Some biogeochemical features of soils in steppe specially protected natural areas (Samara Region, Russia)

Natal'ya Prokhorova[1*], *Yana* Ryazanova[1], and *Oksana* Kuzovenko[1]

[1]Samara National Research University, 1, Akademika Pavlova str., Samara, 443068, Russia

Abstract. The paper considers the features of arsenic (As) accumulation in the steppe soils of the Samara region (Russia) and its four specially protected natural areas. It has been established that As is one of the most toxic elements and belongs to the first hazard class. The work uses quantitative indicators of As content in the upper humus horizon of steppe soils of the Samara region (in the period from 1991 to 2005). The data on the accumulation and distribution of As in virgin soils of the studied protected areas, obtained in 2023, are analyzed. A relatively high level of As content in the studied soils has been established. The reasons for the active accumulation of As in virgin soils of the steppes are substantiated. It is suggested that the increased content of As in the humus horizon of soils may affect the phytodiversity of virgin steppes.

1 Introduction

The features of modern migration and accumulation of huge masses of chemical elements, including heavy metals and metalloids, have become an acute environmental problem. These processes have not yet transformed the global biogeochemical cycles that maintain the integrity and stability of the biosphere, but the chemical composition of natural environments has been significantly changed towards increasing concentrations of particularly toxic elements in some areas. This process is especially important in relation to the soil cover, as an environment that actively deposits pollutants, which can manifest itself in unpredictable reactions of living organisms, up to the depletion of biodiversity [1-3].

The steppe territories of the Samara region (Russian Federation) of a particular interest in terms of environmental protection and biodiversity conservation. In this regard, our research was carried out in the south of the Samara region, where steppe communities are most widespread. Presently, they have been mostly plowed and used in agricultural production, but at the same time small areas of virgin steppes with a rich floral composition have been preserved, allocated to specially protected natural areas (SPNAs). Some of them are used as reference polygons in research on decoding Earth remote sensing data to identify preserved virgin steppe areas. The chemical composition of soils significantly affects biota, including vegetation cover, changing its reflectivity and species diversity,

*Corresponding author: natali.prokhorova.55@mail.ru

which can affect the visual appearance of steppes in satellite images [4-5]. This aspect requires special study, the initial stage of which is terrestrial ecological and biogeochemical studies of soils.

The soil cover of the Samara region steppes is mainly represented by ordinary and southern chernozems, as well as dark chestnut soils. These soils are formed under meadow-steppe and steppe herbaceous vegetation during the sod soil formation process, part of which is the biogeochemical cycle of chemical elements that make up the soil, including toxic heavy metals and metalloids. They enter the humus horizon of soils from natural and man-made sources and largely determine the ecological and biogeochemical features of steppe landscapes [1]. Heavy metals and metalloids deserve special attention from environmentalists, which in Russia belong to the 1st hazard class (As, Hg, Pb, Cr, Cd, Zn), and in other countries are also considered the most toxic [3, 6].

The levels of heavy metals and metalloids in the soils of natural and anthropogenically transformed landscapes are largely determined by the nature of regional technogenesis, in particular, the chemical composition of pollution flows from industrial enterprises, transport systems, and applied agricultural chemicalization technologies. Ecological and biogeochemical monitoring is carried out to assess their content in natural environments, including soil [2].

The features of accumulation and distribution of heavy metals in the soil cover of the Samara region were previously (1991-2005) relatively well studied, but metalloids were not given sufficient attention in these studies. Only general information was published on the content of As in the soils of the Samara region as a whole, as well as in the soils of the forest-steppe and steppe within its borders [7].

Due to the importance of the problem of biodiversity conservation the role of SPNAs is very important, it was decided to analyze the previously obtained regional materials on As (1991-2005) and carry out new ecological and biogeochemical studies of the accumulation and distribution of this element in virgin soils of some SPNAs of the Samara region.

