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Participation of Small Mammals in the Biogenic Transit of Trace Elements under Chemical Pollution of the Environment

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Abstract—The paper considers the participation of small mammals (SM) in the migration of essential (Cu, Zn) and toxic (Cd, Pb) trace elements (TEs) in forest ecosystems under conditions of severe industrial pollution of the environment (1990–2000) by a large copper smelter (Middle Urals, Russia) and after a significant reduction of its emissions (2010–2019). The peculiarity of transit food flows (TFF) in the pollution gradient was determined by the composition and abundance of animals of different trophic groups (phytophages, mixophages, zoophages), as well as the specifics of their diet. The reduction of emissions was accompanied by positive changes in the SM communities expressed in an increase in the abundance of some species and structural rearrangements of trophic groups (TG), which led to partial changes in the composition and amount of food consumed, as well as the concentrations of TEs in them. By the end of the observation period in the background zone, the animal-controlled TFFs remained stable for most TEs (Cu, Zn, Cd), and decreased by a factor of 2 for Pb, but not as a result of reduced emissions. At the polluted areas, the TFF value has not changed for Zn, has increased for Cd, and has decreased for Cu and Pb. It was concluded that in the taiga zone the main contribution to the dynamics of biogenic TEs flows in time and space was made by a group of mixophages that dominated in the pollution gradient.

Keywords: environmental pollution, transit food flow, copper, zinc, cadmium, lead, zoophages, phytophages, mixophages

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INTRODUCTION

The most important role in functioning natural biogeocenosois (BGC) is played by food chains of living organisms, which provide the transfer of matter and energy from sources (autotrophs) to consumers (heterotrophs). Separate links of food chains including organisms with similar feeding type are united in trophic levels, each of which fulfill certain functions in a complex interrelated system (Vernadsky, 1994; Koval'sky, 1974; Pokarzhevsky, 1985, and others).

Small mammals (SM) are traditionally considered as model objects of diverse ecological studies and united into two trophic levels: consumers of the first (phytophages) and second (zoophages) orders. The former includes rodents (order *Rodentia*) with a wide range of forage from dedicated species (herbivorous, granivorous) to mixophages, which consume both vegetarian and animal objects. The second level is represented by insectivorous (order *Eulipotyphla*) and small carnivorous (order *Carnivora*) animals, which are fed mainly by animal food, supplementing the diet by vegetation forages. The flows of chemical elements through SM populations is the main form of their participation in the matter circulation provided by element transit with forage through the gastrointestinal tract, as well as deposition of elements in animal organisms with their subsequent death (Bezel et al., 2007; Ermakov and Tyutikov, 2008; Pokarzhevsky, 1985).

Under prolonged anthropogenic impact on natural BGC, the stability of migration flows of chemical elements is disturbed, thus leading to the deformations of initial biogeochemical cycles. These changes resulted in a disbalance of the global system of mass exchange and energy between organisms and environments, which underlies the existence of biosphere (Koval'sky, 1991).

Analysis of consequences of environmental pollution for living organisms is frequently limited by monitoring of chemical elements in deposition media (soil and snow cover, litter) and a limited set of indicator species, which represent diverse biota components serving as TEs accumulators (mosses, lichens, vascular plants, invertebrates, and mammals). Under these conditions, the theory of Koval'sky (1982) about biogeochemical food connections as a priority approach to the monitoring of environmental state is of particular importance. Such an approach makes it possible to estimate the variably preserved components of biota to fulfill biocoenotic functions, and first of all, to support the necessary level of biogenic exchange. The steady functioning of natural systems is determined by integral trophic structure of BGC, because its higher levels serving as factor of intensification and stabilization of TEs biogenic cycles are frequently subjected to maximum toxic impact.

Using SM of two trophic levels inhabiting in the vicinity of a large copper smelter (Middle Urals, Russia) during the period of high emissions, it was shown (Bezel et al., 2007) that the deformation of animal-controlled biogenic flows is caused by not only elevated influx of TEs with food, but also mostly determined by the abundance of local populations of SM and position of the species in the trophic structure of BGC. Analysis of long-term (1990–2020) dynamics of SM communities led us to conclude that the multifold (by 50 times over 30 years) reduction of industrial emissions of MUCS initiated in them recovery processes, but positive shifts were different for diverse trophic groups (TG) and depended on the pollution level of the areas, which indirectly affected the quality of habitats (Mukhacheva, 2021). Will the biogeochemical exchange of TEs through SM population after significant reduction of industrial emissions? What is the role of separate TG in the transit flow of essential and toxic TEs in different periods?

The purpose of this study was to analyze the dynamics of transit flow of TEs (Cu, Zn, Cd, Pb) through SM populations inhabiting forest biocoenoses in the vicinity of the large copper smelter during high and almost terminated emissions. Two hypotheses were verified: (1) transit food flow of TEs through sympatric SM populations of above mentioned trophic groups was different and determined by both specifics of food and abundance of animals; (2) gradual restoration of biota components, which began after emission reduction, will equalize the quantitative parameters of transit food flows of the studied TEs through SM community of the at the background and polluted areas.

METHODS

Source of Emission

The studies were carried out in the vicinities of the Middle Ural Copper Smelter (MUCS), the Russia’s largest primary copper smelter and a plant for producing sulfuric acid, located 50 km west of Yekaterinburg. During the long period of its uninterrupted operation (since 1940), a contrasting technogenic geochemical anomaly with heavy metal contents 10–100 times exceeding the background levels was formed in soils around it. The characteristics of MUCS as a point emission source is given in the publications (Vorobeichik and Kaigorodova, 2017; Kozlov et al., 2009). In 1970s, the gross emissions reached peak values, which made the enterprise to be one of the main sources of industrial pollution of Russia. Starting from 1980s, the volume of emissions gradually reduced and does not exceed 2.5–5 thou t/yr after modernization in 2010. Over the past 30 years, the gross emissions of the smelter have been reduced by more than 50 times, with SO_2 concentration decreasing the most (80 times), Cu (3000 times), Zn (15 times), and Pb (8.5 times). The studies were carried out during periods of high (1990–2000, period I) and almost terminated (2010–2019, period II) emissions.

