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Biogeochemical Indication: Current State and Development Outlooks

S. F. Tyutikov
Vernadsky Institute of Geochemistry and Analytical Chemistry (GEOKhI), Russian Academy of Sciences, Moscow, 119991 Russia
e-mail: tyutikov-sergey@rambler.ru
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Abstract—The paper presents analysis of the current state of the biogeochemical indication of the status of heavy metals and vital trace elements in various environmental objects in relation to physiological reactions of organisms. Aspects of the application of different methods of phyto- and zooindications are assessed, and integral techniques are reviewed that are based on the use of homogeneous living matter and molecular biogeochemical markers for the purposes of ecological monitoring of the environment at various anthropogenic impacts.

Keywords: biogeochemical indication, heavy metals, trace elements, ecological monitoring
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INTRODUCTION

Methods of *biogeochemical indication* (BGCI) were applied in for centuries. For example, as far back as the 17th century, English miners successively found Zn ore mineralization using certain plant species (*Viola calaminaris* and *Thlaspi calaminaris*), which grow on surfaces above the dissipation aureoles of such orebodies (Ermakov and Tyutikov, 2008). Now BGCI is understood as monitoring the states of provinces and anomalies with a deficit, excess, or misbalance of major and trace elements (TE) and ecological objects of various level (from the molecular to cenotic). Understanding specific reactions of the biota on environmental biogeochemical factors of natural and anthropogenic origin makes it possible to highly accurately determine the trends of processes and timely apply various correcting measures. The classification of BGCI into three major chapters (Fig. 1) is related not only to the use of indicators (also referred to as markers) belonging to a certain realm of living matter and its organization level in monitoring the states of provinces and anomalies. Currently more and more importance is attached to the assessment of the biota itself in the veterinarian, sanitary, and medical aspects (Tyutikov and Ermakov, 2010; Ermakov, 2015).

An important outcome of the application of BGCI techniques is the possibility of understanding the laws of the transition from variations in the chemical composition of individual organisms at extremal geochemical circumstances to those in the populations and biocenoses (Moiseenko, 2009). However, it is practically impossible to describe transition algorithms from biologically rigid systems through a critical bifurcation point to a newly reached relatively stable state by means of modifying emergent relations in biological communities without identification of the changes at the level of individuals. Modern BGCI methods are aimed at detecting these changes.

THEORETICAL ANALYSIS

Current BGCI Techniques

Currently utilized BGCI techniques are classified according to the nature of the used parameters (variations in biogeochemical parameters, fatality, and changes in the appearance, behavioral features, and population and biocenotic indexes) and the level of organization (molecular, cellular, organism, and sys-

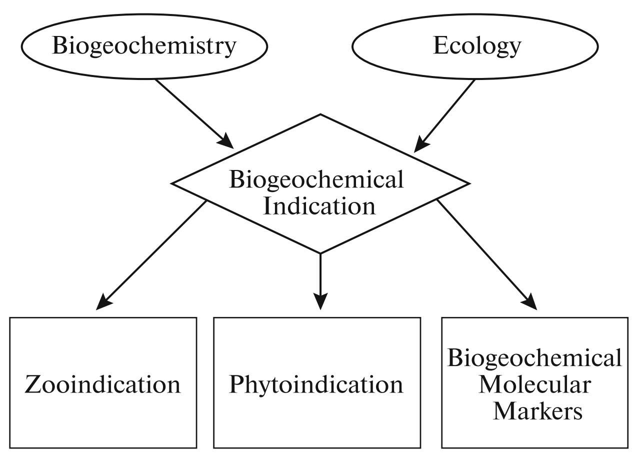

Fig. 1. Schematic representation of the genesis and subdivision of biogeochemical indication.

tem). BGCI methods are classified according not only to their methods but also their goals. Nowadays BGCI methods are widely applied in ecological monitoring of territories (Ermakov et al., 2016), including situations when regions of endemic microelementoses of domestic animals should be outlined.

