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# Bioaccumulation of trace elements in vegetables grown in various anthropogenic conditions

**Anatoly P. Kaledin**[1], **Marina V. Stepanova**[2,*]

[1] Russian State Agrarian University – Moscow Timiryazev Agricultural Academy, Moscow, Russia
[2] Moscow State University of Food Production, Moscow, Russia

* e-mail: stepanova-marina@bk.ru

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**Abstract:**
Hazardous compounds accumulate in plants and animals as a result of anthropogenic impact. Trace elements, such as heavy metals, move up in the system of snow – soil – water – plant – animal. When contaminants accumulate in plants that serve as animal feed, they eventually accumulate in the animals that consume the feed because heavy metals usually enter living organisms via digestive tract, i.e., with food.

In 2003–2021, we studied fodder plants grown and harvested by urban zoological organizations, e.g., zoos, nature corners, etc. This research covered the Central Federal District represented by the cities of Moscow, Ivanovo, Yaroslavl, and Uglich. The empirical part of the study relied on a combination of modern ecological, biochemical, and statistical methods. A KVANT-2AT atomic absorption spectrometer was used to define the trace elements and their quantities.

Broccoli proved to be the most resistant feed vegetable to all the toxic elements in this study. Kohlrabi, sweet potato, and dill had low content of lead and cadmium, while garlic was highly resistant to cadmium and arsenic. Spinach, fennel, potatoes, beets, and bell peppers, which were used as fodder in metropolis conditions, exceeded the maximal permissible concentration of heavy metals. The samples obtained from the Moscow Zoo contained by 1.98 times more zinc, by 1.06 times more copper, and by 89.47 times more lead than average. The samples from Ivanovo accumulated the greatest extent of iron, which exceeded the average level by 3.26 times. The vegetables from Uglich and Ivanovo had the lowest concentration of zinc, which was by 67.86 and 62.70% below the average, respectively. The samples from Yaroslavl contained by 33.08% less copper. In 2003–2021, feed vegetables grown in the Central Federal District had an average increase in zinc, copper, and lead by 1.13, 1.45, and 2.80 times, respectively. The level of iron stayed almost the same throughout 2018–2021, while that of arsenic gradually decreased in concentration. The accumulation level of zinc, copper, iron, and arsenic in feed vegetables appeared to depend on the concentration of their water-soluble metal forms in the soil.

Therefore, forage agriculture in urban areas requires constant chemical and toxicological tests to prevent contaminated feed from entering animal diet.

**Keywords:** Vegetables, trace elements, heavy metals, arsenic, migration, deposit media, pollution

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## INTRODUCTION

The growing anthropogenic impact increases the content of hazardous compounds in feed and animals that are subject to veterinary supervision. Accumulation of heavy metals has been the focus of scientific attention for many years, and the mechanisms of their biogeochemical behavior are clear. However, the jury is still out on the maximal permissible concentration of heavy metals in various environmental objects. As a result, foreign and domestic researchers are busy studying the content of hazardous macro- and microelements in water, soil, and atmosphere [1–7]. Most studies of depositing environments involve urban areas with a high anthropogenic load, e.g., metal-processing industrial wastes, industrial emissions, fuel combustion products, vehicle exhaust fumes, pesticides, phosphate and organic fertilizers, etc.

The content of trace elements in the environment depends on the anthropogenic load on the particular territory. Contaminants follow the snow – soil – water – plant – animal chain to enter food of plant origin [8]. Unfortunately, very few comprehensive studies feature the accumulation and migration of trace elements and heavy metals from the surface soil to plant products. The most prospective research directions in this area include the following topics: the range of chemical contaminants; their content in food and organisms vs. their background concentrations in the soil; their transition to the aqueous soluble phase; their accumulation in plants; etc.

Chemical and toxicological tests are an obligatory stage according to all standardization documents and technical regulations. Such documentation is usually based on foreign and domestic studies on the maximal permissible concentration of toxic elements in objects of veterinary supervision [9, 10]. Yet, such issues as antagonism and synergy of composite pollutants, the migration of metals, and their cumulation in plant products receive very little scientific attention [11]. Therefore, the complex nature of pollution should underlie all comprehensive environmental studies, i.e., interrelations of heavy metals, their migration, the negative impact of their excessive level on environmental objects, etc.

