Natural and technogenic changes in geochemistry of soils in the Ciscaucasian steppe landscapes

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Abstract. The work is based on landscape-geochemical studies, uniformly conducted in the Ciscaucasian region on a scale from 1:500,000 to 1:10,000. Analyses of over 15,000 samples allowed to consider natural and technogenic factors affecting migration and accumulation of elements. The greatest technogenic geochemical changes occurred in the soils of the landscapes during the plowing of steppe. The intensity and direction of the studied regional processes of influx and loss of elements depend mainly on such natural factors as the zonal type of steppes, geomorphological features of the sites, and the intensity of wind erosion. Depending on the land topography, the influence of wind erosion on the geochemical features of steppe soils was described. The impact of dumpsites located at different distances from discrete parts of the steppe landscapes and the post-steppe arable lands were studied alongside the impact of sedimentation tanks of chemical enterprises on the steppe soils.

1. Introduction
The Ciscaucasian region is one of the most developed territories in Russia. All biogenic landscapes account for only about 10% of its territory [2]. The largest area among them is taken by the landscapes of the steppes. However, these landscapes are distinguished somewhat conditionally, since they are largely subject to man-made impact. At present, the steppes are preserved mainly in the south-east of the studied territory. In the western parts of the region, fragments of steppes stand out as separate small "spots", often located in river valleys. The spatial location of the steppes in the region contributed to the development of specific geochemical features under the influence of several natural and man-made factors, and, first of all, the features of the prevalence of some metals in the soils of the steppes [1, 2, 6]. The identification of these features is one of the main goals of this work. The revealed geochemical patterns can and should be used in the search for deposits and in solving a number of environmental problems.

2. Materials and Methods
The main part of the data used in the preparation of this report was obtained as a result of landscape-geochemical mapping at a scale of 1:500,000 in the center and south of European Russia: Voronezh and Rostov Oblasts, Krasnodar and Stavropol Krai, and the republics of the North Caucasus. The authors of this work directly participated and supervised it at all stages of research. According to the
results of the work carried out, maps of geochemical landscapes of the scale 1:500,000 were published (State Publication) [7, 8, 9]. The work under consideration included testing of rocks (if possible), soils, and major plants on a 5x5 – 5x7 km grid. Besides, samples were taken after regional studies on quite numerous areas of detail, where the sampling step thickened from 200 to 2-5 m. In the completely plant-covered areas, pits were dug, wells were drilled, and clearing operations were carried out. In total, more than 15,000 samples were collected during the work. Control testing was carried out in the amount of 3-5%. In this paper, changes in the prevalence and distribution of nine chemical elements in soils are considered. For four of them (Pb, Ti, Cr, and Ni), biogenic accumulation was found either practically absent or insignificant, for the remaining five (V, Mn, Co, Cu, and Zn) it played a significant role in their history [5, 11].

The lithochemical and biogeochemical (plant ash) samples were subjected to spectral analysis in the certified Central Testing Laboratory of the North Caucasus Production Geological Association. Intra-laboratory and external control each accounted for 3-5% of the number of ordinary analyses. For external control, laboratories of the Research Institute of BiosphereGeochemistry (Novorossiysk), Magadangeology (Magadan), the Institute of Geology of Ore Deposits (Moscow), and the Research Institute of Physical and Organic Chemistry of the Southern Federal University (Rostov-on-Don) were selected. The calculation of the values of the average random relative deviation of concentrations (<1.4) allowed us to consider the work of the laboratory as good. When identifying geochemical landscapes, the contents of rock-forming elements were also taken into account, established by X-ray fluorescence and neutron activation methods in the laboratories of the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry RAS (Moscow), the Southern Federal University (Rostov-on-Don), and Kavkazgeolsyomka (Essentuki). The research methodology is described in the textbook on Ecological Geochemistry, recommended by the Ministry of Education of the Russian Federation for university students studying in natural science specialties [1].

