

# Geochemical Ecology of Small Mammals at Industrially Polluted Areas: Is There any Effect of Reduction in the Emissions?

V. S. Bezel<sup>a,\*</sup> and S. V. Mukhacheva<sup>a,\*\*</sup>

<sup>a</sup>*Institute of Plant and Animal Ecology, Ural Branch, Russian Academy of Sciences, Yekaterinburg, 620144 Russia*

\**e-mail: bezel@ipae.uran.ru*

\*\**e-mail: msv@ipae.uran.ru*

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**Abstract**—The paper presents data on the involvement of local populations of bank vole (*Clethrionomys glareolus*) in the biogeochemical cycles of Cu, Zn, Cd, and Pb at territories strongly chemically polluted by large non-ferrous metallurgical plant in the Middle Urals (in 1990–1992) and after a significant decrease in its emissions (in 2015–2017). At maximally polluted areas (impact zone), the animal-controlled transit Cu, Cd, and Pb flows approached their background values by the end of the study period, and the Zn flow simultaneously twofold decreased compared to the background areas. At moderately polluted areas (buffer zone), no significant changes in the metal fluxed were detected for any of the elements. The specifics of the transit flows of the elements at variably polluted areas are controlled by the concentrations of these elements in the diet of the animals and by the abundance of voles. Thereby the manyfold (fifty-fold) decrease in the emissions did no result in an equivalent decrease in the concentrations of the metals in the animal rations at the polluted areas. The main reason for the changes was a structural transformation in the community of the small mammals, which led to a drastic decrease in the bank vole population in the impact zone. The simultaneous effects of the analyzed factors over the study period of time (25 years) resulted in intensification (in the background zone), retardation (impact zone), and stabilization (buffer zone) of the biogeochemical exchange of the elements.

**Keywords:** biogeochemistry, industrial pollution, emission decline, transit flow of elements, Cu, Zn, Cd, Pb, bank vole

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## INTRODUCTION

The ubiquitous tendency toward a reduce in the emissions of industrial plants thanks to technological advancements or work stoppages over the past decade led to that much attention was focused on the rehabilitation of the human-disturbed areas (Vorobeichik et al., 2014; Kalabin and Moiseenko, 2011; Koptsik et al., 2016; Lyanguzova and Maznaya, 2012; Mukhacheva, 2017; Chernen'kova and Bochkarev, 2013; Camizuli et al., 2018; Juknys et al., 2003). Many pollutants [heavy metals (HM) among others] are retained for a long time in ecosystems surrounding pollution sources (Vorobeichik and Kaigorodova, 2017; Douay et al., 2009; Kabala et al., 2008). In the absence of targeted rehabilitation actions, these pollutants can continue to circulate through the food chains (Gall et al., 2015) and adversely affect the biota (Mukhacheva and Bezel', 2015; Berglund et al., 2011; Kozlov and Zvereva, 2011). No consensus has been reached so far about the rates and intensity of processes of the natural rehabilitation of areas disturbed due to anthropogenic activities. Some researchers are prone to believe that ecosystems shall rapidly reach their original states as soon as the industrial emissions are reduced (Chernen'kova

and Bochkarev, 2013; Berglund et al., 2012; Juknys et al., 2003), whereas others think that the rehabilitation shall take a long time even after the emissions are completely terminated (Vorobeichik et al., 2014; Laynguzova and Maznaya, 2012; Mukhacheva, 2017; Berglund et al., 2011; Camizuli et al., 2018). Some authors argue that an ecosystem affected by pollution does not tend to its original state upon its toxic pollution is decreased but is instead modified and acquires new stability characteristics (Moiseenko, 2011). The complicatedness of interpretations of these changes stems from the need for unambiguous identification of their driving forces: whether these changes are caused only by the reduction in the emissions or also by other factors, including anthropogenic ones, which are not directly related to the toxic impact on the animals.

Long-term studies of dynamic changes in various biota components in the surroundings of the Middle Ural Copper Smelter (MUCS) at the same sites and periods have shown that even when the industrial emissions were manifold reduced, the trees continue to die off, and the ground vegetation (Vorobeichik et al., 2014), soil macrofauna communities (Vorobeichik et al., 2012), and those of small insectivore mammals and murine rodents (Vorobeichik and Nesterkova,

2015; Mukhacheva, 2016) show no signs of recovery. A suppressed state of the forest ecosystems is reportedly explained by the very sluggish removal of heavy metals from the upper soil layers, the occurrence of thick forest litter, and suppressed processes of the destruction and subsequent mineralization of plant residues. In this condition it was particularly interesting to gain an insight into the mechanisms and to estimate the intensity of the natural recovery processes of the biogeocenoses (BGC), including the biogeocenotic cycles.