The accumulation of contaminants in feed plants trigger their accumulation in animals, since most hazardous chemical elements enter the body through the alimentary route, i.e., with food [12–14]. Almost all animal diets center on plants or at least include them as additives. Urban zoological institutions, e.g., zoos, circuses, petting zoos, stations for young naturalists, etc., usually use roughage, vegetables, fruits, grain, etc.

Modern physical and chemical methods make it possible to monitor the content of chemical elements in animal diet and identify their residual amounts. Such studies reveal the general trend in heavy-metal contamination, which may be used to update regulatory documents on animal feed safety. Essential elements in animal feed also require a thorough control because they affect their vital activity [11, 15–17].

The present research objective was to determine the content of some trace elements, including heavy metals, in feed vegetables, as well as to study the effect of anthropogenic load on their accumulation and migration ability.

## STUDY OBJECTS AND METHODS

This research lasted from 2003 to 2021 and covered some urban areas of the Central Federal District with different anthropogenic load, namely the cities of Moscow, Ivanovo, Yaroslavl, and Uglich. The study relied on an integrated approach which combined modern environmental, biochemical, and statistical methods. The vegetable samples were obtained from the subsidiary farms of zoos in Moscow, Ivanovo, and Yaroslavl, as well as from a station for young naturalists in Uglich.

The sampling followed the procedure specified by the recommended practice for Moscow zoos and animal stations MosMR 2.3.2.006-03.

The research featured the microelement composition of tubers (potatoes, sweet potatoes), roots (carrots, beets, turnips, daikon, celery), cabbages (white cabbage, broccoli, kohlrabi), lettuce and spinach cultures (endive, spinach), spice plants (parsley, dill, fennel), bulbs (onion, garlic, lettuce, leek), fruit vegetables (tomatoes, cucumbers, bell peppers, eggplant), and cucurbits (pumpkin, zucchini).

The samples were tested for iron, copper, lead, cadmium, zinc, and arsenic by acid mineralization using nitric acid. The sampling procedure followed State Standard GOST 26929-94, while the tests themselves followed State Standards 30178-96 and 51766-2001 [2]. The heavy-metal test involved a KVANT-2AT atomic absorption spectrometer.

The samples weighed 20 g. They were charred on an electric stove with concentrated nitric acid and potassium or magnesium oxide, depending on the element. The charring lasted until the smoke emission ceased, which depended on the moisture content. Then, the samples were heated up to 250°C in a muffle furnace for 30 min, and the temperature was maintained at the same level for another 30 min. After that, the temperature was gradually increased by 50°C every 30 min and maintained so for 30 min. The maximal temperature was 450°C (500°C for cereals). After that, the crucibles were taken out, and samples with black ash were returned in the muffle furnace for another combustion cycle. Samples with white ash were processed in the spectrometer. The crucibles were cooled, and a base solution was added to dissolve the ash. The dissolved and filtered sample was poured into a 100-mL volumetric flask with a blue-ribbon filter. The base solution went in until the sample reached 100 ml. After that, the sample was tested in the spectrometer.

The experiment included 107 samples and 1764 measurements.

All the tests were performed in triplicates with intermediate precision. The obtained data underwent metrological processing according to State Standard R ISO 5725-6-2002.

The migration in the snow – soil – water – plant system was assessed based on the contingency between traits and the distribution of compatibility data by the Shapiro-Wilk W test. To determine the interdependence between two or more samples, we used regression analysis and the Spearman's Rank correlation coefficient. The significance level was 5% for all types of statistical analysis. The primary research materials entered the databases of Microsoft Office Excel 2010, Statistica version 10.0, Windows XP.

