, Pb and F. In the Dniester water In 2001, 2002, 2005, 2018, cases of exceeding the established Pb limits with a maximum value of 2 MPC were observed. In the period 2010-2022, on average, the frequency of exceeding the MPC for total Fe in the Dubossary reservoir varied from 82.9 to 91.7%, and below the hydroelectric dam – from 75.7 to 93.3%. The location of the maximum frequency of Fe pollution at the entrance to the reservoir indicates a significant intake from the upper sections of the Dniester. An episodically fixed pollutant in the waters of the Dniester was Mn, for which MPC exceedances were detected in Dubossary town in 2014, in Tiraspol city in 2013 and in 2018, and in the area of Bendery town in 2013, 2014, 2019.

The greatest spatial variability is characterized by the concentration of Fe which fluctuated in the range of 0.17–11.13 MPC. However, high concentrations of Fe were found only in the Dniester River and the

Kuchurgan reservoir. The water bodies with low anthropogenic load, fed by local runoff, and in wells, the Fe content turned out to be quite stable and did not exceed 50 μg/l.

In distinction of Fe the greatest variations of Ni were observed in local water bodies and groundwater, but still the maximum average concentration of Ni (5.150 μg/l.) was recorded in the Kuchurgan reservoir, which is under the influence of thermal power plant. Wide fluctuations of Mn concentrations were recorded in the waters of the Dniester River (41-217 μg/l), the Kuchurgan reservoir (9-172 μg/l) and urban ponds (μg/l). In other water bodies, the amount of Mn remained stable and varied within the range of 48-58 μg/l. The Zn content in all water bodies of Moldova varied in a narrow range (7-33 μg/l). If abnormal values associated with local pollution are not taken into account, then low concentrations in surface waters of Pb (0.842 μg/l), Cd (0.042 μg/l), Cu (less than 1 μg/l) can be noted. Large concentrations of Se were observed in the waters of Moldova. The Se content in the waters varied in the range of 0.200–6.090 μg/l, and the average values were 1.831 μg/l for surface waters and 1.795 μg/l for groundwater (Kapitalchuk I. et al., 2012).

Table1. Content of elements (mg/kg) in sediments of water bodies and soil of the Dniester valleys

Fe	Mn	Zn	Cr	Ni	V	Cu	Pb	Se
Sediments								
3700–39600	17,0–5620	1,0–992	8–263	7–217	0,7–257	4–398	0,5–137	0,089–3,937
Soils								
12300–37700	150–2250	10–166	25–145	5–75	15–165	2–400	5–30	0,01–0,86

Source: Kapitalchuk I. et al., 2015.

An important depositing medium for chemical elements in subaqual landscapes are bottom sediments, which are of practical importance. Bottom sediments can be used as a meliorant to restore eroded soils. About 200-240 million tons of bottom sediments have accumulated in ponds, small rivers and temporary watercourses of Moldova. This amount of bottom sediments is sufficient for reclamation of 75 thousand hectares of washed away soils (Soil erosion, 2001). In this regard, the content of trace elements in the bottom sediments of Moldova was investigated (Kapitalchuk et al., 2015).

It follows from Table 1 that the upper limit of the range of variation of trace elements in bottom sediments exceeds similar limits for soils. According to some estimates (Kirilyuk 2006) from the list of trace elements considered here for Moldova, bottom sediments are contaminated with Mn, Cu, and Ni, sometimes they are contaminated with Cr and V, not contaminated with Zn and Pb. Despite significant discrepancies in the data on the amount of trace elements in bottom sediments obtained by different researchers for the territory of Moldova, it can be noted that the amount of trace elements in bottom sediments is greater than in the soils of the catchment area.

Bottom sediments of different water bodies differ in the content of elements. For example high concentrations of Fe, Mn, Zn, Cr, Cu are observed in sediments of small reservoirs and small rivers, Fe, Mn, V in the Dubossary reservoir and Ni, Cu, Se in the Kuchurgan reservoir. The amount of trace elements in sediments of water bodies in Moldova can be 20-25% higher than in soils in the catchment area.

Concentrations of Zn, Cu, Pb, Ni, Mo, V at the bottom sediments of the Kuchurgan reservoir are 2-7 times higher in comparison with soils. However in small water bodies located on the left bank of the Dniester River the metal content at the bottom sediments is usually less than their concentration in undisturbed soils. This difference for the corresponding elements is: Fe – 8%, Zn – 5%, Cr – 45%, Ni – 16%, V – 68%, Cu – 8%, Pb – 62%. Only the amount of Mn at the bottom sediments was 9% higher compared to the soils of the region. Thus the bottom sediments of water bodies on the territory of Moldova are an important source of trace elements for the restoration of washed away soils (Kapitalchuk I. & Kapitalchuk M., 2022).