BGCI of environmental contamination with *heavy metals* (HM) and other anthropogenic pollutants seems to be nowadays one of its most demanded uses in ecological monitoring (Brunn et al., 1991). Trivial methods of ecological monitoring, which are now widely applied, involve monitoring of the ecological state of population centers, as well as large enough regions, within broad ranges of parameters, regardless of the pollution sources. The system of data acquisition involves groups of sensors to control the ecological conditions, control and dispatching centers of wastes discharged from industrial facilities, a central control unit, a space communication center with a network of ecological monitoring satellites, and vehicular prompt-action units that are equipped with corresponding groups of sensors and linked to the central unit via communication networks. These systems for collecting ecological information are able to assay the ecological state of a large territory but are multistage, time- and labor-consuming, and extremely expensive (Tytikov, 2016).

Another approach is the assessment of environmental conditions over large enough territories, including determining the quality of industrial atmospheric emissions, pesticides introduced into the soils, and contaminants in the liquid wastes. In this approach, the amounts of contaminants are identified by the levels, the integral index of ecological contamination is calculated, and these values are used to assay the ecological state. A disadvantage of this approach is that it is highly labor-consuming and costly.

Nowadays, along with chemical techniques of determined various toxic elements in the environment, a number of biological estimates of the contents of hazardous pollutants in natural environments are utilized. According to literature data, biological techniques that are most widely utilized to test waters involve daphnids (ISO/6341:1989 (E)) as the test organisms. A disadvantage of these techniques stems from the fact that daphnids are not resistant enough to variations in the concentrations of toxic chemical elements in the environment.

Various express methods are also currently used to estimate the quality of water contaminated with industrial, agricultural, and/or domestic toxicants and/or their mixes in the course of ecological assessment, mapping, and monitoring of surface and groundwaters. These techniques are usually based on changes in the behavorial reactions of mollusks in the tested waters. One of the test organisms is *Ampulla gigas*, which was bred via closely related breeding in "ecologically pure" laboratory environments. As an alternative, the estimates can be made based on the number of dead frond cells in duckweed after its artificial pigmenting and by constructing an appraising chart of contamination (Ermakov and Tyutikov, 2008). The techniques of this group are extremely labor-consuming and require a great number of test organisms, numerous replicate measurements, and the final labor-consuming statistical processing of the results. Another disadvantage of these techniques is the need to carry out a specialized study and the low representativeness of the results because of the use of low-organization organisms. It is quite obvious that no ecological situation over large enough area can be assayed by these techniques.

For BGCI of HM, we selected wild and *agricultural* (a.c.) cloven-hoofed mammals in view of the following facts. First, these animals are traditional hunting targets in Russia, Western Europe, and North America, and hence, sampling of their organs and tissues is inexpensive and relatively simple to organize. Second, although these animals accumulate toxic elements less intensely that some other plant and animal species, wild cloven-hoofed mammals are suitable as biomonitors because they are the last link of the biogeochemical food pyramid before carnivores and humans. Finally, data obtained on wild species are more representative because a.c. animals (cattle, sheep, and pig) consume only feed grown on fields, whereas wild animals consume very diverse species of wild and domestic plants (Figs. 2 and 3). In spite of significant differences in geochemical features and physiological importance, interrelations were detected between background weighted mean concentrations of chemical elements in the BGC of the food chain in Central Black-Earth Belt. The dependence of concentrations of elements in the biomass of wild cloven-hoofed mammals on the concentrations in plants is much stronger ($r = 0.47$, $p < 0.05$) than the dependence on the concentrations in the soil ($r = 0.24$, $p < 0.05$).

Zooindication Techniques

BGC of HM in natural ecosystems. Our technique (RF Patent 2266537) involves sampling of organs and tissues of wild cloven-hoofed mammals, their analysis for total HM concentrations, and graded estimation of the ecological situation in a given region in compliance with the maximum permissible concentrations of the elements standardized by the Department for State Sanitary and Epidemiological Supervision.

It is expedient to sample organs and tissues of elk (*Alces alces* L.), roedeer (*Capreolus capreolus* L.), and wild boar (*Sus scrofa* L.) for annual monitoring during the time of collective hunts for these animals in October–November. Data obtained by analyzing these samples are the most representative and universal, i.e., are suitable for assaying the chronic (annual and longer) and short-term (during a few past weeks) HM fluxes to the ecosystems. It is also permissible to use as

