Geochemical differentiation of atmospheric aerosols in natural zones of European Russia

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Abstract. Climate and environmental changes on Earth have become modern challenges to humanity. The main factor affecting the landscapes of Russia is an increase in air temperature and a decrease in precipitation. Because of these processes, the amount of aerosols in the near-ground atmosphere of the landscapes of the ETR (European territory of Russia) increases. The aim of the study is to determine the atmogeophysical and atmogeochemical indicators that reveal the interaction of the atmosphere and the diversity of natural landscapes in European Russia. Landscape-geochemical research methods make it possible to study geosystems with the participation of all landscape components and actual migration processes, especially the atmospheric migration of chemical elements. To determine the modern atmogeochemical existence, field comprehensive studies of the potential emission of matter in all natural zones of the ETR were carried out submeridionally - in the landscapes of the steppe, forest-steppe, forest and tundra zones of the ETR. The research results show that in the submeridional profile, the mass concentration of aerosols decreases regularly from south to north, the minimum concentrations of atmospheric aerosols are observed in the forest zone, in the tundra there was a slight increase due to anthropogenic landscapes and the influence of the sea. Analysis of the chemical composition of aerosols revealed that, among the elements of global importance, aluminosilicates naturally increase to the south of the ETR as elements of clay minerals that are widespread in the Russian Plain. The maximum phosphorus content occurs in the residential area with agricultural landscapes. Sulfur concentrations are confined to the semiarid zone of the ETR, then decrease in the forest zone and increase again in the technogenic regions and the tundra belt of the Kola Peninsula, surrounded by the sea. The concentrations of chemical elements of regional and local distribution in atmospheric aerosols are more differentiated on the ETR and depend on the natural and technogenic features of each region. Thus, heavy metals are more common in the Plain territories of the forest-steppe and forest zones of the ETR and are confined to the bedrock and technogenic sources. High concentrations of calcium and strontium are associated with areas of weathering of carbonate rocks. In general, increased concentrations of atmospheric aerosols with an increased content of anthropogenic elements are observed during the western and southern transport of air masses. At the same time, the amount of rainstorm precipitation increases when these aerosols act as condensation nuclei. To assess the current state of the atmosphere at the ETR, it is necessary to continue field measurements and organize European annual and seasonal geochemical monitoring at stationary observation points.

1. Introduction
Climate and environmental changes on Earth have become modern challenges to humanity. The international community, on the UN platform, formulated the Sustainable Development Goals in the
Final Document "Transforming our World: the 2030 Agenda for Sustainable Development". The human habitat and the possibilities of its survival are linked to two goals - Goal 13. Combating climate change and Goal 15: Protecting and restoring terrestrial ecosystems and promoting their rational use, rational forest management, combating desertification, stopping and reversing the process of land degradation and stopping the process of biodiversity loss.

The main factor affecting the landscapes of Russia is an increase in air temperature and a decrease in precipitation as the IPCC reports show. Because of these processes, the amount of aerosols in the near-ground atmosphere of the landscapes of the ETR (European territory of Russia) increases. The aim of the study is to determine the atmogeophysical and atmogeochemical indicators that reveal the interaction of the atmosphere and the diversity of natural landscapes in European Russia.

2. Objects and methods of research
The main factor affecting the landscapes of Russia is the increase in air temperature. Thus, for the period from 1936 to 2018, the average annual air temperature anomaly averaged over the territory of Russia (deviation from the average for 1961-1990) was 1.58°C [1]. Thermal anomalies are observed in the south and north-west of the ETR. In general, the amount of precipitation is increasing. However, in summer and autumn, there is a decrease in precipitation in the central part of the ETR. Snow cover falls later than the average climatic terms and leaves earlier, in 2019 it was practically absent in a significant part of the ETR. Accordingly, the water reserves in the snow are not enough for landscapes. When there is a shortage of water, desiccation and degradation of soils are observed, which cause deflation, which supplies a significant amount of fine material to the atmosphere.

Atmospheric pollution depends on the nature of the earth's surface, which in the ETR is characterized by a wide variety of natural, anthropogenic and technogenic landscapes.