THE INTERRELATION OF TRACE ELEMENTS OF ENVIRONMENT IN MOLDOVA

It is known that the normal functioning of a plant organism depends not only on the amount of biogenic elements in the external environment, but also on their ratio, which can cause antagonistic or synergistic interrelation between them. Antagonistic and synergistic interactions of elements in biota can cause chemical stresses. In this regard, the study of the ratio and interrelation of trace elements in the components of the environment and living organisms is an important aspect of biogeo-chemical research.

The ratio of trace elements in soil, plants (mg/kg) and water bodies (mg/l) of the ecosystems of Moldova is presented in the form of the following sequences (Kapitalchuk I. et al., 2011a):

- for local reservoirs

$n{\bullet}10^{-2}\,Mn > n{\bullet}10^{-2}\,Fe > n{\bullet}10^{-2}\,Zn > n{\bullet}10^{-3}\,Se > n{\bullet}10^{-3}\,Cu > n{\bullet}10^{-5}\,Cd$;

- for the Dniester River

$n{\bullet}10^{-1}\,Fe > n{\bullet}10^{-1}\,Mn > n{\bullet}10^{-2}\,Zn > n{\bullet}10^{-3}\,Se > n{\bullet}10^{-3}\,Cu > n{\bullet}10^{-5}\,Cd$;

- for soils

$n{\bullet}10^{4}\,Fe > n{\bullet}10^{2}\,Mn > n{\bullet}10^{1}\,Zn > n{\bullet}10^{1}\,Cu > n{\bullet}10^{-1}\,Cd > n{\bullet}10^{-1}\,Se$;

- for plants

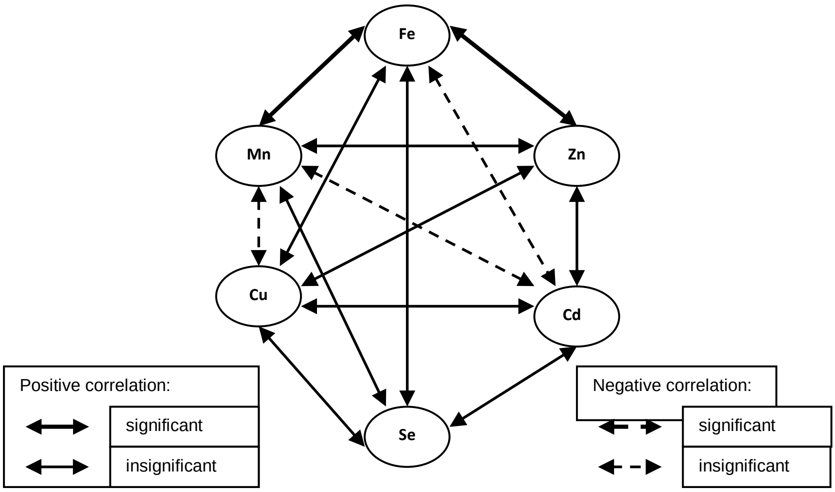
$n{\bullet}10^{2}\,Fe > n{\bullet}10^{2}\,Mn > n{\bullet}10^{1}\,Zn > n{\bullet}10^{1}\,Cu > n{\bullet}10^{0}\,Cd > n{\bullet}10^{-2}\,Se$;

The interrelation between the elements in soils as a rule does not manifest itself. Statistically significant (at a 5% level) positive correlation was established only for the following pairs of elements: Fe-Mn (r=0.79), Fe–Zn (r=0.59), Se–Zn (r=0.57), that is the increase and decrease in the soil of these pairs of elements occur synchronously (figure 5).

In the aboveground part of plants, the sequence of trace elements is the same as in soils. But the amount of Fe in plants is two orders of magnitude less than in soils and becomes comparable to the content of Mn in them. The concentration of Se in plants is an order of magnitude lower compared to soils. The content of Zn and Cu in plants remains commensurate with soils. Depending on the specific geochemical conditions these elements may change places in the sequence as was presented above. The concentration of Cd in plants even exceeds its content in the soil. There was no statistically significant interrelation in plants, with the exception of Fe and Mn, for which a positive correlation was established (r=0.74) (Figure 6).