The choice of As for a deeper analysis is determined not only by the relatively weak knowledge of the characteristics of its content in the soils of the region, but also by its very high toxicity to living organisms and humans. It is considered one of the most important environmental pollutants, for example, it has been established that it is a persistent bioaccumulative carcinogen [3, 8]. Currently, many researchers emphasize the priority of ecological and biogeochemical studies of As in different countries, which is especially evident in China and the USA [9-10].

The purpose of this study is to assess the accumulation of As in virgin soils of four SPNAs located in the steppe zone of the Samara region (Russian Federation) at present time.

2 Materials and methods

Comprehensive ecological and biogeochemical studies of the soil cover of the Samara region were started in 1991 and have been continued until 2005. It was during this period that the database on the content of heavy metals and metalloids in the soils and plants of the region was formed. All quantitative data from this database were obtained by the method of characteristic X-ray radiation (a foreign analogue of PIXE). In 2023, ecological and biogeochemical studies were carried out in the landscapes of four SPNAs located within the Syrtovogo Zavolzh'ya (Sinij Syrt) in the subzone of the middle fescue-feather grass steppes of the Zavolzhsko-Ural'skoj steppe region. All the SPNAs belong to the Bol'shechernigovskij district of the Samara region (Figure 1). Soil samples were taken within a complex geochemical landscape (catena) in geochemically coupled elementary landscapes located on the top of the hill, in the middle and at the foot of its slope in each of

the SPNAs. While, the same methods of selection and preparation of soil samples were used as in earlier studies. Samples were taken from the upper humus horizon (0-10 cm) by the "envelope" method, freed from foreign inclusions (plant residues, stones), dried to an air-dry state. The quantitative analysis of the As content was carried out by atomic absorption spectroscopy (AAS). In parallel, the pH and humus content in the studied soils were determined.

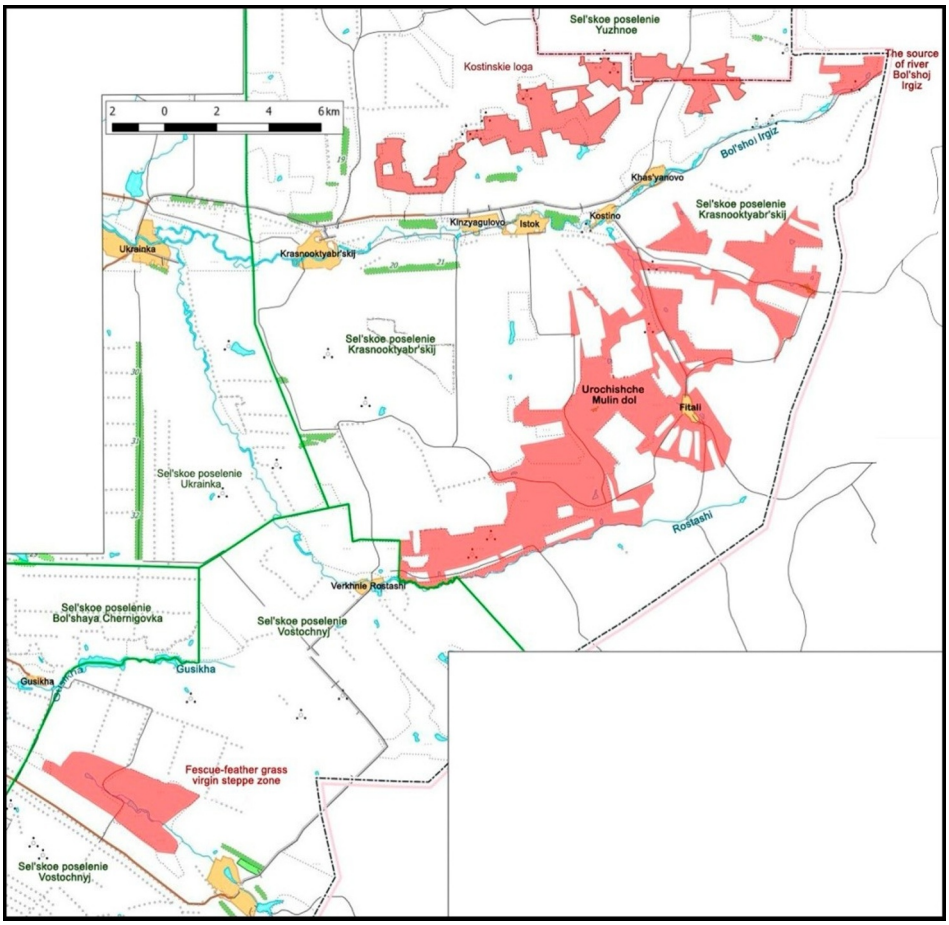

Fig. 1. The location of the studied steppe specially protected natural areas (SPNAs).