Animal Sampling

The SM were collected annually during snowless period (from May to September) according to a single protocol. The traps were arranged in fixed marked lines (25 traps every 5–7 m for 4 days with a single daily checking) in the spruce–fir forests at different distance from smelter: in the impact (1–3 km from smelter, zone of severe pollution), buffer (4–10 km, zone of moderate pollution), and background (20–30 km, conditionally pure zone) zones. The technique of trapping and characteristics of studied areas were described in detail in (Mukhacheva, 2021). Over 70 000 trap-days were treated (34 500 and 36400 trap-days during the I and II periods, respectively) and 3287 animals of fourteen SM species were trapped, including 1231 animals at the background zone, and 2056, in the vicinity of the MUCS (1741 and 1546 animals during the first and second periods).For each of trapped animalits species, gender, age, reproductive status, and based exterior (body weight, length of body, tail, hind foot) and cranial features were evaluated. Latin names of SM species corresponding to the present-day faunal overview on insectivorous, voles (Kryštufek and Shenbrot, 2022) and murine (Pavlinov and Khlyap, 2012) species.

Experimental Animals

Depending on the trophic specialization and taxonomic affiliation, all SM were united into four groups: mixophages, herbivorous, granivorous, and zoophages. The important characteristics of the groups are listed in Table 1.

A group of “mixophages” (M) includes voles g. *Clethrionomys* (*Cl. glareolus, Cl. rutilus*) and g. *Craseomys* (*Cr. rufocanus*), which dominated in all studied areas (from 50 to 75% of the total abundance) and differed in a wide range of forage objects: from vegetative parts of vascular plants, seeds and berries, to mushrooms, moss, lichens, invertebrates, and rarely vertebrate animals. A group of “granivorous” (G) is represented by mice g. *Sylvaemus* (*S. uralensis*) and g. *Apodemus* (*Ap. agrarius*), the proportion of this species was 10–20% of SM total abundance, reaching 40% in the vicinity of smelter in peak years. Main forage is seeds (trees, shrubs, herbaceous plants) and rich fruits, more rarely, berries, mushrooms, and invertebrates.

Table 1. Characteristics of trophic groups of small mammals in the gradient of environmental pollution, during periods of high (I) and almost terminated (II) emissions

Characteristics of the group	Trophic group	Period	Studied zone		
			background	buffer	impact
Species composition of trophic group	Granivorous (G)	I, II	*S_ural, A_agr*	*S_ural, A_agr*	*S_ural, A_agr,*
	Herbivorous (H)	I, II	*M_arv, M_agr, A_oecon*	*M_arv, M_agr, A_oecon*	*M_arv, M_agr*
	Mixophages (M)	I, II	*Cl_glar, Cl_rut, Cr_rfc*	*Cl_glar, Cl_rut, Cr_rfc*	*Cl_glar, Cl_rut, Cr_rfc*
	Zoophages (Z)	I, II	*S_aran, S_caec, S_isod, S_min*	*S_aran, S_caec, S_isod, S_min*	*S_aran, S_caec, S_isod, S_min*
Density of group $(N_i)^1$, individuals/ha	G	I/II	2.31/3.05	2.28/3.44	2.92/2.33
	H	I/II	2.33/2.00	1.89/1.98	1.83/1.91
	M	I/II	14.63/20.16	7.44/11.27	5.81/4.68
	Z	I/II	4.29/4.50	2.65/3.92	2.68/2.87
	Total	I/II	23.57/29.71	14.28/20.61	13.24/11.78
Weight of body of "model" individual², g	G	I/II	18.14 ± 0.86 / 17.37 ± 0.52	17.31 ± 0.67 / 17.61 ± 0.43	19.07 ± 0.55 / 18.91 ± 0.44
	H	I/II	33.59 ± 0.93 / 31.68 ± 0.74	26.74 ± 1.03 / 26.60 ± 0.75	26.75 ± 1.64 / 21.82 ± 0.71
	M	I/II	20.91 ± 0.21 / 20.09 ± 0.14	20.48 ± 0.23 / 20.36 ± 0.17	19.92 ± 0.29 / 19.83 ± 0.23
	Z	I/II	7.52 ± 0.43 / 7.23 ± 0.31	5.80 ± 0.39 / 5.79 ± 0.30	5.19 ± 0.58 / 4.75 ± 0.40
Daily forage consumption by "model" individual $(M_i)^1$, g of dry mass	G	I/II	2.86/2.76	2.80/2.83	2.89/2.88
	H	I/II	3.97/3.67	3.39/3.34	3.49/3.13
	M	I/II	3.06/2.95	3.02/2.98	2.98/2.97
	Z	I/II	1.49/1.33	1.01/1.02	1.07/0.81
Analyzed sampling	G	I/II	40/62	66/79	96/47
	H	I/II	34/16	28/21	11/43
	M	I/II	642/750	548/391	341/209
	Z	I/II	156/124	188/137	89/80
	Total	I/II	872/952	830/628	537/379

S_ural – herb field mouse, *A_agr* – striped field mouse, *M_arv* – common vole, *M_agr* – field vole, *A_oecon* – root vole, *Cl_glar* – bank voles, *Cl_rut* – northern red-backed vole, *Cr_rfc* – gray red-backed vole, *S_aran* – common shrew, *S_caec* – Laxmann's shrew, *S_isod* – even-toothed shrew, *S_min* – pygmey shrew; (1) geometric mean, (2) arithmetic mean ± error.

A group of "herbivorous" (H) includes voles g. *Microtus* (*M. agrestis, M. arvalis*) and g. *Alexandromys* (*A. oeconomus*), their proportion in SM communities in most of areas was insignificant, and preferable forage is vegetative parts of herbaceous plants (shoots, leaves, stems), as well as berries, seeds, bark, and invertebrates. Being consumers of the first order, M, G, and H groups serve as biocatalysts, passing consumed primary production through digestive tract, which facilitates more complete and intense involvement of TE in biogenic exchange (Pokarzhevsky, 1985).

"Zoophage" group (Z) represented by shrews (g. *Sorex*) and mole (g. *Talpa*) occupies a special position. The shrews are characterized by the wide zone of foraging and various spectrum of animal forages (worms, insects, spiders, mollusks, more rarely, small vertebrates). Under extreme conditions, they are able to partially consume vegetarian forage. In all zones, the group has similar composition (*S. araneus, S. isodon, S. caecutiens, S. minutus*) and its proportion did not exceed 15–20%, reaching 40–50% in peak years.

European mole cardinally differs from above mentioned SM species. This is the sole long-lived stenotopic species, which eats mainly earthworms, lives underground, and significantly affects the environment owing to its burrowing activity. But it was excluded from further analysis due to the uneven distribution in forest habitats in general and its complete absence in the vicinity of smelter.