The Indicator of Absolute Accumulation (IAA) used in this work allows us to determine the mass of a chemical element (its compounds) accumulated (removed) per unit area in a specific part of the geochemical landscape, as a result of a certain process:

\[ \text{IAA} \left( \text{t/km}^2 \right) = \left( C_2 - C_1 \right) \cdot K, \]

where \( C_1 \) is the background content before the start of the processes under consideration or the abundance; \( C_2 \) is the average content after the end of the processes under consideration; \( K \) is the coefficient showing what mass of an element corresponds to an increase (decrease) in the content of chemical elements by a certain amount. If we determine the value of IAA in \( \text{t/km}^2 \), then with the thickness of the soil layer with a changed content of 30 cm and when determining the contents in \( n \cdot 10^{-3} \%) \), the \( K \) coefficient for the soils of the region is 6. The thickness of the soil layer was not chosen by chance. It was found experimentally that 30 cm is the thickness of the layer in the region, which is characterized by the greatest intensity of geochemical processes occurring during pollution. Therefore, this value of the soil layer is most often taken as the main one in environmental geochemical studies. Also, 30 centimeters is the usual depth of the arable layer, which is subjected to constant processing in many agricultural operations (experience shows that environmental studies are often conducted within agricultural landscapes).

In practice, this means that an increase in the average content of the element in the soil by \( 1 \cdot 10^{-3} \% \) leads to the accumulation (removal) of 6 tons of this element on an area of 1 km\(^2\) [1].

3. Results and Discussion

The main part of the data used in the preparation of this report was obtained as a result of landscape-geochemical mapping at a scale of 1:500,000 in the center and south of European Russia: According to the composition of the vegetation cover in the region, there are two main subzonal types of steppes: 1 – typical steppes (herb-bunchgrass and bunchgrass steppes); 2 – semi-desert bunchgrass and suffruticulose-bunchgrass steppes [10]. The flora of the steppes includes more than 1,600 species. The main background of the vegetation cover of herb-bunchgrass and bunchgrass steppes is formed by
narrow-leaved grasses of feather-grass (Stipa) and fescue (Festuca). The biomass of the steppes is usually 20-25 t/ha. The annual biopродuctivity is significant.

In the semi-desert bunchgrass and suffruticulose-bunchgrass steppes, the total number of species decreases with an increase in the number of xeromorphic grasses and semi-shrubs, ephemera, and ephemeroïds (Artemisia austriaca Jacq., Kochia scoparia (L.) Schrad., etc.). These steppes are characterized by lower biomass (13-14 t/ha) [3, 4]. These features lead to differences in the biological cycle of chemical elements.

The steppe landscapes of the region were (and still are) subjected to the greatest technogenic change in terms of the occupied area when arable land was created in their place. As can be seen from the data given in tables 1 and 2, all the studied elements (regardless of their biological role) during the plowing of the steppes and the subsequent use of the plowed land as arable land, i.e., under the influence of technogenic processes on the steppes, changed their concentration in the soils. The accumulation of elements in the upper 30 cm layer ranges from 0.6 t/km² to 391 t/km². The level of this accumulation, according to tables 1 and 2, is associated with a number of natural factors and, first, with the subzonal type of steppes. Thus, the Indicator of Absolute Accumulation (IAA) of Ni in the soils of plowed transaccumulative landscapes of semi-desert bunchgrass steppes (1.2 t/km²) is five-fold less than the IAA in the soils of transaccumulative landscapes in the place of bunchgrass steppes. Consequently, in the soils of arable lands formed after the steppes, the content of accumulated metals largely depends on the type of these steppes.

Table 1. Changes in the concentrations and IAA of a number of metals in the upper layer of soils of semi-desert bunchgrass steppes after plowing.

| Elements | Pb | Ti | Cr | Ni | V | Mn | Co | Cu | Zn |
|----------|----|----|----|----|----|----|----|----|----|
| Steppes  |     |    |    |    |    |    |    |    |    |
| Eluvial  | 2.7 | 481| 8.9| 4.8| 9.6| 63.0| 1.9| 5.4| 7   |
| Transeluvial | 2.9 | 448| 9.8| 4.4| 9.5| 61.7| 1.6| 4.8| 6.3|
| Transaccumulative | 0.9 | 417| 12 | 4.2| 8.8| 51  | 1.6| 4.4| 5.5|
| Dry arable land, plowed steppes |     |   |    |    |    |    |    |    |    |
| Eluvial  | 2.6 | 435| 9.3| 4.9| 10.3| 67.9| 1.7| 5.0| 6   |
| Transeluvial | 2  | 414| 8.2| 4.6| 9.9| 61.4| 1.8| 4.8| 5.3|
| Transaccumulative | 1.5 | 448| 5.7| 4.4| 6.1| 39  | 1.8| 4.6| 6   |

The intensity of element accumulation in the soils also changes depending on the terrain of the landscapes of the plowed steppes. This is seen in the example of vanadium. When plowing the bunchgrass steppes of near-watershed landscapes, its content in the soils of the emerging arable lands (1.8t/km²) is five-fold less (9.6 t/km²) than when plowing the same steppes belonging to transaccumulative landscapes (table 2).