SPNA 1 *Fescue-feather grass virgin steppe zone* is located in the south-east of Bol'shechernigovskij district, 3 km northwest of the village Vostochnyj. Its total area is about 931.95 ha. The relief of this SPNA is a plain dissected by shallow gullies, with grass-meadow associations on their bottom. These reference fescue-feather grass steppes and mixed-grass fescue-feather communities are common on the tops of the slopes. The soil cover is represented by southern carbonate chernozems and dark chestnut soils with a close occurrence of groundwater, which contributes to local salinization and the formation of halophytic vegetation [11].

SPNA 2 *Urochishche Mulin dol* represents the southeastern part of the Syrt watershed of the Bol'shoj Irgiz and Rostashi rivers. Its area is about 5090.02 ha. The relief is represented by a flat-topped, steep hill with deep dissection and gentle slopes. The soil cover is also characterized by southern carbonate chernozems. It is dominated by fescue

and fescue-feather grass associations, dry saline-wormwood-cereal, cereal-wormwood and stony steppes in places [11].

SPNA 3 *Kostinskie loga* is a typical ravine-girder system for the Syrtovogo Zavolzh'ya, covering an area about 1763.7 ha. It is located in the upper reach of the Bol'shoj Irgiz River, which contributes to the close occurrence of groundwater and the formation of coastal plant communities, but on gentle slopes the main types of vegetation are mixed-grass fescue-feather, fescue-feather grass и wormwood associations. Mixed grassland steppes and shrub communities are also found. The soil cover is represented by southern carbonate chernozems, salt lakes are found in places [11].

SPNA 4 *The source of river Bol'shoj Irgiz*, with a total area of 204.5 ha is a wide valley with a shallow gently sloping beam, in the expanded part of which there is a pond. The gentle slopes are covered with dry fescue-feather grass steppes with rare herbage, also mixed-grass-cereals associations of steppes with varying degrees of digression are found in places. Wet meadow and coastal-aquatic associations have formed with the dominance of species from the genus Carex L. in the vicinity of the pond. The soil cover of the SPNA is characterized by southern carbonate chernozems [11].

3 Results

Despite the protected status, all the studied SPNAs are subjected to anthropogenic transformation and synanthropization processes, which may affect their biogeochemical characteristics.

Figure 2 shows the average As content in the soils of the Samara region as a whole (regional background) and in the soils of its steppe zone, which were obtained using a previously created database. This figure also contains new data (2023) on the average As content in the soils of the studied SPNAs.

The background indicator of As content in the soil cover of the Samara region as a whole is 7.36 mg/kg. It is calculated based on the results of the analysis of 816 soil samples. The background indicator for the steppe zone is close to the regional background is 7.66 mg /kg. At the same time, the proportion of high concentrations of As in the steppe is quite significant, up to 102 mg/kg, although the prevailing concentrations do not exceed the background indicator for the Samara region (Figure 2).

In 1996, relatively high concentrations of arsenic are characterized the steppe soils of the Kalinin Collective Agricultural Enterprise with its center in the village of Novyj Sarbaj in the Kinelsky district of the Samara region. All soil samples were taken from its farmland. The average arsenic content was 27.3 mg/kg.