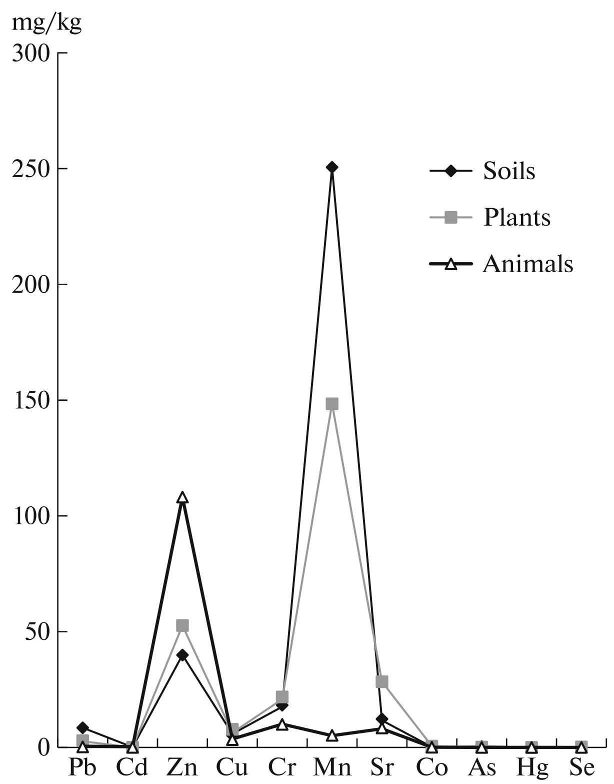

Fig. 2. Weighted mean HM and TE background concentrations in soils, plant feed, and the biomass of cloven-hoofed mammals in the State Voronezh Biospheric Reserve. Concentrations are in mg/kg of air-dry weight for plants and in mg/kg of wet weight for animals.

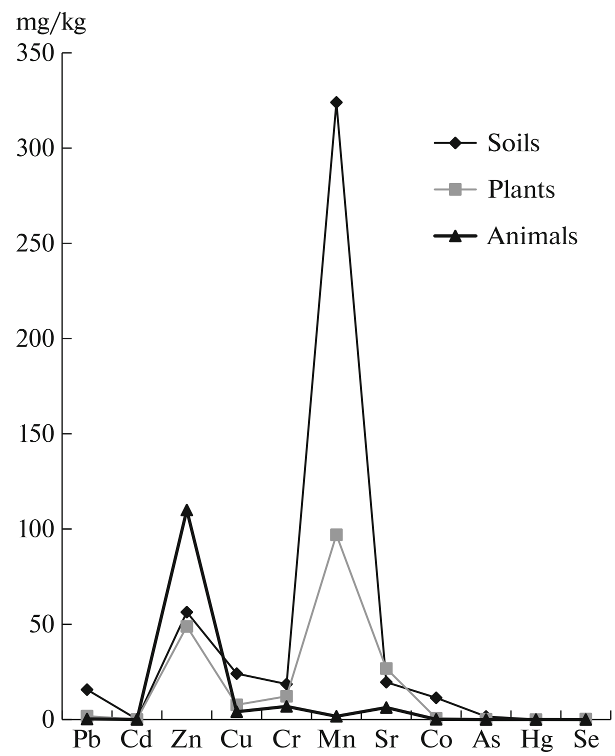

Fig. 3. Weighted mean HM and TE background concentrations in soils, plant feed, and the biomass of cloven-hoofed mammals in Chernyanskii district, Belgorod oblast. Concentrations are in mg/kg of air-dry weight for plants and in mg/kg of wet weight for animals.

biomonitors organs and tissues of animals provided by killing of animals conducted on a regular basis from July to February. It is only impossible to use organs of male animals killed during estrums because of principal changes in the feeding behavior of the animals and their feed consumption and may make the information thus obtained unreliable. The sampling routine, techniques of the primary instrumental preparation of the samples, and analytical techniques are describe in the Patent.

The most complicated issue in ecological monitoring of HM is interpretation of the analytical data to obtain graded assessment of the situation in the area. The currently adopted four-grade scale (I for the zone of relative prosperity, II for the risk zone, III for the crisis zone, and IV for the zone of ecological disaster) is convenient enough and enables the researcher to roughly assay the scale of the anthropogenic impact on the natural communities. Obviously, to assign a territory to categories III or IV (crisis and disaster zones, respectively), it is needless to utilize such sensitive biomonitors as wild cloven-hoofed mammals. Experience has shown that the HM concentration levels in surface waters, atmospheric air, and the uppermost soil horizon in zones of ecological disaster can exceed the approved sanitary standard by as much as one order of magnitude and more. It is much more difficult to identify the initial disturbance of the natural self-regulation of ecosystems and the transition from the prosperity to risk zones. In such situations, it is expedient to utilize living organisms as indicators of the purity of the environment. Table 1 lists the determined indicator capabilities of various organs of wild cloven-hoofed mammals.