The participation of animals in biogenic exchange includes the "animal waste" in the form of dead individuals, a transit flows of chemical elements (that includes the consumption of the primary production and the outflow of vital activity products), and burrowing and nest-building activities. With reference to mammals, the major flows of chemical elements are related mostly to trophic activities (Ermakov and Tyutikov, 2008; Ermakov et al., 2018; Pokarzhevskii, 1985).

We have previously evaluated the transit flows of some major and trace elements through populations of small mammals (with reference to bank vole) at variably polluted areas in the vicinities of MUCS. It has been demonstrated that the deformations of the animal-controlled biogenic flows were not only induced by the enhanced intake of the elements with diet, but also (and largely) depended on the abundance of the local populations (Mukhacheva and Bezel', 2004; Bezel' et al., 2007). These studies were performed during a period of intense environmental pollution by plant emissions in the 1990s. Over the past two and a half decades (first of all, after the modernization of the plant was completed in 2010), the total emissions from MUCS manifold (fifty-fold), reduced and thereby the SO<sub>2</sub>, and HM (Cu, Zn, and Pb) concentrations were maximally decreased. It was interesting to understand whether the significant reduction of the industrial emissions led to any changes in the biogeochemical exchange of these elements through the populations of small mammals (SM).

Our study was focused on estimating the dynamic changes in the transit flows of elements (Cu, Zn, Cd, and Pb) through SM populations inhabiting MUCS vicinities upon the significant reduction of MUCS emissions. All studies were carried out using the same technique, at the same sites, in 1990–1992 and 2015–2017 (i.e., 25 years after the first period of measurements). We suggested that the gradual recovery of the biota, which began after the emissions were reduced (Vorobeichik et al., 2012, 2014, 2017), should have equalized the quantitative parameters of the transit flows of the elements at the compared areas.

## METHODS

### *Emission Sources*

The Middle Ural Copper Smelter (MUCS) located in the suburbs of Revda, 50 km west of Yekaterinburg (56°51' N, 59°53' E) is Russia's largest primary copper

smelter and a plant for producing sulfuric acid. It started operating in 1940, and its the annual total emissions (mostly SO<sub>2</sub> and dust with HM and metalloids) reached 150–225 × 10<sup>3</sup> t in the 1980s, were 95–100 × 10<sup>3</sup> t in the 1990s, were diminished to 30 × 10<sup>3</sup> t in the mid-2000s, and were no higher than 2.5–5 × 10<sup>3</sup> t in 2010 (upon modernization) (Vorobeichik et al., 2014). Over the past two and a half decades, emissions from the plant were thus reduced almost fifty-fold. A particularly significant decrease was reached in the concentrations of SO<sub>2</sub> (80 times), Cu (3000 times), Zn (15 times), and Pb (8.5 times) (Vorobeichik and Kaigorodova, 2017). The period of time when the monitoring was carried out can be provisionally subdivided into two periods of (I) stable high (in 1990–1992) and almost terminated emissions (2015–2017) emission.

### *Experimental Animals*

The model animal used in this study was bank vole (*Clethrionomys glareolus* Schreber, 1780), a typical forest mammal of the taiga zone, which was dominant in the SM community throughout the whole study period of time at both background (close to 75% of the total abundance) and polluted (>50%) areas. Bank vole is highly ecologically plastic and is characterized by a wide range of forage objects, mostly vegetative parts of herbaceous plants, seeds, berries, mushrooms, mosses, lichens, various invertebrates, and occasionally small vertebrate animals (*European Bank Vole*, 1981; Hansson, 1985). Being dominantly herbivorous, it plays a role of a biocatalyst, and when passing the consumed primary production through its digestive tract, it facilitates the more complete and intense involvement of various chemical elements in biogenic exchange.

### *Trapping the Animals*

The animals were trapped annually during the snowless period of time (from May through September) in three sessions, following a unified scheme. The snap-traps (25 traps spaced 5–7 m apart, 4 days exposure, checked daily) were deployed along stationary lines, which were laid out in 1990 westward of MUCS (against the dominant wind) in spruce-fir forests in the impact (within 1–2 km from the emission source), buffer (4–5 km), and background (20 km) zones. The animals were trapped simultaneously at all zones, along three to nine lines (spaced 100 to 1000 m apart) in each zone. The field work amounted to more than 26000 trap-days (13800 and 12300 trap-days during the first and second periods of time, respectively), 764 bank vole were trapped, including 463 at the background zone and 301 in the vicinities of MUCS (461 during the first period of time and 348 during the second one). For each of the trapped animal, its sex, age, and reproductive status were determined. Based on a set of features, the animals were classified into three groups: overwintered, immature, and mature.