## RESULTS AND DISCUSSION

The results obtained were compared with the maximal permissible levels specified in Technical Regulation of the Customs Union TR TS 021/2011 "On food safety" and the interim hygienic standards for certain chemical elements in basic food products No. 2450-81, as well as with the temporary maximal

**Table 1** Trace elements in feed vegetables in zoological institutions of the Central Federal District

| Product | Trace elements, mg/kg | | | | | |
|---|---|---|---|---|---|---|
| | Zn | Cu | Fe | Pb | Cd | As |
| Maximal permissible concentration in vegetables | 10.00 | 5.00 | 50.00 | 0.50 | 0.03 | 0.20 |
| Tubers | | | | | | |
| Potato | 4.18 ± 1.42 | 0.90 ± 0.71 | 13.05 ± 1.63 | 0.60 ± 0.19 | 0.02 ± 0.02 | 0.02 ± 0.01 |
| Sweet potato | 1.07 ± 0.01 | 0.71 ± 0.04 | 0.61 ± 0.02 | 0 | 0 | 0.02 ± 0.00 |
| Roots | | | | | | |
| Carrot | 1.65 ± 0.93 | 0.79 ± 0.47 | 15.04 ± 1.31 | 0.25 ± 0.15 | 0.01 ± 0.01 | 0.02 ± 0.00 |
| Beet | 3.61 ± 1.83 | 0.82 ± 0.77 | 24.31 ± 3.09 | 0.13 ± 0.07 | 0.03 ± 0.01 | 0.05 ± 0.06 |
| Turnip | 2.35 ± 0.01 | 0.89 ± 0.01 | 4.76 ± 0.02 | 0.19 ± 0.01 | 0 | 0.01 ± 0.00 |
| Celery | 0.65 ± 0.00 | 0.28 ± 0.00 | 0.07 ± 0.01 | 0 | 0 | 0.01 ± 0.00 |
| Daikon | 3.55 ± 0.03 | 1.72 ± 0.01 | 2.98 ± 0.02 | 0.36 ± 0.01 | 0 | 0.01 ± 0.00 |
| Cabbages | | | | | | |
| White cabbage | 0.93 ± 0.38 | 1.04 ± 0.59 | 6.96 ± 3.95 | 0.06 ± 0.02 | 0.01 ± 0.01 | 0.01 ± 0.00 |
| Broccoli | 4.48 ± 0.15 | 0.10 ± 0.01 | 1.19 ± 0.03 | 0 | 0 | 0 |
| kohlrabi | 2.29 ± 0.00 | 0.59 ± 0.01 | 2.96 ± 0.02 | 0 | 0 | 0.01 ± 0.00 |
| Lettuce and spinach | | | | | | |
| Spinach | 13.69 ± 0.06 | 2.29 ± 0.02 | 10.66 ± 0.01 | 0.63 ± 0.07 | 0.02 ± 0.00 | 0.01 ± 0.00 |
| Endive | 5.55 ± 0.04 | 2.42 ± 0.05 | 6.42 ± 0.07 | 0.38 ± 0.02 | 0.01 ± 0.00 | 0.01 ± 0.00 |
| Spice plants | | | | | | |
| Dill | 3.96 ± 0.04 | 0.28 ± 0.01 | 0.13 ± 0.00 | 0 | 0 | 0.01 ± 0.00 |
| Parsley | 3.27 ± 0.08 | 0.37 ± 0.00 | 0.03 ± 0.01 | 0 | 0.01 ± 0.00 | 0.01 ± 0.00 |
| Fennel | 3.80 ± 0.01 | 0.65 ± 0.02 | 3.91 ± 0.03 | 0.52 ± 0.01 | 0 | 0.02 ± 0.00 |
| Bulbs | | | | | | |
| Onion | 0.70 ± 0.55 | 0.34 ± 0.04 | 26.92 ± 0.01 | 0.05 ± 0.01 | 0.01 ± 0.00 | 0.01 ± 0.00 |
| Leek | 1.03 ± 0.02 | 0.22 ± 0.02 | 2.06 ± 0.09 | 0 | 0.03 ± 0.00 | 0.01 ± 0.00 |
| Lettuce | 3.39 ± 0.00 | 0.70 ± 0.02 | 5.53 ± 0.00 | 0.39 ± 0.02 | 0 | 0.02 ± 0.00 |
| Garlic | 7.07 ± 0.02 | 0.07 ± 0.02 | 5.97 ± 0.02 | 0.01 ± 0.00 | 0 | 0 |
| Cucurbits | | | | | | |
| Zucchini | 0.68 ± 0.55 | 0.44 ± 0.26 | 7.29 ± 6.59 | 0.07 ± 0.09 | 0.01 ± 0.01 | 0.02 ± 0.01 |
| Pumpkin | 2.13 ± 0.01 | 0.46 ± 0.03 | 0.24 ± 0.02 | 0.03 ± 0.01 | 0 | 0.01 ± 0.00 |
| Fruit vegetables | | | | | | |
| Bell pepper | 0.84 ± 0.44 | 1.20 ± 1.02 | 12.44 ± 4.43 | 0.15 ± 0.05 | 0.04 ± 0.03 | 0.01 ± 0.01 |
| Cucumbers | 1.08 ± 0.02 | 0.29 ± 0.01 | 7.68 ± 0.26 | 0.05 ± 0.00 | 0 | 0 |
| Eggplants | 0.88 ± 0.00 | 0.20 ± 0.02 | 3.07 ± 0.18 | 0.01 ± 0.00 | 0.01 ± 0.00 | 0 |
| Average | 2.52 ± 1.51 | 0.78 ± 0.15 | 9.34 ± 1.03 | 0.19 ± 0.12 | 0.01 ± 0.00 | 0.02 ± 0.01 |