BGCI of the TE status and possibilities of its corrections. Along with the BGCI of HM over large territories, ecological assessment of the status of TE over large areas and at agropedocenoses of relatively small area is currently an essential constituents of nature-protection measures and rational management of natural resources (Ermakov and Tyutikov, 2008). Unlike HM, TE play very definite biological roles by being involved in physiological processes in plant and animal organisms. It is necessary to take into account the fact that intense agro-industrial production is associated with the withdrawal of much mobile TE species from the agropedocenoses (soil–plant complexes of the fields and hay-fields) and, hence, their depletion in these cenoses. In view of this, the assessment of the TE status is a necessary measure, which makes it possible to adequately estimate the situations and select

Table 1. Species of wild cloven-hoofed mammals and organs used as indicators of environmental pollution with toxic elements

Species of wild cloven-hoofed mammals	Indicator organs		
	muscle tissue	kidney	liver
Long-term (chronic) pollution			
Moose deer	–	Pb, Cd	–
Roe	–	Cd	–
Wild boar	–	Hg	Pb
Short-term (single-time) pollution			
Moose deer	Pb	Hg, Cd	Hg, Pb, Cd
Roe	Pb, Cd	Hg, Cd	Hg, Pb, Cd
Wild boar	Hg	Hg, Cd	Hg, Pb, Cd

means for their improvement. From this viewpoint, our method is part of regional ecological monitoring and can provide practical guidelines for intense agricultural production (RF Patent 2280869).

The method is underlain by determining the TE status of a large territory (administrative distinct or oblast) by means of BGCI with the use of organs and tissues of wild cloven-hoofed mammals, analogous monitoring of the local agropedocenosis using a.c. animals (cattle *Bos taurus* L., sheep *Ovis aries* L., and swine *Sus scrofa domestica* L.) and the subsequent integral assessment of the situation. In the case of a crisis situation, we suggest a complex of measures aimed at a correction of the TE status of the agropedocenosis depending on the degree of the ecological trouble. The procedures of sampling, conservation, and primary treatment of organs and tissues of wild cloven-hoofed mammals correspond to those described above. The a.c. animals should be fed on the assayed agropedocenosis, i.e., their feeds should originate from a given field or hey-field.

It is worthwhile to start assaying the TE status with determining the level of TE concentrations in the muscular tissue of wild cloven-hoofed mammals. In contrast to HM, both the upper and the lower critical concentrations of TE are standardized. In other words, the quality of the hunt killings, as well as the determined quality of the natural environment, worsens with both increased and decreased (to below the standardized values) trace-element concentrations in the organs. We assume the following critical levels (lower/upper) for TE concentrations in the muscle tissue (mg/kg wet weight): 0.5/5.0 for Cu, 10.0/70.0 for Zn, 0.1/2.5 for Mn, and 0.05/1.0 for Se. With regard for the feeding specifics of wild cloven-hoofed mammals, which feed mostly at natural biocenoses, comparison of the actual TE concentrations in the muscle tissues with the standardized values makes it possible to adequately assay the TE status of the territory as a whole. The analogous assessments are made for the agricultural lands (agropedocenoses of the ploughed field, hey field, and/or grazing land). If reasonably accurately “alimentarily” correlated with the analyzed agropedocenosis, these data are more representative than TE concentrations in the soil–plant complex.

Obviously, if the levels of TE concentrations in the muscle tissue of a.c. animals lie outside the ranges of optimal concentrations between the upper and lower critical levels, the TE status of the agropedocenosis needs corrections, which are the greater, the greater the deviations of the actual concentrations (toward either greater or lower values). If the TE concentrations in the muscle tissue is 1.5–2 times higher than the upper critical level, we recommend to stop the exploitation of this agropedocenosis because its production cease to comply with the sanitary standards.

If the concentrations of one or more TE in the muscle tissue of the a.c. animals are lower than the standardized values, and these concentrations in the flesh of the wild cloven-hoofed mammals are normal (this situation is typical of actively exploited agrocenoses), measures should be undertaken to correct the TE status using a grading approach to preclude overdoses of fertilizers and pollution of the agricultural lands with excess biologically active chemical elements.