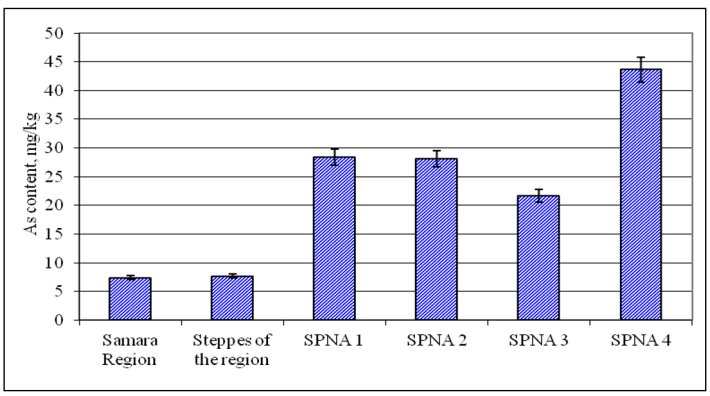

Fig. 2. The average As content in the soils of the specially protected natural areas (SPNAs).

The results of studies of virgin soils of steppe SPNAs carried out in 2023 revealed one feature common to them, which is a high As content exceeding the regional background and the maximum permissible concentration (MPC) of the gross form of As, equals to 2 mg/kg, accepted in Russia. The existing standards suggest using the MPC As taking into account the regional background, therefore, this indicator is 9.36 mg/kg, but it is also significantly exceeded in the soils of the studied SPNAs in the Samara region. Fig. 2 shows, the average As content for the soils of all four SPNAs falls within the range of 21.7 mg/kg in the soils of the SPNA-3 *Kostinskie loga* to 41.7 in the soils of the SPNA–4 *The source of river Bol'shoj Irgiz*. These indicators exceed the regional maximum permissible concentration for arsenic by 2.3-4.5 times.

Soil samples within the studied SPNAs were taken in three different geochemically coupled relief positions: slope-top, slope-mid and slope-foot. Figure 3 shows the average of As concentrations in the soils of individual elementary landscapes for each SPNA.

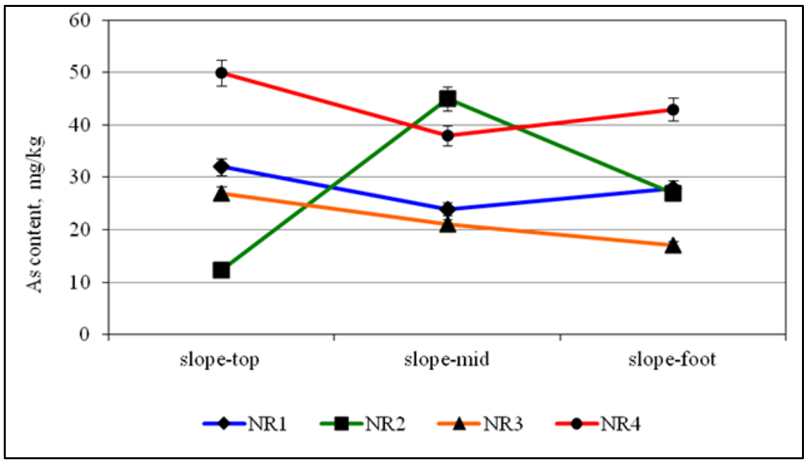

Fig. 3. The average As content in the soils of the SPNAs, depending on the position of the elementary landscape in the relief.

Figure 3 demonstrates the nature of the change in As concentrations depending on the relief is similar and consists in its higher content in the soils of the eluvial landscape at the slope-top and decreasing concentrations towards the slope-mid for SPNA 1, 3 and 4. The distribution of As is different: in the eluvial landscape, the concentration of As is lowest, and then it rises sharply towards the slope-mid in the soils of SPNA 2. The As accumulation in the soils of accumulative elementary landscapes at the slope-foot manifests itself in different ways. Its content decreases in comparison with the slope-mid in the soils of such elementary landscapes of SPNA 2 and 3, increases in the soils of SPNA 1 and 4. At the same time, As concentrations in the soils of all elementary landscapes of each SPNAs exceed the regional MPC level (9.36 mg/kg) by 1.3-5.3 times.

4 Discussions

The differences in As migration and accumulation in the soils of the studied SPNAs are obviously related to their typological features, agrochemical characteristics, as well as the nature of vegetation, in particular its species composition, the height of the herbage, the density of its underground and aboveground parts.