permissible level for certain chemical elements and gossypol in farm animal feeds and feed additives and with some scientific publications [2].

Table 1 presents the main results of the study. The average accumulation levels of trace elements in the feed samples decreased as Fe > Zn > Cu > Pb > As > Cd, which was consistent with the available publications on this matter [5, 15].

Monitoring results from other regions of Russia showed that the degree of contamination in the areas covered by this research had a much lower average heavy-metal content: Cu – by 2–4 times, Zn – by 4–12 times, Pb – by 12 times, Cd – by 2 times, and As – by 2–8 times [15, 19–21]. Iron, copper, zinc, and manganese also were in lower concentrations compared to the average Russian data (Table 1).

However, we registered higher-than-average concentrations for some heavy metals. Tubers contained 3.81 ± 1.33 mg/kg of Zn and 0.01 ± 0.00 mg/kg of Cd. Roots had 15.02 ± 1.31 mg/kg of Fe and 0.01 ± 0.00 mg/kg of Cd. Lettuce and spinach demonstrated 0.01 ± 0.00 mg/kg of Cd. Spice vegetables had 3.68 ± 0.32 mg/kg of Zn. Lettuce and spinach vegetables had a high content of Zn and Cu: 9.62 ± 1.46 and 8.54 ± 2.33 mg/kg, respectively. Tubers had 0.51 ± 0.01 mg/kg of Pb while lettuce and spinach vegetables had 0.53 ± 0.12 mg/kg. Fruit vegetables contained a lot of Cd (0.02 ± 0.00 mg/kg). Cucurbits demonstrated the lowest accumulation level of all trace elements but Cd. Cabbages were also low in all the toxic elements but Cu (Fig. 1), which confirmed the results obtained by an Iranian research team [5].

The content of Pb in tubers, as well as in lettuce and spinach plants, exceeded the maximal permissible concentration by 1.06 and 1.02 times, respectively. Probably, the concentration was so high because the samples were obtained from such a big industrial metropolis as Moscow. However, the results were consistent with those obtained in Serbia [22]. Other