**Table 1.** Variations in the population density (individuals/ha) and daily forage consumption by an “abstract” individual (g per dry weight) in an anthropogenic pollution gradient

Distance from smelter, km	Study area	Study period (years)	
		I (1990–1992)	II (2015–2017)
Density of bank vole, individuals/ha			
20	Background	12.6 ± 3.6	17.9 ± 5.50
4–5	Buffer	8.0 ± 1.8	10.8 ± 3.80
1–2	Impact	4.2 ± 0.5	2.7 ± 0.60
Forage mass consumed by an “abstract” individual, g/day			
20	Background	3.01 ± 0.05	2.96 ± 0.03
4–5	Buffer	2.96 ± 0.09	2.86 ± 0.02
1–2	Impact	3.02 ± 0.05	2.89 ± 0.07

Arithmetic averages and errors of the averages are reported.

### *Evaluating the Animal Numbers*

We used data on the absolute number of the animals (individuals/ha), which were calculated according to the method (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 these coefficients depending on the numbers of the animals. In the zone of boreal forests at middle latitudes, the bank vole is known to show pronounced cyclic variations in the population size (*European Bank Vole*, 1981). To level off these differences for each of the periods of time, we used data on three sequential years, including all phases of the population dynamics (depression, growth, and peak). Trapping the animal throughout the whole snowless period of time (spring, summer, and autumn) allowed us to take into account the seasonal variations in the number of the animals. In the later calculations, we used data on the whole snowless period of time averaged over three years (Table 1).

### *Daily Forage Consumption*

According to literature data, the consumption intensity during the snowless period of time significantly (up to 30% and even more) varies for animals of different sex, age, and reproductive status (Voronov, 1955; Kuznetsov and Mikhailin, 1985; Mukhacheva, 2005). In view of this, we used data on the daily food consumption by an “abstract” individual animal. The values were calculated from weighted average values (Table 1), with regard for the demographic structure of the local bank vole populations during periods I and II, the size-weight parameters of the animals, and the amount of forage consumed by them.

### *Chemical Analysis of the Samples*

To estimate the accumulation levels of the HMs (Cu, Zn, Cd, and Pb) in the forage of the animals, we used the contents of their stomachs. If the ration was of complicated composition and plastic, the animals

actively moved, and the pollution showed a mosaic distribution, the most accurate approach was (in our opinion) to determine concentrations of elements in the stomach content (Mukhacheva, 2005). The samples were taken with clean plastic spreaders, individually for each animal. The material was then placed onto an object glass, dried in a air bath at a temperature of 75°C to air-dry mass, and packed in pressure-tight plastic bags. The samples were then homogenized, weighted (approximately 0.1 g) on a KERN-770 analytical balance accurate to 0.00001 g, and placed into Teflon bombs with a mixture of 7 mL 65% HNO<sub>3</sub> (ultra high purity) and 1 mL deionized H<sub>2</sub>O, incubated for 30 min, and incinerated in a MWS-2 (Berg-hof, Germany) microwave oven. Upon cineration, the sample volume was adjusted to 10 mL with deionized H<sub>2</sub>O. Concentrations of HMs (µg/g per dry weight) were measured on an AAS vario 6 (Analytik Jena, Germany) atomic absorption spectrometers with flame (for Cu and Zn) or electrothermal (for Cd and Pb) atomization. Analysis was conducted at the Laboratory of Ecotoxicology of Populations and Communities (Institute of Plant and Animal Ecology, Ural Branch, Russian Academy of Sciences) certified for technical competence (certificate no. ROSS RU.0001.515630). The quality of the measurements was estimated with the internationally certified standard reference sample CRM 185R (bovine liver). The extraction percentages were 93.2% for Cu, 99.8% for Zn, 114.2% for Cd, and 94.4% for Pb; the respective detection-limit concentrations 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 got analyzed 487 samples of stomach contents.