The main anthropogenic sources of atmospheric pollution are enterprises for the extraction and processing of minerals, the largest enterprises of metallurgy, enterprises of the fuel and energy complex, the chemical industry, the woodworking and paper industry, transport [2]. Currently, the program "Clean Air" and "Ecology" is being implemented in the Russian Federation. According to measurements for the period from 2012 to November 2019, the concentration of air pollution in the highways decreased. As a result, in the areas located along the highways, pollution decreased by 2.3 times compared to the data obtained 8 years ago.

However, all modern studies are based on remote sensing data and stationary indicators with an incomplete list of pollutants. In the context of growing natural and technogenic risks, areal ground measurements of pollution, including atmospheric aerosols, are required. To fully assess the environmental impact of aerosols in the natural and anthropogenic landscapes of European Russia, taking into account the mechanisms of in situ emission and transboundary transfer of matter, an expeditionary study of surface aerosols in natural zones of the EPR was carried out in 2020 and their geochemical differentiation was revealed. The main objects of research are aerosols, atmospheric precipitation, as well as soils and rocks.

Landscape-geochemical methods make it possible to study geosystems taking into account the state of all landscape components and actual migration processes [3]. When choosing key observation points (PO), we used complex atlases for the study areas, remote sensing data and field data from drone. For aerosol measurements, typical landscapes were selected in all natural zones of the ETR submeridionally (Table 1). At the observation points, a mobile aerosol complex of measuring equipment operated, including a field aspiration aerosol sampler, a mobile meteorological station, thermo-hygrochrones and navigation devices. Primary processing of aerosol characteristics data during expeditions based on satellite data using backward trajectories (NOAA HYSPLIT) has been carried out.
Table 1. Key points of observation of atmospheric aerosols in the EPR in 2020.

| Natural zone | Name, location of PO | Types of landscapes |
|-------------|----------------------|---------------------|
| Caucasus Mountain | Kislovodsk high-mountain scientific station of the IAP RAS, height 2077 m above sea level | Subalpine steppe |
|              | Kislovodsk, 850 m above sea level | Urbolandscapes |
| Steppe | Tsimlyansk Scientific Station of IAP RAS (CNS), height 60 m above sea level | Natural-anthropogenic steppe |
| Forest-steppe | Kursk Biosphere Station, IG RAS (KBS), height 250 m above sea level | Forest-steppe and agricultural landscapes |
| Southern taiga | Central forest state reserve (CFSR), Height 281 m above sea level | Coniferous and deciduous forests, swamps, postagrogenic landscapes |
| Northern taiga | Karelia, height 241 m above sea level | Coniferous forests, swamps |
| Tundra | Murmansk region, Height 215 m above sea level | Tundra |

The mountainous landscapes of the Caucasus are represented by high-mountainous moderately humid subalpine meadows in the city of Shatzhatmaz and in the urban landscapes of the city of Kislovodsk.

The steppe zone is characterized by the European soddy-grass steppes in the interfluve of the Volga and Don rivers, where loose Neogene-Quaternary deposits occur, represented mainly by loess-like loams and in some places blown by a sand cover [4]. The steppe zone has been considerably developed.

The forest-steppe zone corresponds to the southern watershed part of the stratal-denudation loess Russian Plain [4]. Analysis of meteorological data from the HMS Kursk indicates a steady increase in temperature, with an increase in the deficit of atmospheric precipitation, the number and duration of dry periods [5] The lack of sufficient atmospheric moisture in forest-steppe landscapes is one of the active factors affecting landscape degradation, leading to the emission of aerosols. Moreover, the chernozem zone is significantly plowed up, the zonal vegetation is 5% and is represented by meadow grass-forb steppes in combination with forests. There is practically no river runoff. There is a significant dissection of the ravine-girder network. The landscapes are represented by European forest-steppes.

The southern taiga in the Central Forest State Reserve (CFGR) remained practically the only site with broad-leaved-dark coniferous primary forests with the participation of pine forests on sod-podzolic soils, not subject to anthropogenic influence. The main watershed of the Baltic and Caspian Seas on the Russian Plain, where the headwaters of the Volga and Western Dvina rivers are formed, passes through the territory of the CFGR.