Evaluating the Animal Numbers

We used data on the absolute number of animals (density, individuals/ha), which were calculated using the technique (Bernshtein et al., 1995). To translate the relative parameters (individuals/100 trap-days) into absolute ones, we applied coefficients proposed by these researchers and corrected them depending on the abundance of the animals. To level off the influence of cyclic variations of species abundance, which are typical of most SM species of the boreal forests at middle latitudes, data on ten sequential years were used, including all phases of population dynamics (depression, growth, and peak). Trapping the animals during three tours (spring, summer, and autumn) allowed us to take into account the seasonal variations in the demographic composition and number of populations during snowless period. Data for each year summated over tours were used as a statistical unit. The average values of SM population density in the environmental pollution gradient in different periods are given in Table 1.

Daily Forage Consumption

The intensity of the forage consumption by animals during the snowless period significantly depends on their age, gender, and reproductive status (Kuznetsov and Mikhailin, 1985; Mukhacheva, 2005). Therefore, for each trophic group (with allowance for the pollution zone and observation period), we estimated the daily forage consumption by a "model" individual (M_i), which was calculated from weighted average values with regard for their demographic structure of local populations TG and the size–weight parameters (Table 1). For rodents (M, G, H), technique proposed by (Kuznetsov and Mikhailin, 1985) was applied. Calculations for shrews (Z) were based on the literature data on the daily consumption by different species (Wołk, 1969) and body weight of experimental animals.

Chemical Analysis of the Samples

The content of stomach was used as an integral parameter of TEs ingress in organism with food (Mukhacheva, 2005). Samples for chemical analysis were collected according to a single protocol during the entire observation period. The content of stomach (for each individual) was extracted, dried in air bath at a temperature of 75°C to air-dry mass, packed in sealed plastic bags and stored to the beginning of analytical investigation. Then, the samples were homogenized, weighted (near 0.1 g) on a KERN-770 analytic balance (accurate to 0.0001 g), and placed into Teflon vessels with a mixture of 7 mL 65% HNO_3 (ultra-high purity) and 1 mL deionized H_2O, incubated for 30 min, and then incinerated in a MWS-2 microwave oven (Berghof, Germany). After ashing, the volume of samples was adjusted to 10 mL by deionized H_2O. The concentrations of Cu, Zn, Cd, and Pb (μg/g per dry weight) in samples were measured by atomic absorption using an AAS6 Vario spectrometer (Analitik Jena, Germany). The quality of measurements was evaluated according to the international reference sample of CRM 185R (bovine liver). The extraction accounted for (in %): 93.2 Cu, 99.8 Zn, 114.2 Cd, and 94.4 Pb; the corresponding detection limits were 0.013, 0.005, 0.001, and 0.013 μg/mL. If an element concentration was below the detection limit, a value equal to half of the detection limit was used for statistical calculations. We have analyzed 1217 samples of stomach content (Table 2). Sample preparation and chemical analysis were carried out during 2015–2017 and 2019 according standard protocols in the Laboratory of Ecotoxicology of Populations and Communities, Institute of Plant and Animal Ecology, Ural Branch, Russian Academy of Sciences.

Transit Food Flow of Trace Elements

The transit food flow of element (TFF, mg/ha day per dry weight) through SM community represented total TFF through distinguished TG of animals, which were calculated for each observation year with allowance for pollution level (zone) and observation period. The TFF value for each group (i) was calculated as daily forage consumption by "model" individual (M_i), concentration of element in its diet (C_i), and the total density of local species populations composing TG (N_i):

$$\mathrm{TFF}_i = M_i C_i N_i.$$

Statistical Analysis

Since the distribution of TEs concentrations in most cases was close to lognormal one, further analysis was carried out with the logarithms of the concentrations (Log_{10}). Geometric averages mean and maximum/minimum values were calculated for parameters of animal density, daily forage consumption, concentrations of TEs in diet, and TFF values. The possible differences between zone and periods of study in terms of these parameters were identified using analysis of variance (a two-way ANOVA). In the statistical tests, differences were considered to be significant at

Table 2. The concentration of TEs (μg/g per dry weight) in the stomach content of SM of different trophic groups in the pollution gradient during the period of high (I) and almost terminated (II) emissions of MUCS

Element	Study period (years)					
	I (1990–1998)			II (2010–2019)		
	Study area			Study area		
	background	buffer	impact	background	buffer	impact
Granivorous						
Copper	16.06 / 4.47–103.79	56.95 / 14.35–991.36	65.50 / 2.74–706.50	16.50 / 3.32–92.11	20.73 / 4.78–122.76	41.30 / 134.59–217.52
Zinc	71.31 / 27.04–560.30	122.58 / 45.23–614.38	126.00 / 36.04–652.21	72.91 / 24.86–492.31	78.57 / 35.58–167.40	106.65 / 37.99–311.57
Cadmium	0.29 / na–3.68	1.21 / 0.03–8.06	1.52 / 0.33–18.52	0.31 / na–2.60	0.47 / 0.05–5.59	1.12 / 0.05–5.49
Lead	2.13 / na–31.48	11.99 / 2.55–254.68	17.75 / 2.96–226.43	1.38 / na–14.40	2.97 / 0.29–29.40	5.33 / 0.12–57.02
n	25	18	35	44	55	28
Herbivorous						
Copper	29.81 / 8.71–131.40	113.06 / 35.28–752.40	108.79 / 40.30–750.84	10.01 / 3.80–24.36	27.23 / 8.12–83.31	61.43 / 19.93–229.56
Zinc	110.54 / 27.04–560.30	192.69 / 45.23–614.36	187.87 / 2.74–736.50	56.30 / 16.72–128.71	139.65 / 35.54–237.03	162.22 / 78.49–364.36
Cadmium	2.28 / na–27.72	1.63 / 0.16–22.78	1.63 / 1.61–22.70	0.54 / 0.09–4.08	1.06 / 0.05–28.97	1.57 / 0.10–3.47
Lead	24.83 / na–85.58	16.51 / 6.31–27.20	16.42 / 6.05–36.75	2.89 / 0.36–15.38	4.79 / 0.45–26.94	18.78 / 2.65–109.91
n	16	11	11	15	14	10
Mixophages						
Copper	18.56 / 2.29–223.25	75.29 / 6.52–1048.80	101.09 / 4.11–831.78	16.19 / 3.74–70.76	41.03 / 9.83–164.22	95.63 / 12.76–699.98
Zinc	90.10 / 18.26–416.30	139.00 / 22.98–531.40	182.41 / 14.43–810.91	94.12 / 25.99–317.46	132.38 / 7.65–608.05	193.17 / 64.52–820.25
Cadmium	0.59 / na–23.60	2.59 / na–25.06	3.46 / 0.35–88.63	0.86 / na–9.23	2.54 / 0.03–46.39	7.54 / 1.52–56.46
Lead	4.61 / na–97.84	16.85 / 0.16–207.47	25.92 / 0.63–287.38	2.36 / na–48.36	10.42 / 0.06–78.82	25.76 / 0.10–657.69
n	238	152	131	157	93	62
Zoophages						
Copper	19.51 / 9.70–77.00	70.04 / 40.70–145.00	63.37 / 48.50–215.50	18.75 / 8.37–86.64	61.1 / 9.8–161.5	74.4 / 34.2–442.0
Zinc	138.83 / 57.79–472.40	159.86 / 74.20–254.20	133.57 / 72.74–259.80	164.18 / 48.65–492.31	176.68 / 104.61–434.86	155.75 / 94.56–271.04
Cadmium	4.89 / 0.80–19.76	4.68 / 0.18–7.68	4.01 / 1.83–9.39	4.33 / 0.16–24.75	11.54 / 0.42–79.68	3.09 / 0.16–11.29
Lead	10.50 / 3.15–30.41	27.35 / 5.54–115.00	13.97 / 4.69–36.80	4.57 / na–36.20	25.66 / 6.42–233.32	10.81 / 1.31–92.85
n	17	12	9	37	19	24