### *Calculation of the Transit Flow of Chemical Elements*

The transit flows of elements (mg/ha × day per dry weight) through the local bank vole populations ( $P_i$ ) at various zones ( $i$ ) were calculated from the known absolute number of the animals ( $N_i$ ), concentration of a

given element in the ration ( $C_i$ ), and the forage amount consumed by an "abstract" individual animal ( $M_i$ ):

$$P_i = C_i N_i M_i.$$

#### *Statistical Analysis*

The distribution of element concentrations was commonly close to a lognormal one, and hence, the further analysis was carried out with the logarithms of the concentrations. Geometric averages and maximum/minimum values were calculated for the concentrations of HMs and their transit flows, and arithmetic averages and errors of averages were used in processing data on the number of the animals and forage consumption. The possible differences between zones and periods of time in terms of these parameters were identified using analysis of variance (ANOVA). In the statistical tests, differences were assumed to be significant at  $p < 0.05$ . The calculations were made with the JMP v.11 program package.

## RESULTS

### *Bank Vole Population Density*

Data on the dynamic variations in the population density of bank vole at different distances of the emission source are summarized in Table 1. As the technogenic load increased, the density of animals gradually decreased ( $F = 6.67$ ,  $p = 0.011$ ), whereas the differences between study periods within a given zone were statistically insignificant ( $F = 0.69$ ,  $p = 0.421$ ). Note that the reasons for the increase in the differences from the buffer (from two- to threefold) and background (from four- to sevenfold) areas during period II were the unequal trends: a 40% increase in the number of the animals at the background and moderately polluted areas and a simultaneous 60% decrease in this number at the impact zone.

### *Daily Forage Consumption by Bank Vole*

The calculated forage consumption by a single "abstract" individual bank vole indicates that no significant differences occur between these parameters for the different zones ( $F = 1.49$ ,  $p = 0.264$ ), whereas the dynamic variations in this parameter were significant at all areas ( $F = 7.76$ ,  $p = 0.017$ ). From the observation period I to II, the registered forage mass consumed by the animals everywhere decreased (Table 1). The probable reason for this was the overall "rejuvenation" of the populations. Analysis of the demographic structure of the local populations of bank vole shows that a decline in the emissions at all of the zones was followed by an increase in the percentage of young animals (immature): the increase was close to 20% at the polluted areas and close to 50% at the background zone. At the same time, the percentages of overwintered individuals consuming 20–30% more forage decreased.

### *Concentrations of the Elements in the Rations*

Data on accumulation of the elements in the rations of the bank voles trapped during the snowless periods at different distances from the emission source are presented in Table 2. The concentrations of all HMs systematically increased toward MUCS ( $p < 0.0001$ ). For example, the concentrations of Cu, Cd, and Pb during period I at the impact areas were five to six times higher than the background values, and the Zn concentration was two times higher. During period II, the range of the Zn concentrations remained at the same level, and the Cu concentrations decreased by a factor of 4.6 times away from the smelter. Conversely, the differences for the toxic elements seven- to tenfold increased (for Cd and Pb, respectively). As a result of the reduction in aerial emissions from MUCS, the decrease in the concentrations in the animal ration (during period II as compared to period I) was significant only for Cu ( $F = 23.42$ ,  $p < 0.0001$ ) and Pb ( $F = 9.18$ ,  $p = 0.003$ ). Simultaneously, Cd concentration in the animal rations increased, and the Zn concentration remained at the same level. The effect of elevated Cd concentrations in bank vole diet and the probable reasons for this increase were discussed in our earlier paper (Mukhacheva, 2017).

### *Transit Flow of the Elements through the Populations*

The calculated transit flows of each of the elements during the studied periods are presented in Table 2. During the snowless period, the daily biogeochemical exchange in the spruce–fir forests (per ha) due to the consumption of primary production by the bank vole populations involved 0.9–7.1 mg Zn, 0.4–3.2 mg Cu, 0.01–0.13 mg Cd, and 0.04–0.9 mg Pb. Thereby the differences between the flows at the zones were statistically significant for all of the elements (Table 3). For Cu, Cd, and Pb, nonlinear changes with maximum in the buffer zone were registered during both of the periods of study, whereas the Zn concentrations monotonously decreased toward the emission source. At the same time, obvious dynamic changes in the transit flow from period I to II (according to data of single-factor ANOVA), in the form of a decrease in the biogeochemical exchange intensity by a factor of 2.5, were registered only at the impact areas for Cu ( $F = 11.33$ ,  $p = 0.028$ ) and Pb ( $F = 11.04$ ,  $p = 0.029$ ).