The northern taiga zone in Karelia occupies structural-denudation ridge uplands of the ancient Scandinavian shield [4].

In the north of the Murmansk region, there are tundra and forest-tundra European landscapes of the middle mountains of Fennoscandia. Mountain relief formed on crystalline rocks of the Baltic shield and complicated by glacial deposits of the last glaciation [6]. A vertical zonation forms, represented by three main belts of vegetation - mountain-forest, birch crooked forests and mountain-tundra, and on high
peaks and plateaus there are fragments of cold loach deserts, in which bryophytes and lichens prevail. Very large areas, especially in the east of the region, are occupied by swamps [7].

3. Results and discussions
The measurements of the mass concentrations of surface aerosols and soils for the natural zones of the ETR were carried out in the summer of 2020 at maximum air temperatures (July-August) with a predominant transfer of air masses, and their geochemical composition was determined.

The soils of the regions under study correspond to the zonal soil types. Geochemical differentiation by observation points shows that the maximum amount of aluminosilicates is confined to mountainous areas with close occurrence of rocks. The increase in the content of Na₂O, CaO and especially MgO is confined to the anthropogenic landscapes of the Kola Peninsula, where there are outcrops of bedrocks. The calculation of the concentration clarkes in soils (the content of the element in the soil / the clarke of the earth's crust) made it possible to calculate the intensity of the accumulation of elements in the soils of the observation regions, which are presented in the table 2.

Table 2. Intensity of accumulation of elements in the soils of the observation areas, 2020

| Natural zone          | 1-10 | 10-50 |
|----------------------|------|-------|
| Caucasus Mountain   | Cs, Zn, As, Mo, Cd, Hf |       |
| Southern taiga       | Zn, As, Pb, Zr, Cd, Hf |       |
| Northern taiga       | V, Co, Pb, Sc, Mo, Cd, Hf | Cr, Ni, Cu, As, Se |

Natural waters and atmospheric precipitation in key regions of the EPR were studied, if possible, at all observation points (Table 3).

Table 3. PH and mineralization of atmospheric precipitation and river waters of the ETR, 2020.

| Natural zone          | pH  | g/l | T°C |
|----------------------|-----|-----|-----|
| Caucasus Mountain   | 7,53| 0,02 | 10,9|
| Forest-steppe        | 6,87| 0,13 | 24,9|
| Southern taiga       | 5,81| 0,18 | 24,9|
| Tundra               | 7,61| 0,02 | 11,5|
| River Volga          | 7,68| 0,16 | 20,1|

The atmospheric precipitation of the high mountains of the Caucasus and high latitudes is clean and the pH value is neutral or slightly alkaline. The rains on the Russian Plain are more acidic and noticeably mineralized.

During the period of aerosol measurements in the high mountains of the Caucasus, according to the NOAA HYSPLIT model, northern air mass transfer was observed. The mass concentrations of surface aerosols in Kislovodsk at an altitude of 5 m and in the city of Shatzhatmaz at heights of 2 m and 0,5 m are presented in Table 4.

Table 4. Mass concentrations of surface aerosols at KVNS, 2020/

| Observation points | mg/m³ |
|--------------------|-------|
| Kislovodsk         | 0,0562|
| Shatzhatmaz (2 м)  | 0,0589|
| Shatzhatmaz (0,5 м)| 0,0204|

Measurement data on weight gain on filters show that presumably one air mass was recorded in the foothill zone and in the highlands. This is confirmed by similar concentrations of chemical elements of global, regional and local significance.
The ETR steppe zone has been studied in detail in Kalmykia in previous years [8]. Studies show that dusting of the atmosphere occurs during convective removal of in situ and pollution with heavy metals during transboundary transport. The same situation was observed in the central nervous system in 2020.

The forest-steppe zone is represented by steppe, forest and agricultural landscapes of the KBS. Measurements at all points were carried out at a height of 2 m. During the measurement period according to the NOAA HYSPLIT model, a west-northwest transfer of air masses was observed. Mass concentrations in natural landscapes are very similar (Table 5). In agrolandscapes, surface cementing of soil aggregates and good air permeability were observed.