Field studies revealed that the transformation of steppe vegetation in the Samara region varies depending on the seasons. In spring, farmers carry out annual burning of dry grass

residues, which contributes, on the one hand, to the introduction of ash into the soil and improvement of its properties, on the other hand, destroys the woody shoots of rare steppe plants and old-age individuals of the feather grass (*Stipa* sp.). However, these activities have a positive effect on the development and fruiting of spring ephemeral plants and ephemeroids (*Tulipa schrenkii* Regel, *Valeriana tuberosa* L., etc.). The greatest depression of vegetation is observed in the second half of summer, which is associated with poorly regulated grazing of livestock. Almost complete degradation of meadow and coastal-aquatic vegetation occurs in watering places, which subsequently inhibits the renewal of terrestrial vegetation, reducing the diversity and biological productivity of the phytocenosis. Native species are replaced by adventive representatives (*Tripleurospermum inodorum* (L.) Sch. Bip., *Sonchus arvensis* L., *Lactuca tatarica* C.A. Mey., etc.) in such places. In the depressions between the steppe hills, when precipitation are sufficient, a rich variety of grass of the meadow-steppe type develops, but annual haymaking transforms its floral composition – an adventitious faction is being introduced to replace the typical zonal representatives (*Euphorbia virgata* Waldst. et Kit., *Cirsium incanum* (S.G. Gmel.) Fisch., etc.). Agricultural arable lands and roads, pipelines have the most pronounced transformative effect on steppe biomes. During seasonal work, machinery repeatedly enters areas of SPNAs, completely destroying natural communities, during the time they are populated by aggressive invasive species (*Cyclachaena xanthiifolia* (Nutt.) Fresen., *Cannabis sativa* L.). Such a local anthropogenic impact can also have a certain effect on the ecological and biochemical parameters of the protected virgin steppes areas, significantly changing the nature of their reflection on satellite images. In particular, it is known that steppe plants are able to accumulate a large amount of As in their organs, especially in the roots, which contributes to its accumulation in the upper horizon of the soil [12].

Steppe soils of the Samara region are characterized mainly by neutral and weakly alkaline pH values and a fairly high Fe and Mn content with a maximum concentration of 60796 mg/kg and 1785 mg/kg accordingly. Arsenical pesticides were widely used in the steppe farmlands of the Samara region before the ban in the Soviet Union in 1978. The low migration ability of As in the soils of the studied SPNAs (mobile form < 1 mg/kg) has been established, which also contributes to the consolidation of As in them.

The obtained quantitative results of soils in SPNAs can be explained by the presence of natural sources of As, namely, the soil-forming rocks of Sinij Syrt rich in Fe and Mn, which, in turn, are able to bind As [13]. Many authors point out to the predominantly lithogenic origin of As in soils [1]. Possible technogenic sources of As for the steppe soils of the extreme south of the Samara region cannot be ignored. They include some fertilizers and pesticides with As [14], as well as emissions from various industrial enterprises, motor vehicles, and agricultural machinery entering the soil cover of the steppes with regional atmospheric transport. The same process may be associated with the impact on the steppe ecosystems of the Samara region of mining and processing plants processing non-ferrous metal ore containing As in the territory of the neighboring Orenburg region.

5 Conclusion

Obviously, the main reason for the enrichment of the steppe virgin soils of the As region is related to natural factors, such as the characteristics of the soil-forming rocks, the acid-base regime of the soils and the high content of Fe and Mn, compounds of which are able to bind As firmly. The anthropogenic factor also contributes to the quantitative characteristics of the As content in the SPNAs soils. Anthropogenic transformation of steppe landscapes, accompanied by biogeochemical changes in their soil and vegetation cover, significantly affects the overall appearance of the steppes that are parts of regional SPNAs used as reference polygons for remote sensing of the Earth. The results of modern ecological and

biogeochemical studies in the future may become an important addition to the characteristics of these reference polygons, which are used in the interpretation of remote sensing materials.

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