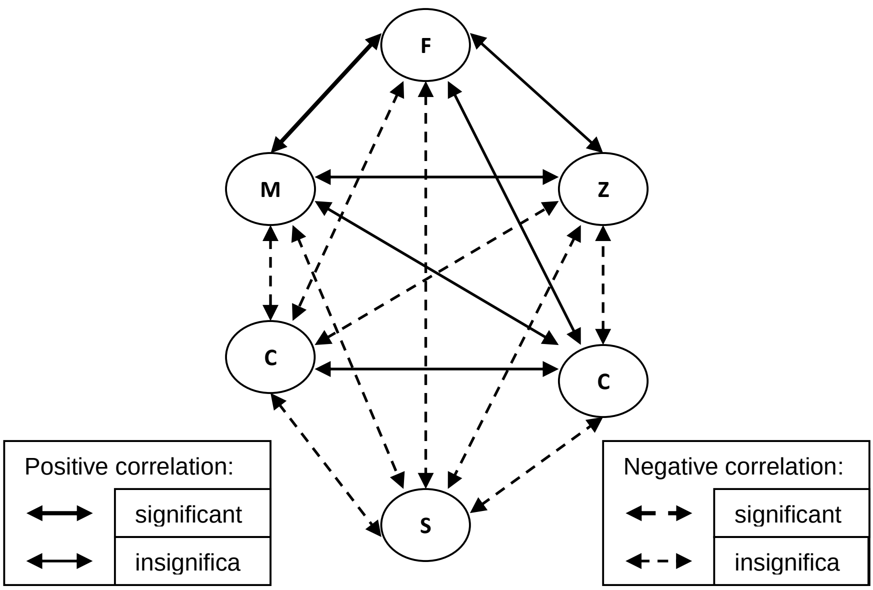
The most interesting is the assessment of the dependence of the accumulation of elements by plants on their ratio in the soil. Usually the gross content of trace elements in the soil rarely correlate with their concentration in plants. Nevertheless in the geochemical conditions of Moldova, a statistically significant (at a 5% level) positive interrelation was revealed between the gross Mn in the soil and the amount of its accumulation by plants (r=0.53), between the gross Cu in the soil and Zn in plants (r=0.53), between the gross Cd in soils and Cu in plants (r=0.54).

Figure 5. The interrelation of trace elements in the soils of Moldova



Source: Kapitalchuk I. et al., 2011b.

Figure 6. Interrelation of trace elements in plants



Source: Kapitalchuk I. et al., 2011b.

The ratio of trace elements in small reservoirs which depends on the chemical properties of the environment of local catchments indirectly reflects the presence of soluble forms of these elements in soils and soil forming rocks in the catchment area. In addition, information on the ratio of trace elements in reservoirs allows to identify us the introduction of elements into the studied territory by transit watercourses.

The above sequence of elements for local reservoirs differs significantly from similar ratios for soils and plants. In the water of local reservoirs, Fe gives way to Mn, the status of Zn increases, the concentration of which becomes of the same order with Mn and Fe. The place of Se in the sequence changes dramatically, which becomes not only one-order with Cu, but on average even outstrips it in quantitative terms. At the same time, the status of Cd in local reservoirs decreases by two orders of magnitude compared to its content in plants.

In Moldovian part of the Dniester River due to anthropogenic impact and the transit component, the content of Mn and Fe increases by an order of magnitude compared to local reservoirs. Fe occupies the first place in the sequence of elements and the location of the remaining elements in the sequence has not changed.

BIOGEOCHEMICAL PROVINCES

Based on the analysis of the content of I, Co, Zn, Cu, Mn in soils, agricultural plants and natural waters, Ya.V. Bumbu (1981) identified several biogeochemical provinces on the territory of Moldova. The most significant biogeochemical province is associated with an insufficient amount of I and partly Co in environmental objects. In Moldova the spread of endemic goiter among the population was noted and with a lack of Co the same disease and acobaltosis in animals. One of the causes of physiological deficiency I is called an unbalanced excess of the gross Mn content in soils, plants and natural waters. Ya.V.Bumbu considers the low content of I in the components of the environment to be characteristic of the entire territory of Moldova, but it manifests itself to varying degrees for different regions of the country. The lowest I content in soils, waters and plants was found in the northern forest–steppe soil province, and the highest in the southeastern steppe soil province.

Researcher by E.S. Feldman (1977, pp. 77-80) also studied biogeochemical provinces. During the medical and geographical zoning of Moldova, E.S. Feldman associated the spread of endemic thyroid pathology with certain classes of geochemical landscapes in which iodine deficiency was observed. Thus, the greatest risk of goiter endemia of III–

IV degree (increased danger) was noted in the Tsentralnomoldavsky forest district and the Codru forest district. The Central Moldavian forest geochemical landscape is located on the Cambisoils, and the Codru forest geochemical landscape is located on the Humic Luvisoils. Both areas belong to the transitional class of landscape from acidic to calcium.