## DISCUSSION

A key factor controlling SM involvement in biogeochemical exchange is the level of food-related transit of chemical elements through the populations. The intensity of this exchange depends on the concentrations of the elements in the animal rations, the consumed forage amounts, and the local population density of the species. Inasmuch as the forage mass daily consumed by an "abstract" individual animal during each of the study periods did not show any significant

**Table 2.** Concentrations of chemical elements ( $\mu\text{g/g}$  per dry weight) in the ration of bank vole and the transit flows of the elements ( $\mu\text{g/ha day}$ ) through the local populations in the gradient of pollution

Element	Study period (years)					
	I (1990–1992)			II (2015–2017)		
	Study area					
	Background	Buffer	Impact	Background	Buffer	Impact
Concentration of elements in the ration, $\mu\text{g/g}$ per dry weight						
Copper	$\frac{18.6}{3.3-223.6}$	$\frac{79.5}{6.5-1048.8}$	$\frac{105.7}{4.1-831.8}$	$\frac{16.4}{4.5-48.0}$	$\frac{61.1}{9.8-161.5}$	$\frac{74.4}{34.2-442.0}$
Zinc	$\frac{90.6}{18.3-416.0}$	$\frac{139.7}{23.0-1824.8}$	$\frac{185.3}{19.2-810.9}$	$\frac{91.0}{37.1-194.7}$	$\frac{122.8}{20.6-608.0}$	$\frac{181.9}{81.6-395.4}$
Cadmium	$\frac{0.56}{na-14.40}$	$\frac{2.56}{0.11-18.34}$	$\frac{3.44}{0.09-88.63}$	$\frac{0.81}{na-9.23}$	$\frac{2.36}{0.25-20.09}$	$\frac{5.88}{1.55-25.26}$
Lead	$\frac{4.56}{na-43.16}$	$\frac{18.53}{0.10-207.47}$	$\frac{24.21}{0.63-287.38}$	$\frac{1.82}{na-13.70}$	$\frac{16.82}{1.97-78.82}$	$\frac{17.25}{4.64-83.01}$
<i>n</i>	234	131	104	75	24	18
Transit flow through population, $\mu\text{g/ha} \times \text{day}$						
Copper	$\frac{652}{438-1072}$	$\frac{1722}{1145-2637}$	$\frac{1328}{1077-1550}$	$\frac{759}{352-1280}$	$\frac{1670}{1057-3233}$	$\frac{543}{367-846}$
Zinc	$\frac{3137}{2131-5219}$	$\frac{3133}{2011-4614}$	$\frac{2329}{1889-2719}$	$\frac{4218}{1958-7111}$	$\frac{3357}{2126-6498}$	$\frac{1328}{898-2069}$
Cadmium	$\frac{20}{13-32}$	$\frac{57}{37-85}$	$\frac{43}{35-50}$	$\frac{38}{17-63}$	$\frac{65}{41-125}$	$\frac{43}{29-67}$
Lead	$\frac{160}{107-263}$	$\frac{413}{267-612}$	$\frac{304}{247-355}$	$\frac{84}{39-142}$	$\frac{460}{291-890}$	$\frac{126}{85-196}$

Nominators are geometric averages, denominators are the minimum and maximum values, *na* means concentrations below the detection limits, and *n* is the numbers of analyzed samples.

differences between the zones, it is reasonable to believe that the intensity of the biogeochemical exchange of each element depended on its concentration on the ration and the number of the bank voles. Our calculations indicate that the transit flows in an industrial pollution gradient were significantly different for all elements (Tables 2, 3). This result seems to be quite evident, because both of the main parameters (the density of the animals and the concentrations of the HMs in the rations) are significantly modified in a pollution gradient. Conceivably, it is the combined effect of these factors that controls the nonlinear variations in the transit flows of Cu, Cd, and Pb (Table 2).