First of all, the deficit coefficient of a trace element in the muscle tissue of the a.c. animals should be determined as

$$K = Ll/Ac,$$

where K is the deficit coefficient, Ll is the lower permissible level of the concentration of the TE, and Ac is its actual concentration (in mg/kg in wet weight of the tissue) of the TE in the muscle tissue of the a.c. animals at the agropedocenosis in question.

Our experiments conducted in 1999–2003 at the territory of the Niva private company in the Chernyanskii district, Belgorod oblast, allowed us to suggest measures for correcting the TE status of the agropedocenosis. Depending on the value of the deficit coefficient, certain measures and operations were suggested to correct the TE status of the agropedocenosis. As the TE deficit of an agropedocenosis

Table 2. Selection of measures for correcting TE status of an agropedocenosis

Type of agropedocenosis	Deficiency coefficient			
	0.5 or less	from 0.5 to 1.5	from 1.5 to 2.0	more than 2.0
Ploughed field	Stop introducing mineral fertilizers, lime application	Introduce mineral fertilizers	Introduce mineral fertilizers	Introduce specialized TE fertilizers
Hay field	Sow multicut perennial plants	Limited exploitation	Introduce organic fertilizers	Introduce mineral fertilizers
Pasture	Regulate hay harvesting regime	Limited exploitation	Introduce organic fertilizers	Introduce mineral fertilizers

increases, TE should be introduced into it first as organic and then as mineral and specialized TE fertilizers.

In certain situations, beneficial effects can be reached by changing the exploitation regime of the agricultural lands. The introduction of TE fertilizers should be minimized. The optimal measure for correcting the TE status of an agropedocenosis is dressing with a sufficient amount of organic fertilizers and limiting the exploitation of the lands (Table 2). This approach is adapted to assessment and correction for Cu, Zn, Mn, and Se.

Phytoindication Techniques

In search for biogeochemical markers, we suggested a number of BGCI techniques with the use of plant organisms and their communities as biomonitors. It is expedient to take them into account because, along with zooidentification techniques, they significantly widen the potentialities of territorial assessments by both a wide circle of chemical elements and the specifics of the biocenoses themselves.

Using willow in BGCI of environment pollution with Cd. We focused our efforts on increasing the representativeness of monitoring results and ensuring the possibility of regular biogeochemical appraisal of practically unlimited territories at reduced labor inputs. An important advantage of this technique (RF Invention Patent 2486507) over its analogues is the possibility of appraising such complicated environmental targets as floodplains of rivers of long length and relatively small width. In addition, we managed to extend the list of marker species for BGCI of environmental objects for Cd (Ermakov et al., 2015).

An illustrative example of the application of the method is the assessment of Cd pollution in the valley of the Ardon River, North Ossetia–Alania, downstream of the tailing dump near the village of Nizhnii Unal. We sampled leaves of goat willow (*Salix caprea L.*) and/or snap willow (*Salix fragilis L.*), dried them to a constant mass, obtained an averaged sample, analyzed it for Cd, and compared these data with the approved standards. If the concentrations extended outside the approved ranges, the degree of Cd pollution of the territory was determined. The routines of sample preparation and analyses were in compliance with the Patent.

Based on results of long-term studies at the Laboratory of Environmental Biogeochemistry at the Vernadsky Institute, we assumed the following gradation for Cd concentrations in willow leaves: (1) conventionally background territories, with Cd concentrations in the leaves no higher than 0.6 mg/g of air-dry weight; (2) territories of risk, with Cd concentrations of 0.6 to 1.2 mg/g of air-dry weight; and (3) territory of crisis, with Cd concentrations in willow leaves form 1.2 to 2.8 mg/g of air-dry weight.

Based on this grading, we have outlined river valley areas that are crisis, risk, and background territories. The territory of ecological disaster with Cd concentrations >2.8 mg/kg (up to a tens of mg/kg of air-dry weight) were identified only at the dam of the tailing dump and at the water discharge site from it. Monitoring such territories is, however, senseless because of the obvious degradation of the vegetation (Ermakov et al., 2016).