The risk of endemic thyroid enlargement of the I and II degree (medium danger) was associated with forest-steppe geochemical landscapes of the following types: carbonate; transition from acid to calcium; carbonate-gley and salt-gley classes on Luvic chernozems and Haplic chernozems. These types of landscapes are common in the North Moldavian, Dniester-Prut, Baymakli, Sredneprutsky and Balti medico-geographical areas. E.S. Feldman considered steppe geochemical landscapes of the Xeric chernozems are not dangerous for thyroid diseases associated with a lack of iodine in the environment. Steppe geochemical landscapes of the carbonate class on Xeric chernozems prevail in Southern Moldova. However, on the territory of steppe medico-geographical areas, local areas with an average risk of thyroid pathology can be observed.

On the territory of the central forest and southeastern steppe soil provinces of Moldova Ya.V. Bumbu (1981) identified a biogeochemical province with an insufficient amount of zinc and the spread of rosette disease in fruit trees.

In the southern part of Moldova, where soils rich in carbonates are common, Ya.V. Bumbu also identified a biogeochemical province with an increased amount of copper, which is characterized by the spread of chlorosis of the vine. As the main reason for the high copper content in this province, Ya.V.Bumbu considers the long-term use of copper preparations against pests and diseases of grape and garden plantings. Thus, this biogeochemical province has not a natural, but an anthropogenic origin.

E.S. Feldman (Atlas of the Moldavian SSR, 1978; Feldman, 1977) identified areas of caries and fluorosis on the territory of Moldova. These areas correlate well with the lack and excess of F in drinking water. E.S. Feldman also conducted zoning of the territory according to the probable risk of cardiovascular diseases, lithiasis and diseases of the gastrointestinal tract, depending on the hydrochemical factor.

According to J.E. Kreidman (1992) soils with an average content of F predominate throughout Moldova, the geochemical province with a high content of this trace element mainly covers the Balti steppe plain and the forest-steppe Priprut upland. Soils with a very high F content are confined to floodplains of rivers.

FUTURE RESEARCH DIRECTIONS

Today the problem of biogeochemical zoning of the territory of Moldova cannot be considered definitively solved, since there are a number of fundamental contradictions in this issue. Conclusions about the availability of microelements for biota and the population may be erroneous if based only on the study of the content of trace elements in soil forming rocks, soils, waters and plants. This has been well demonstrated by systematic studies of Se in the components of the Moldovan environment.

When systematic studies of Se content in the environment of Moldova were just beginning and researchers received the first results of Se content in different types of soils, they concluded that there was not enough Se in the ecosystems of Moldova and selenium deficiency in the population was possible (Bogdevich et al., 2005; Toma et al., 2006). But further studies of the content of Se in plants, fungi, bee products, food products of plant and animal origin, animals of aquatic and terrestrial ecosystems have shown a high availability of Se. Moreover, abnormally high concentrations of Se (exceeding MPC) were observed in aquatic ecosystems both in aquatic vegetation and in animals. Thus, in the ecosystems of Moldova, against the background of a low gross Se content in soils, a high Se content in biota is observed. The biomagnification of Se along food chains is particularly pronounced in aquatic ecosystems (Kapitalchuk M. et al., 2013; Kapitalchuk M. et al., 2019).

Nowadays there are also numerous contradictions on the content of I and Fe in plants, animals and the availability of these biogenic elements of the population of Moldova (Kapitalchuk M. et al., 2013a; Sturza, 2016; Kapitalchuk M., 2018; Kapitalchuk I. et al., 2020). Recent publications (Kapitalchuk M. et al., 2018; Sheshnitsan et al., 2018; Kapitalchuk M. et al., 2019a; Kapitalchuk I. et al., 2019; Kapitalchuk M. et al., 2022) suggest that it is necessary to clarify the ecological status in the ecosystems of Moldova of such elements as Cr, Cu, Mn, Mo, Zn, Cd and Pb. These problematic issues determine the directions for further biogeochemical research in Moldova.

CONCLUSION

The nature of the distribution of trace elements in soil forming rocks, soils, waters and plants has its own characteristics. The ratio of trace elements in the ecosystems of Moldova is mostly optimal, since there are no pronounced antagonistic reactions between the elements.

Biogeochemical provinces of I, Co, Zn, Cu, Mn, F have been identified on the territory of Moldova, but this aspect requires clarification. Modern research shows the complex nature of migration and distribution of trace elements in ecosystems. Therefore, further studies of trace elements should cover all components of the environment and trace the migration of chemical elements in the system: soil forming rock – water – soil – plants – fungi – animals – the human body.

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