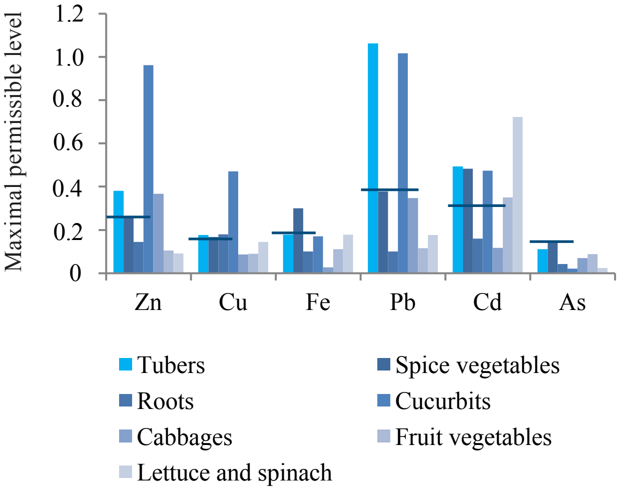

**Figure 1** Accumulation of trace elements and heavy metals in feed vegetables in zoological institutions of the Central Federal District

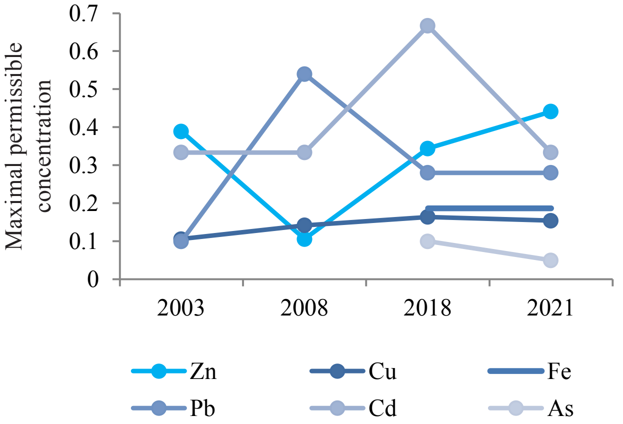

**Figure 2** Accumulation of heavy metals and other trace elements in the Yaroslavl Region, 2003–2021

**Table 2** Intercorrelation of trace elements in feed vegetables of the Central Federal District: a correlation analysis, mg/kg

| Element | Cu | Fe | Pb | Cd | As |
|---|---|---|---|---|---|
| Zn | 0.21** | –0.02 | 0.12 | –0.15 | –0.12 |
| Cu | – | 0.52*** | 0.53*** | 0.04 | 0.46*** |
| Fe | | – | 0.38*** | 0.54*** | 0.42*** |
| Pb | | | – | 0.12 | 0.06 |
| Cd | | | | – | 0.25* |

* significant difference ($P < 0.05$)

** significant difference ($P < 0.01$)

*** significant difference ($P < 0.001$)

groups revealed no excess of maximal permissible concentration, but Zn in the lettuce and spinach samples had an upward trend.

We performed a pairwise correlation analysis to check the possible interdependent accumulation of metals (Table 2). Cu and Fe had a direct relationship ($R = 0.52$ at $P < 0.001$), and so did Cu and Pb ($R = 0.53$ at $P < 0.001$), Cu and As ($R = 0.46$ at $P < 0.001$), Fe and Pb ($R = 0.38$ at $P < 0.001$), Fe and Cd ($R = 0.54$ at $P < 0.001$), and Fe and As ($R = 0.42$ at $P < 0.001$). Zn and Cu ($R = 0.21$ at $P < 0.01$) and Cd and As ($R = 0.25$ at $P < 0.05$) demonstrated a trend to symbatic accumulation level. The pairs Cd-As and Cu-Fe showed a mutual dependency similar to research conducted on other territories [15, 20].

We registered a significant increase in the content of all the elements in the samples from Moscow, compared with the average indicators: Zn – by 1.98 times, Cu – by 1.06 times, and Pb – by 89.47 times. On the contrary, Fe had the highest accumulation level in the samples from Ivanovo, the textile capital of Russia, where it exceeded the average content by 3.26 times. The lowest level of Zn belonged to the samples from Uglich and Ivanovo: they were by 67.86 and 62.70% below the average, respectively. The lowest content of Cu was in the samples from Yaroslavl: it was by 33.08%) below the average level (Tables 1 and 3).

A comparative analysis for 2003–2021 in the Central Federal District revealed an increase in the content of Zn, Cu, and Pb by 1.13, 1.45, and 2.80 times, respectively (Table 4). The content of Fe was approximately at the same level in 2018–2021, while As demonstrated a downward trend (Fig. 2). These data were found consistent with the general trend registered for the content of these elements in the Central Federal District and with our previous studies [2, 3].