BGCI of the ecological status of territories according to the Se concentration (RF Invention Patent 2430355). This method differs from others in the means of phytoindicator sampling, obtaining an averaged sample by quartering (one to five times depending on the original material amount), treatment of the pulverized sample (collected at three surfaces) by ethanol, its analysis for Se concentration, and comparison of these values with the approved standards. If the values extend outside the limits, the ecological status of the territory is determined. It is principally important that the plant samples are not dried because up to 70–85% of the total Se concentration can be lost in the form of volatile compounds with released moisture. The phytoindicators are hay cuttings of wild plants of meadow–steppe vegetation or annual or perennial a.c. plants. These values are compared with the minimum critical Se concentration in the air-dry hay cuttings of the wild vegetation: this is 20 μg/kg of native mass for the forest zone, 30 μg/kg for the forest–steppe zone, and 50 μg/kg for the steppe zone.

These critical Se concentrations were assumed based on the results of long-term studies conducted at

Table 3. Identification efficiency of endemic microelementoses of cattle by hair chemical composition

Chemical element	Deficit	Excess
Zn	Intermediate	No data
Cu	Intermediate	High
Mn	Intermediate	Intermediate
Sr	No data	High
Co	Intermediate	High
Mo	Intermediate	High
Se	High	High

the Laboratory of Environmental Biogeochemistry at the Vernadsky Institute. The total Se background concentration in the average hay cuttings of wild plant species in the meadow–steppe zone and in the terrestrial biomass of annual and perennial a.c. herbaceous plants was determine to be no lower than 20 μg/kg of native material in the forest zone and no lower than 30 μg/kg in the steppe zone. The application of this method allowed us to identify a number of Se-deficient territories in eastern Transbaikalia.

BGCI of the ecological status of territories according to the Sr concentration (RF Invention Patent 2375710). The sampling routine of this method is quite similar to that for BGCI of Cd pollution but principally differs from the latter in separating Sr from an averaged sample by extraction with concentrated HNO_3 and the subsequent analysis of the extract by electrothermal atomic absorption spectrometry.

The data thus acquired are then interpreted using the background Sr concentration of the air-dry material of averaged hay-cuttings within the range of 20–500 mg/kg. This range of Sr concentration was assumed based on the results of long-term studies of extremal and background territories. Our earlier publication and literature data indicate that a low (much lower than the minimum background Sr concentration of 20 mg/kg) Sr concentration in the averaged hay-cuttings of single-crop a.c. plants adversely affects the development of the bone tissue of animals and humans, whereas Sr concentrations in the averaged hay-cuttings of wild meadow–steppe plants above 500 mg/kg lead to the development of Sr rachitism in the a.c. animals and achondroplasia in the animals and humans. Excess Sr concentrations adversely affect first of all the bone tissue, liver, and blood.

Application of this method in studies of territories in the vicinities of villages with endemically very high incidence rates of the Urov (Kashin–Beck) disease in Gazimurozavodskii district in Transbaikalia made it possible to identify hazardous areas with Sr concentrations of 650–700 mg/kg of air-dry weight of averaged wild-plant hay cuttings. This parameter for the middle-endemical villages varied within 530–650 mg/kg (Tytikov, 2016).

INTEGRATED BGCI METHODS

In order to track and estimate local and global natural geochemical processes, identify natural–anthropogenic and biogeochemical anomalies, and assess the states of animal organisms utilized to provide foodstuffs for humans, it is necessary to apply BGCI. This is understood as searches for such solutions whose implementation results in dualistic effects: first, the possibility of adequately identifying a certain group of noncontagious metabolic diseases of animals due to an excess, deficit, or misbalance of one or more trace elements is (or proving the absence of such diseases); and second, the possibility of estimating how much the territories where these animals are bred are troublesome from the ecological–geochemical viewpoint.

Diagnostics of cattle microelementoses based on the chemical composition of *the animal hair* (RF Invention Patent 24774830). Our and literature data indicate that the chemical composition of animal chair can be efficiently utilized to identify hypo- and hyperelementoses. For example, concentrations of TE play a leading role in the identification of such diseases in provinces with anomalously high Mo, Cu, and Se concentrations. Data on Mn and Zn concentration in animal hair are less informative, but concentrations of these elements are also analyzed under extremal geochemical circumstances.