The data obtained (tables 1 and 2) also indicate that almost all the elements under consideration can be either accumulated in the soils during plowing of the steppes or removed. Much more often and in larger quantities, metals are removed when plowing dry steppes (from 0.6 t/km² to 275 t/km²). Plowing of bunchgrass steppes did not lead to the removal of Ni, V, Mn, Co, and Cu in various geomorphological conditions, for which (except for Ni) biogenic accumulation is essential.

In the region under consideration, the natural deflation process affects the geochemical changes in the steppe soils and embraces the largest areas. When the wind of the usual speed is almost constant for the southern part of the region, the lightest particles that have not sorbed metals in any large quantities are carried out. As a result, the soils are enriched with metals [1, 2, 6]. This process is largely associated not only with the movement of air masses carrying light soil particles but also with the geomorphological features of the region. The removal of light particles from the soil occurs more
intensive from watershed (eluvial) landscapes, which are more prone to deflation, as compared to the landscapes of the foothills (transaccumulative).

**Table 2.** Changes in the concentrations and IAA of a number of metals in the upper layer of soils of bunchgrass steppes after plowing.

| Elements                  | Pb  | Ti  | Cr  | Ni  | V   | Mn  | Co  | Cu  | Zn  |
|---------------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Landscapes                |     |     |     |     |     |     |     |     |     |
| Eluvial                   | 2.9 | 407 | 9.0 | 4.1 | 9.7 | 57.6| 1.2 | 3.9 | 5.0 |
| Transeluvial              | 2.6 | 451 | 8.6 | 4.3 | 9.6 | 60.6| 1.6 | 4.5 | 6.3 |
| Transaccumulative         | 1.9 | 347 | 4.6 | 3.3 | 8.0 | 55  | 1.3 | 4.2 | 3.8 |
| Dry arable land, plowed steppes (n•10^{-3}% wt.) |     |     |     |     |     |     |     |     |     |
| Eluvial                   | 2.6 | 435 | 9.3 | 4.9 | 10.3| 67.9| 1.7 | 5.0 | 6.0 |
| Transeluvial              | 2   | 414 | 8.2 | 4.6 | 9.9 | 61.4| 1.8 | 4.8 | 5.3 |
| Transaccumulative         | 2.5 | 412 | 7.8 | 4.3 | 9.6 | 57.9| 1.8 | 4.5 | 4.9 |

Indicator of Absolute Accumulation (t/km^2)

| Elements                  | Eluvial | Transeluvial | Transaccumulative |
|---------------------------|---------|--------------|------------------|
| Dry arable land, plowed steppes (n•10^{-3}% wt.) | -1.8   | +168         | +1.8             |
| Eluvial                   | -3.6   | -222         | -2.4             |
| Transeluvial              | +3.6   | +391         | +19.2            |
| Transaccumulative         | +4     | +17.4        | +3               |

In areas without wind removal of light soil particles, the migration of heavy metals through the soil horizons mostly occurs under the influence of gravity. As a result, the soil is enriched with metals in the landscapes of the foot of the slopes (transaccumulative) (table 3, figure 1).

**Table 3.** Change in the average content of a number of metals in the soils of conjugate landscapes not subject to wind erosion (n•10^{-3}% wt.)

| Landscape    | Number of samples | Chemical elements with different atomic weights |
|--------------|-------------------|-----------------------------------------------|
|              |                   | Pb (207.0) | Zn (65.3) | Cu (63.5) | Ni (58.7) | Mn (54.9) |
| Eluvial      | 66                | 1.3 | 4.9 | 4.0 | 3.9 | 55.9 |
| Transeluvial | 396               | 1.4 | 4.8 | 4.2 | 4.0 | 55.8 |
| Transaccumulative | 77     | 1.8 | 4.9 | 4.5 | 4.3 | 56.7 |

The relative increase in metal concentrations at the foot of the slopes, %

|                      | 138 | 102 | 112 | 110 | 101 |

**Figure 1.** Changes in the average content of a number of metals in the soils of conjugate landscapes not subject to wind erosion (n•10^{-3}% wt.).