A comparative analysis for 2003–2021 revealed a significant decrease in the content of Zn in the samples obtained from the rural and industrial territories of the Yaroslavl Region by 4.58 and 4.22 times, respectively. The content of Pb and Cd in Uglich samples increased by 3.09 and 4.02 times, while in the Yaroslavl samples it increased by 1.10 and 1.50 times, respectively. The accumulation level of Cu in the Yaroslavl samples increased by 1.10 times, while in Uglich it remained the same.

In 2008, Zn showed a significant accumulation decrease while Pb kept increasing. The highest level of Cd was registered in 2018.

The Central Federal District covers a huge territory, which varies greatly in geographical features and anthropogenic load. Consequently, this fact affects the accumulation level of pollutants in vegetables obtained from different environments. To establish the factors that affect the accumulation of chemical elements in vegetables, we studied the relationship between the content of trace elements and their level in environmental objects, i.e., snow, soil, and natural water bodies. We also investigated their migratory properties along the snow – soil – water – plant system.

The experiments revealed a competition in the transfer from the soil through water-soluble forms of Fe – Zn ($R = –0.27$), Cu – Fe, Cu – Cd, Cu – As

**Table 3** Heavy metals and arsenic in feed vegetables from areas with different anthropogenic load

| Location | Trace elements, mg/kg | | | | | |
|---|---|---|---|---|---|---|
| | Zn | Cu | Fe | Pb | Cd | As |
| Moscow | 4.98 ± 1.29** | 0.83 ± 0.28* | 5.28 ± 0.61** | 0.17 ± 0.12 | 0.01 ± 0.00 | 0.01 ± 0.00** |
| Yaroslavl | 1.14 ± 0.15** | 0.60 ± 0.16* | 12.30 ± 1.84** | 0.31 ± 0.17 | 0.01 ± 0.00 | 0.02 ± 0.01** |
| Ivanovo | 0.94 ± 0.14** | 1.05 ± 0.03* | 30.47 ± 1.86** | 0.25 ± 0.14 | 0.01 ± 0.00 | 0.02 ± 0.00** |
| Uglich | 0.81 ± 0.32** | 0.78 ± 0.19* | 12.40 ± 3.12** | 0.14 ± 0.02 | 0.01 ± 0.00 | 0.02 ± 0.01** |

* significant difference ($P < 0.05$)

** significant difference ($P < 0.001$)

**Table 4** Average content of the trace elements in feed vegetables of the Central Federal District in 2003–2021

| Year | Trace elements, mg/kg | | | | | |
|---|---|---|---|---|---|---|
| | Zn | Cu | Fe | Pb | Cd | As |
| 2003 | 3.89 ± 1.25 | 0.53 ± 0.31 | – | 0.05 ± 0.02 | 0.01 ± 0.00 | – |
| 2008 | 1.06 ± 0.54 | 0.71 ± 0.14 | – | 0.27 ± 0.16 | 0.01 ± 0.00 | – |
| 2018 | 3.44 ± 0.54 | 0.82 ± 0.27 | 9.34 ± 1.03 | 0.14 ± 0.02 | 0.02 ± 0.01 | 0.02 ± 0.00 |
| 2021 | 4.41 ± 0.58 | 0.77 ± 0.16 | 9.33 ± 1.24 | 0.14 ± 0.08 | 0.01 ± 0.00 | 0.01 ± 0.00 |