The geometric mean value is in nominator, the minimum and maximum values are in denominators, *na* - concentration of TE below the detection limit, and *n* is the number of analyzed samples.

$p < 0.05$. The calculations were made using the JMP v.11 program package (Carver, 2014).

RESULTS

SM Population Density of Different Trophic Groups

The total density of SM community depended on the contamination level of the areas ($F = 8.75$, $p = 0.0005$), decreasing by 1.7–1.8 times with approaching smelter, whereas the period of observation and interaction of factors did not affect significantly ($p > 0.05$) on its dynamics. Directed changes by 2–4 ($F = 10.20$, $p = 0.0002$) and 1.2–1.6 times ($F = 5.11$, $p = 0.009$) were noted in mixophages and zoophages groups, respectively. The density of herbivorous groups in all zones was insignificant and almost did not change with time, whereas the granivorous group did not define clear trends, reaching maximum values in the impact (period I) and buffer (period II) zones. Increase in the difference of mixophages abundance in impact zone from buffer (from 1.3 to 2.4 times) and background (from 2.5 to 4.3 times) zones during period II is caused by opposite trends: a 40% increase in their number in the background zone and a 50% increase in buffer zones at a simultaneous 25% decrease in the impact zone (Table 1).

Daily Forage Consumption by Animals of Different Trophic Groups

The results of calculation of daily forage consumption by the single "model" individual (M_i) for every TG revealed significant influence of the level of pollution ($F = 30.61$, $p < 0.0001$), study period ($F = 28.11$, $p < 0.0001$), affiliation to TG ($F = 332.78$, $p < 0.0001$), as well as their interactions ($F = 4.57–23.36$, $p = 0.0001–0.003$). In the series herbivorous > mixophages > granivorous > zoophages, the amount of consumed forage (calculated per 1 individual) gradual decreased with approaching the smelter from period I to period II (Table 1).

Concentrations of Trace Elements in the Forage of Different Trophic Groups

Concentrations of all considered TEs in the stomach's content of consumers of the first order, as well as Cu and Pb concentrations in consumers of the second order natural increased with approaching the smelter ($F = 4.59–330.17$, $p = 0.0001–0.014$).

The content of essential TEs in the forage of SM of all TG from polluted zones exceeded the corresponding background values during the entire observation interval: by 2.5–5.4 times for Cu, by 1.1–3 times for Zn (Table 2). The emission reduction did not lead to the significant decrease of Cu and Zn concentrations in the SM diets in the background and impact zones, whereas moderately polluted areas demonstrated a significant decrease of concentrations of both elements in the granivorous ($F = 14.21–14.69$, $p = 0.003$), and Cu decrease in other TG ($F = 12.07–30.92$, $p = 0.0001–0.003$).

Concentrations of toxic TEs in the stomach's content of different TG showed distinct spatiotemporal variations. In particular, levels of Pb and Cd in the forage of consumers of the first order from polluted areas during the entire observation period was 1.3–11 and 1.5–8 times higher than background values (Table 2). The exception is the herbivorous group, the background species of which during the entire period I consumed 1.5 times more Pb and Cd with forage than those in the vicinity of smelter. The dynamics of accumulation of toxic elements in the second order consumers during the entire time interval was characterized by the non-monotonous changes reaching maximum in the buffer zone, and increase of the differences during period II.

Reduction of emissions (from I to II period) led to the significant ($F = 3.96–15.752$, $p = 0.0001–0.05$) decrease of Pb level by 2–4 times in the granivorous diet (all zones), by 1.5–10 times in mixophages and granivorous (at the background and buffer zones), and by 2 times in zoophages (background zone). The Cd concentrations in the animal forage of most TG did not demonstrate clearly expressed trends, except for granivorous group (a three-fold decrease) and zoophages (three-fold increase) from buffer zone, as well as mixophages from impact zone (two-fold times increase).

Transit Food Flow of TEs

Calculated values of total TFF (mg/ha) of the studied elements through SM communities in the pollution gradient during different observation periods are given in Fig. 1. A contribution of separate TG in TFF structure is shown in Fig. 2. The calculations revealed significant influence of pollution level, study period, and interaction of factors (Table 3).

The value of total TFF monotonously increased (by 1.2–3.3 times) from background to more polluted areas: Cu and Pb during both periods, Cd during period I. During period II, the Cd TFF was characterized by nonlinear changes with maximum in the buffer zone, whereas background and impact values were similar. The exception is Zn, TFF fluctuations of which in space and time did not exceed 20%.