Let us consider the geochemical features of soils in the areas of their removal by wind and in areas that are not subject to wind erosion. These areas are located in similar landscape-geochemical conditions and differ in the development of erosion processes. The data analysis showed that the background contents of Cr, Zn, Pb, Ni, and Mn in the southern part of the region subject to deflation are significantly higher than in the northern part. As it was shown above, in all cases, the distribution of metals in soils is influenced by the geomorphological features of the territories. Let us consider the
example of Pb and Ni: the concentration of metals in the conjugated landscapes changes in areas that are subject to and not subject to wind erosion. To do this, we use the IAA (table 4).

### Table 4. Metal accumulation in the upper 30-centimeter soil layer of eluvial and transeluvial landscapes exposed to wind erosion, compared to non-exposed areas.

| Landscape       | Number of samples | Element | Change in concentration, n\cdot10^{-3} % | Indicator of Absolute Accumulation, t/km^2 |
|-----------------|-------------------|---------|----------------------------------------|-----------------------------------------|
| Eluvial         | 201               | Pb      | 1.3 – 2.6                              | 7.8                                     |
| Transeluvial    | 828               | Pb      | 1.4 – 2.0                              | 3.6                                     |
| Eluvial         | 201               | Ni      | 3.9 – 4.9                              | 6.0                                     |
| Transeluvial    | 828               | Ni      | 4.2 – 4.6                              | 2.4                                     |

As can be seen from table 4, for each km^2 in eluvial landscapes, due to wind erosion, the content of Pb increased by 7.8 tons and by 6.0 tons in the case of Ni. In transeluvial landscapes, these indicators are 3.6 t and 2.4 t, respectively.

We note that the atomic mass of the elements plays an important role in deflation [12]. The larger it is, i.e., the heavier is the element, the more difficult it is for it to be carried by relatively weak (compared to hurricanes) air currents. Consequently, the relative increase in its concentration in watersheds becomes large, compared with the concentration in the soils of transaccumulative landscapes. As can be seen from table 5, the largest increase is typical for lead (144%).

For other elements, the relative concentration decreases to 106-109%, as the atomic mass of the metals decreases from 207 to 54.9. Thus, for the conditions of a particular region, the atomic mass of elements during deflation means no less (and probably even more) than the sorption capacity of soil minerals.

In areas that are not subject to deflation, the relative concentration of elements in the soils of geomorphologically different landscapes also depends on the atomic mass of these elements (table 3). The values (%) of the relative increase in the contents of the metals under consideration in the soils of landscapes subject to and not subject to wind erosion are similar (tables 3 and 5). However, in the latter case, the average contents increase not during the transition from transaccumulative to eluvial landscapes, but during the transition from eluvial to transaccumulative landscapes.

### Table 5. Change in the average content of a number of metals in the soils of conjugate landscapes subject to wind erosion (n\cdot10^{-3} % wt.).

| Landscape       | Number of samples | Chemical elements with different atomic weights | 
|-----------------|-------------------|-----------------------------------------------|
|                 |                   | Pb(207.0)  | Zn(65.3)  | Cu(63.5)  | Ni (58.7) | Mn(54.9) |
| Eluvial         | 196               | 2.6       | 6.0       | 5.0       | 4.9       | 67.9     |
| Transeluvial    | 241               | 2.0       | 5.3       | 4.8       | 4.6       | 61.4     |
| Transaccumulative | 77              | 1.8       | 4.9       | 4.5       | 4.6       | 56.7     |

The relative increase in metal concentrations at the watershed, %

|                   | 144 | 122 | 111 | 106 | 109 |

These features allow us to assume that even with the mechanical movement of substances, the role of internal migration factors (in this case, the atomic mass, and hence the radii of atoms) is quite large.