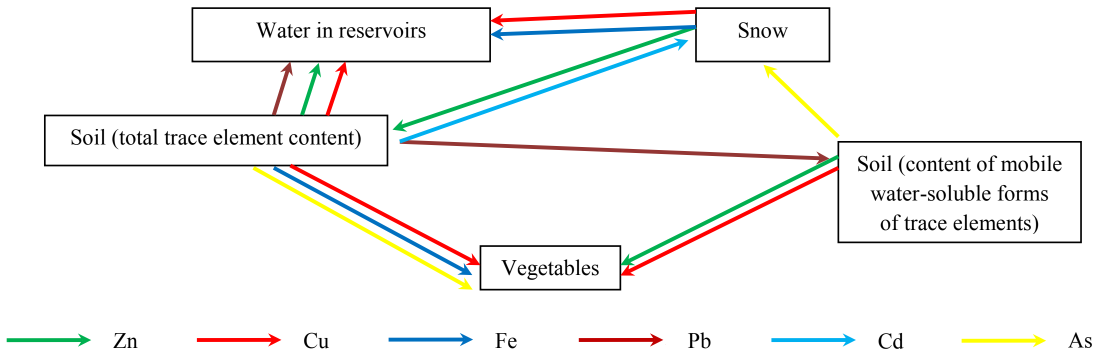

**Figure 3** Intermedia transition of trace elements in the snow – soil – water – plant system in the Central Federal District

($R = -0.52$; $R = -0.46$; $R = -0.30$, respectively), as well as Pb – Cu and Pb – Fe ($R = -0.37$ and $R = -0.49$, respectively). No direct correlation occurred between the chemical composition of snow and water and the accumulation of chemical elements in feed vegetables (Fig. 3).

Zn demonstrated good migration ability in the snow – soil – water – plant system. The level of Zn was low in the deposition media, i.e., soil and snow, as well as in drinking water and food. We also registered a weak and medium direct relationship between the concentrations of Zn in vegetables and environmental objects. The concentration of water-soluble metal forms in the soil affected the level of microelement content in the vegetables. Cu had good snow – water and soil – plants migration ability, which allowed Cu to accumulate in plants in high concentrations. The concentration of metal in vegetables was most affected by the type of soil-forming material and the amount of its water-soluble forms in the soil. These results were found consistent with those reported for the Altai Region [23].

Fe usually entered vegetables from its aqueous solution in the soil, as evidenced by the weak correlation. We revealed no clear migration between environmental objects and plants, which indicates the natural origin of the metal.

The migration tests revealed a strong effect of the As content in the soil, especially its total accumulation, on the As concentration in feed vegetables.

The migratory ability of Pb and Cd had a loose dependance on their content in vegetables, and the intermedia transition was not obvious. We established a high content of Pb in depositing media, i.e., soil and snow, which may indicate its anthropogenic origin.

## CONCLUSION

Broccoli turned out to be the most resistant vegetable to the accumulation of all the toxic elements in this research. Kohlrabi, sweet potato, and dill were highly resistant to toxic heavy metals, namely Pb and Cd, while garlic did not accumulate Cd and As. Spinach, fennel, potatoes, beets, and bell peppers cultivated as feed for animals in the Moscow Zoo exceeded the maximal permissible level of some microelements. Compared with the average indicators, vegetables from the Moscow Zoo demonstrated a significant increase in the content of Zn (by 1.98 times), Cu (by 1.06 times), and Pb (by 89.47 times), but no increase was registered for Fe. The samples from the city of Ivanovo had the greatest accumulation of Fe, which exceeded the average content level by 3.26 times. In the samples from Uglich and Ivanovo, the content of Zn was by 67.86 and 62.70% below the average, respectively, which was the lowest level in this research. The content of Cu in the samples from Yaroslavl was below the average by 33.08%.

The average concentration of Zn, Cu, and Pb increased by 1.13, 1.45, and 2.80 times, respectively, between 2003 and 2021. However, the concentration of Fe remained almost the same in 2018–2021, while the concentration of As demonstrated a downward trend in the same period.

The concentration of water-soluble metal forms in the soil had a major effect on the accumulation of Zn, Cu, Fe, and As in feed vegetables grown in the Central Federal District.

## CONTRIBUTION

The authors were equally involved in writing the manuscript and are equally responsible for plagiarism.

## CONFLICT OF INTEREST

The authors declare no conflict of interest.

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**ORCID IDs**

Anatoly P. Kaledin https://orcid.org/0000-0002-1769-5043
Marina V. Stepanova https://orcid.org/0000-0002-0041-1091