TFF analysis with allowance for trophic specifics showed that the maximum contribution in structure of flows of essential TEs in all zones was made by mixophages group, which amounted from 50 to 80% of total TFF (Fig. 2). Minimum contribution (< 25%) was made by this group in TFF of toxic elements at the background areas during period I. For other TG, a decrease of pollution level (in time and space) was accompanied by 2–10 times decrease of TFFs of the

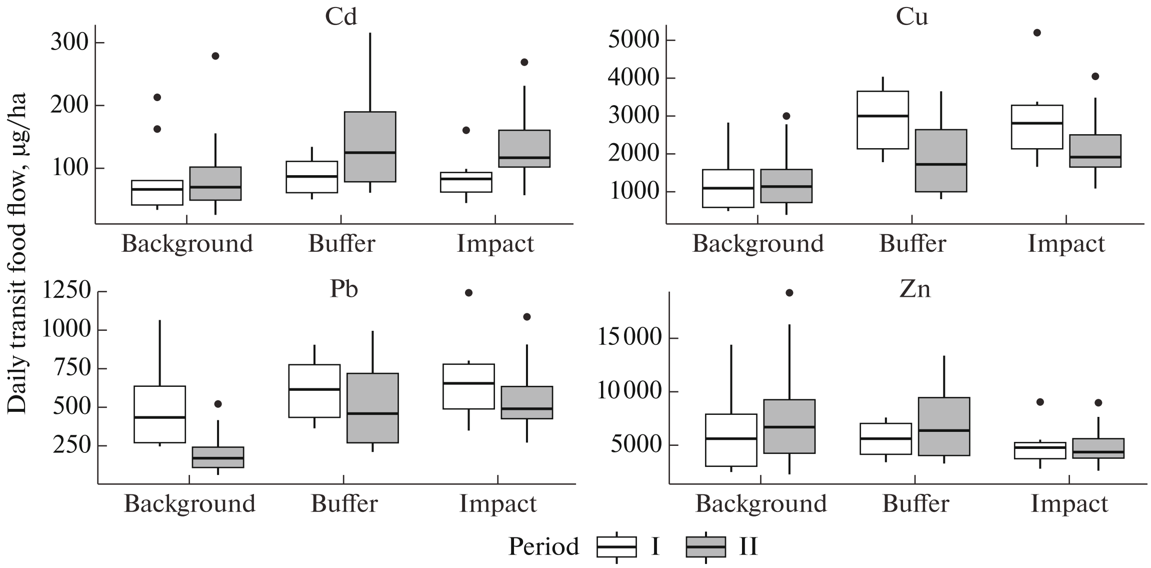

Fig. 1. Total transit food flow of toxic (Cd, Pb) and essential (Cu, Zn) TEs through SM population in the environmental pollution gradient by MUCS emissions during high (I) and almost terminated (II) emissions.

considered elements. The maximum contribution (20–50%) was introduced by these groups in the formation of TFF of toxic TE: granivorous and herbivorous for Pb, zoophages for Cd.

DISCUSSION

According to classical concepts, biota forms and controls flows of matter and energy in the biosphere, thus providing steady environmental parameters (Vernadsky, 1994). Organisms that occupy the different trophic levels are efficiently involved in the stabilization of ecosystems, serving as geochemical barriers and natural depository of chemical elements (Koval'sky, 1974; Pokarzhevsky, 1985; Ermakov and Tyutikov, 2008). Biogenic cycles having constant intensity in natural (unaltered by technogenic impact) BGC can be considered as factor providing their stable functioning, while deformation of cycles under conditions of environmental pollution, as manifestation of destabilizing processes.

It was shown previously that during period of high emissions of MUCS, the involvement of animals in the formation of TEs biogenic cycles was determined by the pollution level, composition of SM communities, their abundance and biomass (Bezel' et al., 2007).

Based on the numerous data, we attempted to distinguish factors that are most important for the formation of the TFF of the essential (Cu, Zn) and toxic (Cd, Pb) elements at significant decrease of technogenic load.

Assuming that the manifold reduction of industrial emissions of the smelter will lead to the partial "purification" of biota components (upper soil horizons, litter, plant, invertebrates), it was expected that a gradual restoration of the environment in the vicinity of MUCS should lead to the increase of the ecological capacity of habitats (first of all, protective–forage properties) for representatives of different TG.

Dynamics of Communities of Small Mammals

The industrial pollution of the environment in the SM communities causes structural rearrangement, the value and direction of which depend on the type of impact, its intensity and duration, as well as peculiarities of species forming to the community (Luk'yanova and Luk'yanov, 1998; Mukhacheva et al., 2010; Mukhacheva, 2013, 2021; Kataev, 2017; Kozlov et al., 2005). Non-ferrous smelters have a strong negative effect on the biota: with their approaching, the species richness and abundance of SM communities show both monotonous (Luk'yanova and Luk'yanov, 1998; Kataev, 2017) and nonlinear changes, reaching maximum in a zone of moderate loads. In particular, in the vicinities of copper (nickel) smelters at the Middle (Mukhacheva, 2021) and South (Mukhacheva et al., 2010) Urals, Kola Peninsula (Kataev, 2017; Kozlov et al., 2005) and Finland (Mukhacheva, 2013) the differences in the SM total abundance reached 1.2–5 times between the buffer and background zones and 5–20 times between the buffer and impact zones. In the vicinity of smelters, the resident population of SM was usually absent (Mukhacheva et al., 2010; Kozlov et al., 2005).

Analysis of long-term dynamics of the SM communities in the vicinity of MUCS showed that the response of animals to industrial pollution has not fundamentally changed over 30 years of observations