In comparing the trace-element composition of animal hair with clinical and subclinical forms of endemic microelementoses in the territory of the Russian Federation, concentrations of Sr, Cu, Mo, and Se in the cattle hair are proved to be moderately important indicators for identifying endemic hypo- and hypermicroelementoses and outlining ecologically–geochemically disadvantageous territories. The efficiency of identification of the diseases by this technique is illustrated by data in Table 3.

Application of this method in searches of areas with endemic microelementoses in the Northern Caucasus and eastern Transbaikalia is illustrated by data in Tables 4 and 5.

BGCI of Cu–Mo and Mo–W misbalance in cattle organisms and in the environment. Copper and molybdenum are “true” TE: they are known to be responsible for both hyper- and hypomicroelementoses. The biological role of W is not as clear. Certain data indicate that Mo and W are antagonistic *in vitro* on a molecular scale when affecting the activity of xanthine oxidase (EC 1.17.3.2). It was experimentally proved that this enzyme is activated by Mo oxide. The isoenzymatic profile of this enzyme was proved to be different in various biogeochemical provinces. Thereby the degree of Mo substitution for Cu depends of the concentrations of the metals in the nutrient budget of the animals and environment (Ermakov and Baboshkina, 2016). Xanthine oxidase is thus a molecular biomarker that can e utilized in integral BGCI of Cu–Mo and

Table 4. Ranges of normal concentrations of chemical elements in cattle hair at assumed background territories

Study area	Concentrations of chemical elements, ppm					
	Zn	Cu	Mn	Sr	Co	Mo
Moscow oblast (*n* = 147)	110–130	7–8	10–20	7–11	0.02–0.04	0.14–0.26
Blekmishevo, Transbaikalia (*n* = 102)	120–130	7–8	16–20	9–12	0.04–0.08	0.08–0.14
Voronezh oblast (*n* = 133)	110–120	8–10	6–8	11–15	0.02–0.04	0.02–0.08
Chegem, Kabardino-Balkaria (*n* = 11)	120–150	7–8	4–16	6–11	–	0.02–0.15

At degrees of freedom $f \geq 30$, $s \approx \sigma$. The confidence interval of the mean value is $\bar{X} \pm n\sigma$ (where $n = 1$ at $P = 68\%$; $n = 2$ at $P = 95\%$; and $n = 3$ at P = 99.8%). At $f < 30$ $\sigma = ts$. In this case, at a specified probability, the confidence interval of the mean value is $\bar{X} \pm ts$ (where t is Student's coefficient).

Table 5. Chemical composition of cow hair in areas with microelementosis cases

Study area	Parameter	Concentration (ppm) of element					
		Zn	Cu	Mn	Sr	Co	Mo
Bylym, KB (*n* =31)	$\bar{X}$	118	6.0	9.1	11.4	0.026	0.19
	$\pm s$	4	0.32	0.84	1.1	0.004	0.044
Tyrnyauz, KB (*n* = 33)	$\bar{X}$	134	6.6	9.1	10.2	0.019	0.80
	$\pm s$	3	0.4	1.5	0.9	0.003	0.11
Nizhnii Unal, NO (*n* = 8)	$\bar{X}$	142	8.5	16.5	8.8	0.089	0.43
	$\pm s$	9	0.3	2.9	2.7	0.027	0.12
Unda, TB (*n* = 2)	$\bar{X}$	148	6.9	22	33	0.10	0.037
	$\pm s$	13	0.3	5	8.9	0.02	0.007
Nerchinskii Zavod, TB (*n* = 3)	$\bar{X}$	116	6.0	4.4	11.2	0.013	0.024
	$\pm s$	5.4	0.5	0.4	3.0	0.007	0.004
Trubachevskoe, TB (*n* = 60)	$\bar{X}$	110	7.0	20.4	24.7	0.088	0.043
	$\pm s$	2	0.1	1.0	1.2	0.006	0.005

Acronyms: KB—Kabardino-Balkaria, NO—North Ossetiya, TB—Transbaikalia.