Our earlier case study of local bank vole populations in the vicinities of MUCS (Mukhacheva and Bezel', 2004; Bezel', 2007) during its persistently high emissions (in 1990–1998) has shown that the involvement of animals in biogeochemical cycles (which were evaluated for 21 chemical elements) is controlled not so much by the level of the industrial pollution of an environment (first of all, animal rations) as by the species

**Table 3.** Results of two-factor analysis of variance of the differences in the transit flows of elements through the local bank vole populations in a pollution gradient at various periods of time

Element	Variability source	<i>df</i>	<i>F</i>	<i>p</i>
Copper	Zone	2	5.73	<b>0.018</b>
	Period	1	1.38	0.269
	Zone $\times$ period	2	1.97	0.182
Zinc	Zone	2	3.96	<b>0.049</b>
	Period	1	0.09	0.771
	Zone $\times$ period	2	1.25	0.321
Cadmium	Zone	2	4.20	<b>0.041</b>
	Period	1	1.26	0.287
	Zone $\times$ period	2	0.78	0.481
Lead	Zone	2	11.44	<b>0.002</b>
	Period	1	4.28	0.061
	Zone $\times$ period	2	1.17	0.222

composition and the number of the community SM. It has been demonstrated that the transit flow during depression periods (when the numbers of animals at contrasting territories differed insignificantly) was controlled, first of all, by the concentration of a given element in the animal ration. An increase in the animal number led to more intense involvement of chemical elements in exchange. The role of the number of the animals increased (this number increased by one order of magnitude and more during the peak years), as was particularly well seen at the background areas.

We expected that the significant (fifty-fold) reduction in the gross industrial emissions from MUCS over the two decades should have led to at least partial purification of biota components, including the vegetation and upper soil horizons. Moreover, we hypothesized that the gradual restoration of the environment should have improved the quality of the habitats, increased their ecological capacities, and indirectly, increased the density of animal populations of various species. As a result of these changes, biogeochemical exchange of the elements through the populations of herbivorous organisms at the polluted areas should have approached its background level.

Analysis of the averaged (over a period of three years) data shows that the transit flows of Zn and Cd at the background areas have increased (by a factor of 1/3 and almost twofold, respectively) over the study period (25 years), the Pb flow has simultaneously decreased (twofold), and Cu flow has not been modified at all. No significant changes in the flows of the four elements have been detected at the buffer areas. Conversely, in the impact zone, the transit flows of most of the elements decreased: by factors of almost 2.4 for Cu and Pb and by a factor of 1.8 for Zn. The only exception is Cd, whose flow has not changed. This led us to conclude that the modern (during period II) Cu, Cd, and Pb flows registered in the impact zone approached the background ones (for period I and/or II) and decreased by factors of 1.7–2.4 for Zn.

Such changes in the biogeochemical situation can be due to various factors. The likely most probable ones are as follows: (1) a drastic reduction in the volumes of pollutants coming to the environment and, consequently, a decrease in the concentrations of the pollutants in components of the biota (including its vegetation); (2) changes in the ration structure (due to a change in the species composition of the plant communities in the course of the reductive succession); (3) selective consumption of less polluted forage by the animals; and (4) changes in the abundance of the local populations.