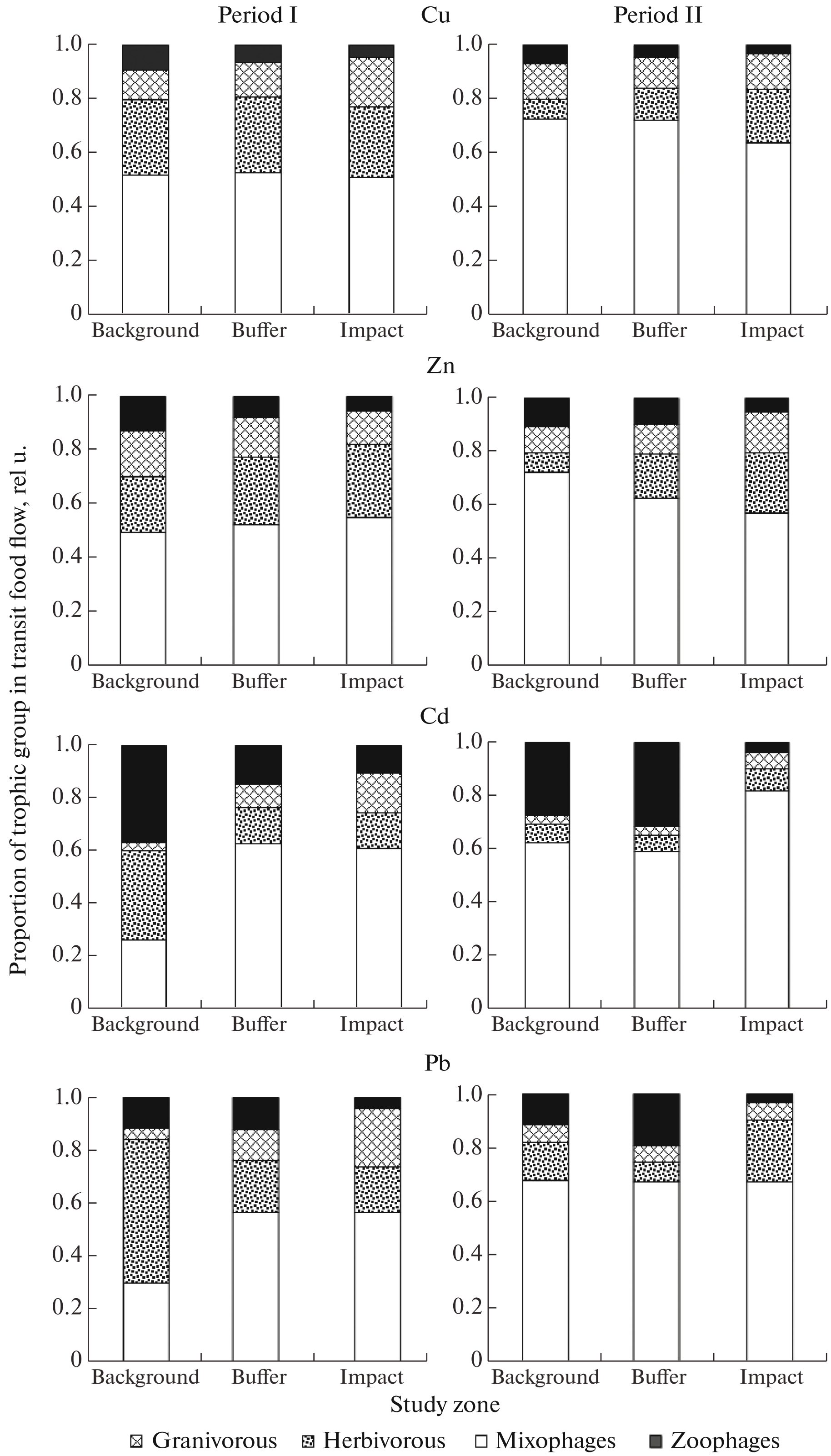

Fig. 2. Contribution of different trophic groups of SM in the formation of transit food flow of essential and toxic TEs in the environmental pollution gradient in the vicinity of the MUCS during stable high (I) and almost terminated (II) periods of the emissions.

Table 3. Results of two-factor ANOVA for the value of transit food flow of the TEs through different trophic groups of small mammals in a pollution gradient at various periods of time in the vicinity of the MUCS (F-test, significance level is shown in parentheses)

Source of variability	df	Cu	Zn	Cd	Pb
			Granivorous		
Zone	2	60.05 (<0.0001)	1.77 (0.180)	108.31 (<0.0001)	126.90 (<0.0001)
Period	1	23.75 (<0.0001)	1.96 (0.168)	14.52 (0.0004)	151.42 (<0.0001)
Zone × period	2	9.97 (0.0002)	6.23 (0.004)	8.53 (0.0006)	5.89 (0.005)
			Herbivorous		
Zone	2	116.69 (<0.0001)	24.14 (<0.0001)	0.86 (0.430)	25.33 (<0.0001)
Period	1	230.56 (<0.0001)	36.63 (<0.0001)	93.07 (<0.0001)	254.61 (<0.0001)
Zone × period	2	12.66 (<0.0001)	9.50 (0.0003)	46.07 (<0.0001)	100.89 (<0.0001)
			Mixophages		
Zone	2	7.39 (0.002)	1.00 (0.371)	11.51 (<0.0001)	14.05 (<0.0001)
Period	1	0.07 (0.797)	3.37 (0.071)	14.79 (0.0003)	0.16 (0.668)
Zone × period	2	1.20 (0.310)	6.74 (0.486)	0.98 (0.383)	0.05 (0.954)
			Zoophages		
Zone	2	1.16 (0.322)	15.76 (<0.0001)	26.65 (<0.0001)	24.03 (<0.0001)
Period	1	8.72 (0.005)	1.17 (0.284)	1.66 (0.203)	5.55 0.022
Zone × period	2	2.04 (0.139)	0.66 (0.529)	10.07 (<0.0001)	4.02 (0.024)
			Total food flow (all trophic groups)		
Zone	2	13.47 (<0.0001)	1.58 (0.215)	2.44 (0.061)	11.23 (<0.0001)
Period	1	3.53 (0.065)	1.00 (0.322)	6.74 (0.012)	12.24 0.0009
Zone × period	2	1.70 (0.192)	0.17 (0.848)	0.89 (0.417)	3.40 (0.041)

(Mukhacheva, 2021). In each of periods, an increase of pollution was accompanied by a significant decrease in the total abundance and α-diversity of communities, whereas the γ-diversity in the background and polluted zones remained similar (13 and 12 species, respectively). The reduction of emissions had no significant influence on the SM community of background zone: the species structure fluctuated insignificantly, the dominant structure did not change (the super dominant, bank voles, annually accounted for over 75% of total abundance), and the increase in the animals abundance by the end of observation period (at the expense of mixophages and granivorous) was related to the successional changes in the vegetation.

The reduction of emissions in the vicinity of smelter, led to the structural rearrangement (a change of dominants), while variation trends of animal abundance were different in the buffer (increase) and impact (absence of changes) zones. An increase of abundance of all TG in the buffer zone was considered as evidence of the initial stages of the recovery of SM communities due to the improvement of protective–forage properties of habitats. In the impact areas, positive shifts in the communities were expressed only in the zoophage group as an increase of proportion and abundance of dominant - Laxmann's shrew (Mukhacheva, 2021).