Table 6. Cu, Mo, and W concentration (μg/L) in cattle milk and buttermilk from anomalous (Tyrnyauz, Bylym) and background (Kudinovo, Zayukovo) territories

Sampling site	Milk			Buttermilk		
	Cu	Mo	W	Cu	Mo	W
Kudinovo	13.1 ± 1.8	8.4 ± 1.0	0.05 ± 0.01	130.2 ± 14	93 ± 10.9	0.4 ± 0.05
Zayukovo	12.5 ± 1.7	14.4 ± 1.5	0.08 ± 0.02	148.3 ± 17.8	189 ± 20.5	0.1 ± 0.01
Bylym	52.4 ± 7.7	42.2 ± 5.8	0.22 ± 0.07	110.8 ± 12.7	174 ± 19.2	2.0 ± 0.3
Tyrnyauz	60.9 ± 8.9	56.6 ± 9.3	0.50 ± 0.09	684.3 ± 80.0	556 ± 73.8	4.3 ± 0.5

Mo–W misbalance in animal organisms and environment.

Our data on Cu, Mo, and W concentrations in soil, vegetation, and cattle milk (Table 6) allowed us to determine the background ratios of the concentrations of these elements in the butter-milk and to develop a technique for monitoring misbalance in the Cu–Mo and Mo–W pairs (RF Invention patent 2542236).

PROMISING BGCI METHODS

Current progress in BGCI is reflected in numerous publications presenting results of experimental studies. BGCI methods were suggested to be utilized to monitor environment pollution with wastes from large plants of the nonferrous metallurgy (Gashkina et al., 2015). Consequences of long-term anthropogenically induced transformations of large lacustrine ecosystems are studied in the Arctic (Moiseenko et al., 2009). BGCI involves microorganisms, algae (chlorella, soil algae, brown algae, and diatoms), insects (fir aphid, wiggle-tail, carabus, and daphnids), moss, lichen, macrophytes, herbaceous plants, trees (birch, larch, spruce, linden, and pine), birds, oligochaetes, earthworms, and several other living organisms and their communities. Fish, mollusks, and crustaceans can be employed as reliable indicators of aquatic pollutions (Moiseenko and gashkina, 2016).

Much interest is also attracted to biogeochemical molecular markers, such as a certain types of enzymes (glutathione peroxidase and xanthine oxidase), low molecular weight proteins (metallothioneins, phytochelatins, and other chelators), pigments, and compounds of other groups (chlorophyll a and b, plastoquinone, and carotenoids). Newly invented biosensor technologies (that make use of DNA and RNA) are more and more widely utilized in ecological monitoring. All of them make it possible to more or less accurately estimate the pollutions of waters, soils, air, and other environments and assess how much a territory is ecologically troublesome.

CONCLUSIONS

In conclusion it should be mentioned that the suggested BGCI methods are in a sense advantageous not only over the mass analyses of natural waters, soils, and air but also over trivial biotesting techniques. BGCI methods are faster, less labor-costly, and yield more representative results. The main reason for this is that BGCI methods are "more ecological", i.e., are able to yield a comprehensive assessment of a biogeochemical food chain using its certain reference links. Also, concentrations of most TE and HM usually show significant and unsystematic lateral variations, as is particularly typical of industrially polluted soils. The patchy character of pollution in water flows and air masses manifests itself with time. In view of this, BGCI of plant and animal organisms and their habitats makes it possible to obtain integrated results, in which the patchiness is smoothed. A basis ensuring the reliability of the methods is the concept of the unanimity of the chemical composition of homogeneous living matter as understood by V.I. Vernadsky, as well as patterns of its variations under the effect of variations in the geochemical environment.

Modern BGCI methods are in essence the tracking of certain parameters of living organisms and their systems at various states and at changes in the geochemical environment with time. Thereby efforts are focused first and foremost on the biological reactions of living organisms in response to variations in environmental biogeochemical factors. At progressively greater anthropogenically induced transformations of nature, the chemical elemental composition of living matter evolves, and biogenic migration of chemical elements varies with time. It tends to a maximum within certain limits, which correspond to homeostasis of the biosphere as a fundamental feature of its stable evolution.

Nowadays practically all living organisms on the planet suffer anthropogenic impacts due to industrial progress. This results first of all in a decrease in the wooded areas, desertification of certain territories, and an increase in areas of industrial, agricultural, urban, and military purposes and those allotted to energy-producing facilities. The degradation of natural biocenoses is directly related to decreasing biological diversity. The parameters and meaning of migration of several chemical elements is modified. Biospheric taxons are appreciably changed, as also are fluxes of atoms. With regard for the importance of geochemical characteristics of the environment, we try to gain insight into their importance for certain living organisms, their populations, and communities and to identify the most important factors and understand their effects on ecological tension.

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