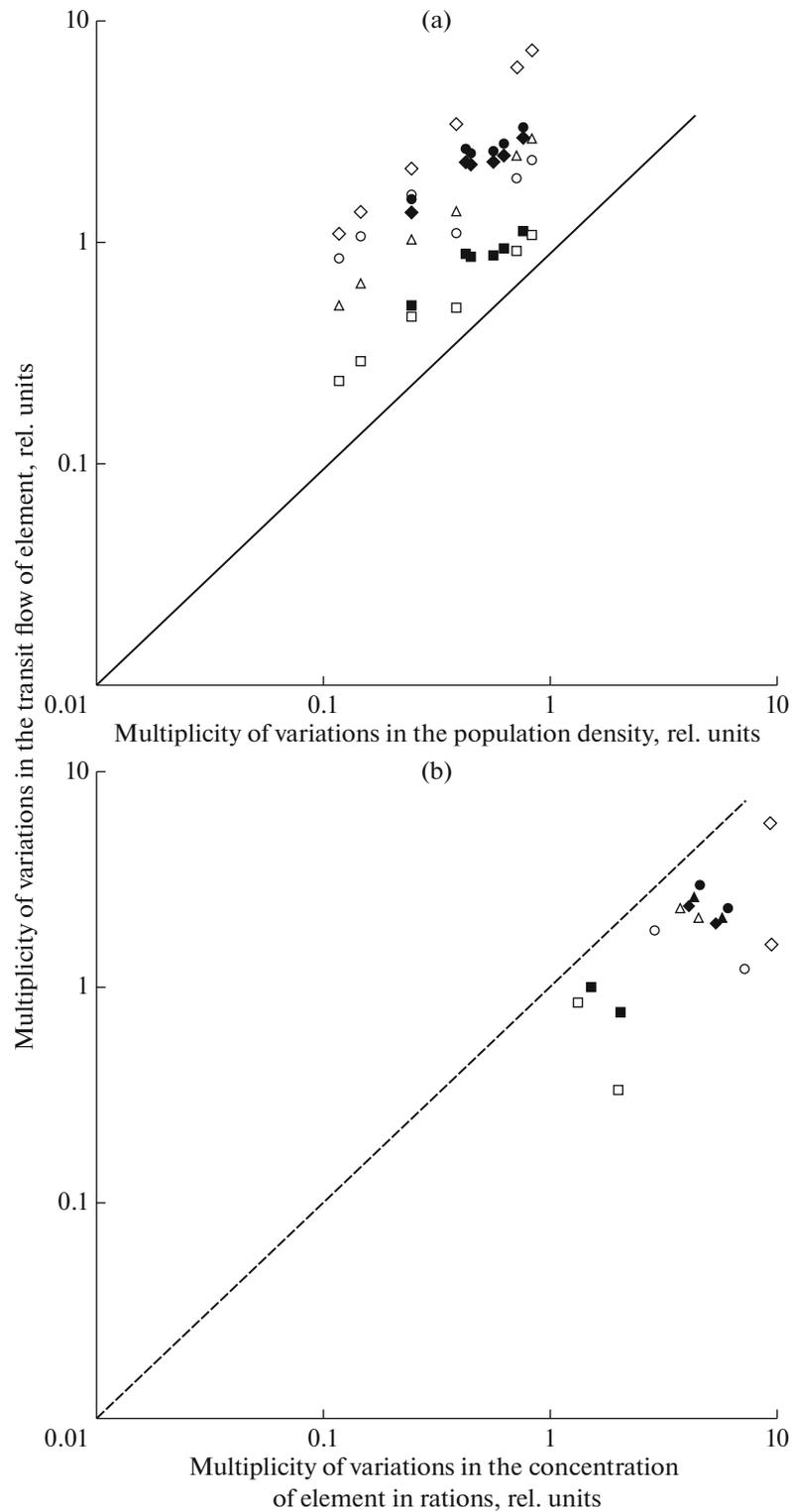
As was proved by our earlier studies (Mukhacheva, 2017), no equivalent changes in the accumulation levels of the elements in the forage of the animals have occurred since the many-fold reduction in MUCS emissions. During the two and a half decades of the observations, the concentrations of the essential ele-

ments (Cu and Zn) in the zone varied insignificantly (by no more than 20%) and did not have clear trends. The trends in the concentrations of the toxic elements (Cd and Pb) were different: Pb concentration in the forage of the animals has everywhere decrease by the end of the study period, whereas Cd has been, conversely, intensely accumulated in the animal forage at the polluted areas.

According to (Vorobeichik et al., 2014), the composition of plant communities in the impact zone has not changed over the period of time in question, and hence, the spectrum of the forage types can also be assumed as not changing. The literature provides information that animals are able to efficiently regulate the intake of pollutants to their organisms. This phenomenon was illustrated by the examples of some species of murine rodents both in the laboratory (Beernaert et al., 2008) and in nature (Zaichenko, 1981; Ozaki et al., 2018): the animals themselves could select less contaminated forage. This factor can, however, be neglected in our situation, because the concentrations of all of the four elements in the bank vole ration at the buffer areas varied insignificantly, and the trends for the impact zone were different but similar to the changes in the soil horizons (Mukhacheva, 2017).

Hence, the biogeochemical specifics of the flows at the variably polluted areas were controlled, first and foremost, by the number of the animals and the concentrations of the elements in the rations. The effects of each of these factors on the variations in the transit flows in a gradient of industrial pollution can be evaluated by comparing the multiplicity of the change in the food transit of chemical elements through local animal populations as a function of the number of the animals (Fig. 1a) and the concentrations of the elements in the ration (Fig. 1b). These dependences show that a decisive role in the exchange of chemical elements through bank vole populations is the density of the populations. These results are well consistent with our earlier conclusions (Mukhacheva and Bezel', 2004; Bezel' et al., 2007).

The number of local populations is an integral parameter, which reflects how birth and death rates and the migration activities of animals are balanced in the populations. This parameter depends both on natural dynamic processes (seasonal and annual) and on the quality of the habitat and its ecological capacity. It has been demonstrated by targeted studies that the potential "capacity" of fragments of forests preserved in the impact zone is only insignificantly (by approximately 20%) lower than that at the undisturbed areas (Mukhacheva, 2007). Under favorable conditions, the density of the local bank vole population at these areas can approach the values for the background zone. We expected that the gradual recovery of habitats in the vicinities of MUCS shall be favorable for an increase in the number of the animals at the polluted areas.