Dynamics of Trace Element Contents in Diets of Small Mammals

In natural SM populations, the TEs accumulation reveals species peculiarity. This means that at equal levels of environmental pollutants, their different content in animal organism is caused by ecological specifics of species, and, first of all, by their forage (Mukhacheva, 2005, 2022; Gall et al., 2015; Pankakoski et al., 1994). Hunter et al (1987) revealed significant differences in TEs content in forage of SM of different TG, which inhabit the surrounding of the copper refining smelter. Recalculating to 1 g of mass body, zoophages consumed more Cu (by 3 times) and Cd (by 12 times) compared to the herbivorous and granivorous, while Zn influx did not depend on the type of feeding. It is believed that the main reason for the observed differences is the high content of TEs in the zoophages forage (invertebrates) at their relatively low levels in plant food. It is also known that rodents are able to control efficiently the TEs consumption by selective sampling of less polluted forage. This phenomenon was demonstrated for several species of mouse-like rodents under laboratory (Beernaert et al., 2008) and nature conditions (Mukhacheva, 2017; Ozaki et al., 2018).

Our data show that among sympatric populations of SM in the background zone, the maximum TEs contents in forage during both periods were found in zoophages, while the minimum concentrations, in granivorous mammals, and mixophages and herbivorous species occupied the intermediate position on accumulation scale. Thereby, recalculating to 1 g of mass showed that shrews (consumers of second order) compared to the rodents (consumers of 1rst order) consumed with forage more both essential elements (Cu, Zn)—by 1.3–5 times and toxic elements (Cd, Pb)—by 2.4–22 times. Similar pattern was also observed on the moderately polluted areas, but the range of essential TEs was narrowed (by 1.1–2.7 times) and that of toxic TE, in contrast, increased (1.7–35 times). At the highly polluted sites, the highest TEs contents in forage were found in diet of mixophages (forest voles). Compared to shrews, the voles daily received with forage (recalculated for 1 g of mass) by 1.1–2.3 times more essential TE, and by 1.4–6.6 times, toxic elements.

We believe that such changes on polluted territories can be caused, on the one hand, by partial change of forage objects within the group, and, on the other hand, by structural changes in TG composition. Both assumptions are confirmed by facts.

In the background and buffer zones, shrews are characterized by similar composition of forage objects, with important significance of the earthworms. However, at the moderately polluted areas, the Cd and Pb concentrations in earthworms are 4–7 times higher than background values (Nesterkova et al., 2014). In addition, their digestive tract contains particles of polluted soil, which significantly increases the influx of toxic TE in shrews with forage. In the impact areas, in contrast, the zoophage diet is characterized by peculiar "purification" compared to the buffer zone, owing to which the average TE levels approach background values (Mukhacheva, 2022). This is related to the fact that in the vicinity of smelters, the earthworms are absent in feeding of all species of shrews, while their diet is mainly based on invertebrates of replacing groups (*Elateridae, Staphylinidae*, *Carabidae*) with the lowered bioaccumulation of toxic TEs (Bezel et al., 2007; Mukhacheva, 2022).

An increase of Cd concentration in stomach content of mixophages inhabiting severy polluted areas nearly of MUCS during period of almost terminated emissions is caused by a general 1.5–4 times increase of the element in vole forage due to the intense Cd accumulation in humic horizon and forest litter (Mukhacheva, 2017), as well as structural rearrangements in the group. The period II is characterized by the rotation of dominants among mixophages: leading position (75% of the group abundance against 15% during period I) is occupied by northern red-backed vole (*Cl. rutilus*), the forage of which compared to bank voles (*Cl. glareolus*), the prevailing species during period I, contains 1.5 times more Cu and toxic TEs.

Structural rearrangements affected also other TG, which are most expressed in the zoophages. The reduction of emissions from period I to period II was accompanied by a 2–11 times decrease of proportion of "major" species (*S. araneus*, *S. isodon*) in shrew population from background and impact zones, respectively. This fact caused a decrease of the average mass of "model" individual (by 4–8%) and daily forage consumption (by 10–24%) within zones. In the pollution gradient, the total decrease of abundance of the TG and proportion of major species (at unaltered species composition) with approaching smelter led to 40–60%-decrease of discussed parameters of impact shrews compared to the background ones (Table 1).

Thus, a decrease of technogenic load in space (moving from smelter) and time (from first to the second period) in most cases was accompanied by the total decrease of TEs concentrations (both essential and toxic) in the animal forage and affected all TG. However, changes that have occurred during 30 year observations are not proportional to the multiple decreases of volumes of gross emissions of MUCS (by 50 times) and contents of the considered TEs (Cu, Zn, Pb) in them (by 8–3000 times).

Dynamics of Transit Food Flows in Space and Time

It was suggested that SM communities are characterized by a broad spectrum of food preferences of consumers of the first and second orders, thus reflecting the composition and level of environmental pollution. At the same time, the total volume of daily consumption of TEs by all species amounting SM communities makes it possible to estimate the participation of animals in local biogeochemical cycles, as well as to reveal possible changes of migration flows of TEs during periods high emissions and natural remediation of environment after their multiple reduction of emissions. Depending on the balance of the processes, the joint action of the considered factors could result in the stabilization, intensification, or slowdown of biogeochemical exchange of TE.

Performed calculations showed that during snowless period, the SM population at each hectare of fir–spruce forests in the background zone through consumption daily involved in the biogenic exchange (depending on the phase of population dynamics) from 2.2 to 19.3 mg Zn, from 0.5 to 3.0 mg Cu, from 0.06 to 1.1 mg Pb, and from 0.03 to 0.3 mg Cd. In the vicinity of smelters, the values of total Zn TFF were close to the background value (2.6–13.3 mg/ha), whereas those of other elements recorded two-fold exceeding of TFF: daily influx of Cu varied from 0.8 to 5.2 mg/ha, Pb—from 0.2 to 1.3 mg/ha, and Cd—from 0.05 to 0.3 mg/ha.

Analysis of generalized (for 10-year intervals) data showed that the character of changes of food transit of the studied TEs had much in common. In the pollution gradient, a decrease of load during both the periods was accompanied by an increase of total Zn TFF by 20–25%, whereas the value of total TFF of other elements, in contrast, decreased (Fig. 1). Zoned differences were maximum for Cu (period I) and Pb (period II), TFF directed decreased by 2.7–3.3 times (respectively) as distance from the smelter increased.