Local technogenic changes in the soils are detected on relatively small areas of the steppes and arable lands formed in their place. They mainly occur under the influence of dumps, sedimentation tanks, rock dumps, and other enterprises [13]. Thus, during the detailed landscape-geochemical studies, biogenic landscapes of the steppes were identified in the immediate vicinity of the mine dump sites (10 m–200 m). The studied dumps and steppes are located on the upper parts of the slopes and occupy significant territories in the region. The data on the element contents in the soils of the steppes exposed to geochemical influence are given in table 6.
Table 6. Content of chemical elements in the soils of steppes and arable lands (n·10⁻³%).

| Elements                      | Ba   | Co  | Cr  | Cu  | Ga  | Mn  | Mo  | Ni  | Pb  | Ti  | V   | Zn  |
|-------------------------------|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Abundance in the Earth’s soils* | 50   | 0.80| 20.0| 2.0 | 3.0 | 85  | 0.20| 4.0 | 1.0 | 460 | 10.0| 5.0 |
| Fieldcrop landscapes          | 49.8**| 1.9 | 7.1 | 4.1 | 1.6 | 61.3| 0.1 | 4.4 | 1.9 | 465 | 7.8 | 5.3 |
| Remainders of steppe landscapes away from waste heaps | 47-55 | 1.3-2.3 | 6.8-8.7 | 4.0-4.8 | 1.5-2.0 | 48.0-90.0 | 0.1-0.15 | 4.3-5.0 | 1.7-2.7 | 333-458 | 7.8-10.6 | 5.0-6.6 |
| Steppe landscape adjacent to the waste heap | 43   | 1.8 | 5.3 | 3.2 | 1.0 | 56  | 0.48| 3.5 | 1.6 | 406 | 6.8 | 1.3 |
|                                                                                      | 62   | 1.8 | 9   | 5.7 | 1.1 | 98  | 0.25| 4.1 | 2.9 | 446 | 12.8| 6.5 |

* after A. P. Vinogradov;
** the numerator indicates the average content, the denominator indicates the minimum and maximum ones.

As can be seen from the above data, the content of Mn, Cu, V, Cr, Zn, Pb, Mo, and Ba in the soils of the steppe landscapes directly adjacent to the dumps is higher not only than in the soils of the steppe landscapes located at the first km away but also higher than in the soils of the pasture farming landscape. This allows us to assume that under the influence of dumps at a distance of 1-2 km, more significant geochemical changes occur in the soils of the steppes than as a result of agricultural land development [14].

Often in the region, the soils of the steppes are contaminated as a result of liquid waste discharges, including cases of special settling tanks [1, 2, 6]. One of these sedimentation tanks was made on the outskirts of Kamensk-Shakhtinsky in the oxbow of the Seversky Donets River. The high level of groundwater associated with the oxbow led to the formation of an evaporative geochemical barrier in the steppe landscapes. Constant drainage from the oxbow, which became a sedimentation tank, contributed to an increase in the concentration in groundwater of several metals, including lead and zinc. The deposition of metals in soils on the evaporation barrier led to the formation (in the direction of groundwater flow from the settling lake to the river) of large metal anomalies. Thus, the size of the contrast Zn anomaly exceeds 1.5 km² and makes up 0.5 km² for Pb. It should be particularly noted that the contents of Zn (up to 10,000 mg/kg) and Pb (up to 200 mg/kg) in the soils of these technogenic anomalies are quite comparable to the industrial contents in ores.

4. Conclusions
The major natural factors of migration and accumulation of chemical elements in the soils of steppe landscapes are the intensity of wind erosion, land topography, and the type of steppe. Depending on the combination of these factors, natural and man-made regional processes lead to the sedimentation and removal of a number of metals.

The accumulation of elements reaches 390 t/km² when plowing, while the removal accounts for 220 t/km². More often and in large quantities, metals are taken out when plowing the semi-desert steppes.

The impact of sedimentation tanks and waste heaps widespread in the region affects the geochemical features of the steppe soils even at a distance of up to the first km. As a result of the impact of mine dumps, the content of Mn, Cu, V, Cr, Zn, Pb, Mo, and Ba in soils increases to abnormal concentrations. Under the influence of sedimentation tanks of chemical enterprises, anomalies of Pb and Zn with contents comparable to those in ores are formed.

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