**Fig. 1.** Variations in the transit flows of elements through the local bank vole populations depending on (a) the density of the population and (b) concentrations of the elements in the ration. Solid symbols—the period of high emissions (1990–1992), open symbols—the period of almost terminated emissions (2015–2017). Triangles—Cu, squares—Zn, circles—Cd, rhombs—Pb. The multiplicity of variations of a parameter is reported relative to background values, which were taken as a unit. The bisectrix corresponds to a direct dependence of the flow on analyzed factors.

In fact, over the two and a half decades of our monitoring, we registered a decline in the absolute number of bank voles in the impact zone from 4.4 to 2.7 individuals/ha (Table 1). However, thereby the density population size of northern red-backed vole, a species with similar ecological requirements, proportionally increased (from 2.6 to 4.2 individuals/ha) at the same areas. Hence, the gross density of both species during the study periods was comparable: 7.0 individuals/ha during period I and 6.9 during period II. The data presented above indicate that the quality of the habitat in the impact zone has not been changed any significantly over the study period, and the decrease in the bank vole population density in the immediate vicinities of the emission source is a result of the competitive replacement of this species by northern red-backed vole. Note that the absolute number of bank voles in the buffer and background zones, conversely, increased by 40% on average (Table 1). The numbers of northern red-backed voles at the same areas have changed similarly but on a scale incomparable with that of bank vole.

The interplay of these factors (the number of the animals and the concentrations of the elements in the food) at a reduction in the industrial emissions may result, depending on the balance of the processes, in intensification, slowdown, or stabilization of the biogeochemical exchange of the elements. Evidence of each of these scenarios can be identified in MUCS vicinities. The intensity of the exchange of most elements in the impact zone twofold decreases compared to the original values, reaches background values (for Cu, Cd, and Pb), or becomes even lower (for Zn). In the buffer zone, the biogeochemical exchange seems to stabilize, since none of the four elements shows any significant changes in the flow values. Thereby it was moderately polluted areas, where the maximum transition flow values were registered for most elements (except Zn), which were 1.7–5.5 times higher than the background values and 1.3–3.7 times higher than the impact zone. In the background zone, biogenic exchange was intensified (except that of Pb), and the transit flow values increased up to twofold compared to the original values.

## CONCLUSIONS

Our studies have shown that the biogeochemical traits of the Cu, Zn, Cd, and Pb transit flow through local bank vole populations at variably polluted areas were controlled by the numbers of the animals and the concentrations of the elements in their ration. The manifold reduction in the volume of emissions from MUCS over the past decades has not resulted in an equivalent decrease in the concentrations of the elements in the forage of bank vole inhabiting the polluted areas. In the impact zone, Cu, Zn, and Pb concentrations in the ration of the animals has not significantly changed, and the Cd concentration has twofold

increased by the end of the observation period compared to the original concentration. No clear directional changes were detected in the concentrations of the metals in the ration of the animals in the buffer zone. The situation with Cu, Zn, and Cd in the background zone was similar, whereas Pb concentration in the bank vole ration decreased by a factor of 2.5 compared to the original concentration. The trends in the density of the local bank vole populations in a pollution gradient were different: the population 40% grew at the background and buffer areas but 60% decreased in the impact zone. The decrease of density the bank vole was due to the interspecific competition of the sympatric species with similar ecologic requirement but not by changes in the quality of the environment. The simultaneous effects of the above factors at a decrease in the industrial emissions could lead, depending on a balance of the processes, to intensification (in the background zone), slowdown (impact zone), or stabilization (buffer zone) of the biogeochemical exchange of elements. Our hypothesis that quantitative parameters of the transit flows of the elements at the polluted and background areas shall equalize has received a partial validation. The transit flows of Cu, Cd, and Pb in the impact zone have close to the background values by the end of the study period, whereas the Zn flow twofold decreased compared to the unpolluted areas. The main reason for these changes was the significant transformation in the structure of the SM community and the ensued drastic decrease in the bank vole population density in the impact zone. The estimated levels of the biogenic exchange of the chemical elements through free living populations of SM and the variations of this exchange in the pollution gradient were not significant enough to any strongly affect the general geochemical status of the territories. The populations of the model species considered herein reflect how animals in natural BGC react to changes in the geochemical background at polluted areas, with an emphasis placed on the role of the habitat quality, including its anthropogenic deformations.

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