At the background zone the reduction of MUCS emissions did not, as expected, lead to a significant decrease of total TFF of Zn, Cu, and Cd. The absence of expressed temporal changes can be considered as stabilization of biogenic exchange of these TEs, which indicates the low level of anthropogenic impact (in particular, pollution) on BGC in the background zone. Indeed, the TEs content in depository environment (in snow cover, soil horizons, forest litter) and other components of biota (vascular plants, wild fruits and berries, and mushrooms) corresponded to the levels of regional background (Bezel et al., 2010; Vorobeichik and Kaigorodova, 2017; Trubina et al., 2013, 2014).

For the same time interval, the value of background Pb TFF compared to the initial value decreased twice, which can be interpreted as the retardation of exchange processes. The main reason for changes was a significant (from 2 to 10 times) decrease of Pb concentrations in forage of SM of all TG inhabiting unpolluted areas. It should be noted that the effect was too high to be compensated even by 40% increase of the total abundance of SM community. We suggest that a sharp decrease of Pb level in biota components in recent two decades was related, first of all, with a total decrease of its content in motor emissions owing to the transition from ethylated petrol to other types of fuel. Remind that all studied zones are intersected by highway with intensive traffic.

The reduction of emissions at the polluted areas (from period I to period II) was accompanied by differently directed trends of TFF changes: a general decrease of Cu and Pb, increase of Cd, and insignificant fluctuations of Zn (Fig. 1, Table 3). A decrease of TFF value is caused, first of all, by the sharp (from 1.5 to 5 times) decrease of TEs concentrations in forage of consumers of the first order in the buffer (for Cu and Pb) and impact (only for Cu) zones. This is well consistent with information that modernization of production resulted in the maximum decrease of exactly Cu and Pb contents in MUCS emissions (Vorobeichik and Kaigorodova, 2017). The main contribution in the formation of TFF of these TEs is made by mixophages. Thereby, during the entire observation period, the value of flows controlled by representatives of this group were supported at the same level (in absolute values), whereas the contribution of other TG compared to the initial values decreased by 1.5–3 times or remained unchangeable (Fig. 2). Thus, the polluted areas demonstrated both stabilization (Zn) and retardation (Cu, Pb) of biogeochemical exchange of TEs.

The time dynamics of Cd TFF at the polluted sites was peculiar in the intensification (by 1.6 times) of exchange processes from period I to period II. Thereby, the formation of Cd flows in different zones was controlled by different mechanisms: its growth is mainly provided by zoophage group at the moderately polluted areas, and by mixophages at the severy polluted zone (Fig. 2).

The elevated contribution of zoophages in the buffer zone is related to the joint action of two factors: the growth of group abundance (by 2.4 times) on the one hand, and equivalent increase of Cd concentrations in their diets (by 2.5 times) due to the partial change of forage. The reasons of such changes were discussed above. Note that our estimates of zoophage contribution in the formation of total TFF of all studied TEs could be slightly underestimated due to the features of the accounting method to shrews. An insignificant increase of Cd TFF in the buffer zone due to mixophages is exclusively caused by changes in the abundance of this group, because the concentration of element in the forage of voles of the buffer zone during the entire observation period did not change. A significant increase of Cd TFF in the zone of severe pollution, in contrast, is related to the two-fold growth of element concentrations in animal forage, because the total abundance of the group during period II even decreased.

Thus, our hypothesis about the TFF specifics of flows through SM population of different TG, which coinhabit the polluted and background areas during the high and reduced emission, was completely confirmed. The assumption about the alignment of quantitative parameters of transit flows of the studied TE due to the multiple reduction of MUCS emissions was confirmed partially, only for Zn and Pb, the level of geochemical exchange of which approached the present-day (period II) or the initial (period I) background values (respectively). The Cu and Cd contents even at the end of period II were two times higher than the initial background values of TFF in the vicinity of smelter.

CONCLUSIONS

We are unaware of any long-term studies of SM communities inhabited in the vicinity of the point source of industrial pollution in the period high emissions and after its reduction, which would provide the direct comparison of the biogeochemical flows of TEs intensity through sympatric populations of mouse-like rodents (eight species) and small insectivorous mammals (four species) from the background and polluted areas was carried out based on the annual registrations of abundance, biodiversity, demographic structure and size–weight parameters of local species populations with involvement of trace-element composition of diets.

The examined hypothesis about peculiarity of biogenic TEs exchange caused by specifics of food and abundance of animals was confirmed completely. It was shown that the value of transit flows of TEs (Cu, Zn, Cd, Pb) through SM communities with allowance for the trophic specialization (granivorous, herbivorous, mixo- and zoophages) of separate species, which coinhabit in the vicinity of the Middle Ural Copper Smelter, was determined by the amount of consumed forage, concentrations tent of TEs in it, as well as the abundance of comparable groups.

The reduction of MUCS emissions was accompanied by a gradual decrease of daily consumption of forage in the series herbivorous > mixophages > granivorous > zoophages with approaching smelter. Thereby, at the background and moderately polluted territories, zoophages were characterized by the maximum TEs content, while granivorous species, by the minimum contents. In the nearly of the smelter, the elevated accumulation of TEs was noted in diets of mixophages, while the minimum accumulation, in granivorous mammals. The observed changes were related to the structural rearrangement in trophic group (a change of dominants) and a partial change of forage. A decrease of technogenic load in space (with increasing distance from smelter) and time (1990–2019) in most cases was accompanied by the total decrease of TEs concentrations (both essential and toxic) and affected all TG. Thereby, changes occurred during 30 year observations were not equivalent to 50 fold decrease of volumes of MUCS emissions for the same period.

Our assumptions about gradual alignment of the quantitative parameters of transit flows of the studied TEs at the polluted and background areas due to the decrease of technogenic load was partially confirmed. The value of total TFF of most TE (Cu, Zn, Cd) at the background areas characterized the stable functioning of the system during the entire time interval, while the retardation of biogenic Pb exchange was not related to the level of industrial pollution. In the vicinities of MUCS, only Zn TFF was characterized by the constant intensity in space and time, whereas TFF dynamics of other TEs can be interpreted as retardation (Cu, Pb) or intensification (Cd) of biogenic exchange through SM population coinhabiting the polluted areas. The main reasons of observed deformations of exchange processes were structural rearrangements in the SM communities, as well as a change of TE concentrations in forage of separate TG.

Natural remediation of anthropogenically disturbed territories is a complex process, which involves a diverse complex of living organisms composing BGC: producers, consumers, and destructors. The role of SM communities during biogenic exchange of TE should be considered as one of the chains, which reflect the intricate processes occurring in space and time.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest and confirm compliance with applicable ethical guidelines for the use of animals in research.

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