### Table 5. Mass concentrations of surface aerosols at the KBS, 2020.

| Observation points          | mg/m³  |
|-----------------------------|--------|
| arable land                 | 0.0262 |
| oak forest                  | 0.0332 |
| forb-cereal steppe          | 0.0331 |

The chemical composition of the atmosphere shows that due to the rains, the dustiness of the atmosphere has been reduced. Only the content of sulfur is increased, which is probably an element of long-range transport. Heavy metals are characterized by an increased content of titanium, copper, nickel and zinc.

In the southern taiga in the CFSR, observation points were established in two typical landscapes - a spruce green moss-sphagnum forest at an altitude of 10 m almost at the upper border of the forest and at a height of 2 m, a herb meadow. During the measurement period according to the NOAA HYSPLIT model, a west-northwest transfer of air masses was observed. The mass concentrations in the forest biome are generally very similar (Table 6). On the post-agrogenic meadow, a powerful grass stand was observed on the abandoned lands of thirty years ago. Here, the increase in mass concentration was influenced by the proximity of the village (fires, arable land).

### Table 6. Mass concentrations of surface aerosols at the CFSR, 2020.

| Observation points                  | mg/m³  |
|-------------------------------------|--------|
| Forest 10m                          | 0.0053 |
| Forest 2m                           | 0.0052 |
| post-agrogenic meadow               | 0.0242 |

In general, the forest ecosystems of the CFSR are weakly differentiated. Increased concentrations of elements of the global value of sulfur, calcium and phosphorus are observed. The proximity of the industrial zones of Europe is the reason for the presence of heavy metals - titanium, nickel, zinc, copper and cadmium.

In the Tver region, preliminary studies were carried out in 2013 to determine the chemical composition of aerosol, snow cover and atmospheric precipitation in the landscape-geochemical system. Key natural points in the forest landscapes of the Tver region, relatively remote from economically developed territories and sources of anthropogenic pollution, were selected as experimental sites [9]. The conducted studies show that the natural landscapes of the Tver region, despite the remoteness from technogenic sources, still experience anthropogenic influence, due to aerial migration. However, a comparison of our data with the background abundances of elements in the atmosphere over the ETR indicates their comparability: the concentrations of most chemical elements in aerosols reflect the natural state of the surface atmosphere. The selected key areas in the CFSR and in previous studies can be considered background, data on the geochemical state of their components can be used in the future for comparative analyzes of the functioning of landscape-geochemical systems of the ETR.
The northern taiga in the Republic of Karelia was selected in a sparsely populated forest area in a spruce-pine forest and on a raised sphagnum bog. The surrounding areas are prone to areal felling, leading to waterlogging of the area. The numerous lakes and rock outcrops of Fennoscandia play a significant role in the formation of landscapes. During the measurement period, according to the NOAA HYSPLIT model, a south-southwest transfer of air masses was observed. The weight gain on the AFA-XA20 filters is very small - 0.0035 mg/m³. Global value items correspond to natural values. Elevated concentrations are characteristic of such chemical elements of regional and global importance as chromium, nickel, copper, zinc and cadmium.

In the Murmansk region, in the tundra landscapes, the observation point was on Mount Supchepakhk. Here, moss-lichen tundra vegetation is formed on coarse-grained red granites. Birch crooked forests are widespread along the river and lake valleys. The calculation of the reverse trajectories of the movement of air masses showed that during the measurements the wind direction was unstable - western, northern and southern intrusions were observed. Field observations have shown that unstable weather forms on the tops of the mountains with low cloud cover and strong winds. The west wind brings lingering precipitation. A southwest and southerly invasion with warm air masses improves the weather. The mass concentration in the tundra was 0.0184 mg/m³. Increased concentrations of elements of global importance mark the weathering of rocks (Fe) and marine influence (S, Ca, Na, Mg). Elements of regional and local significance include Ni, Cr, Mn, Ti Cd, which indicate the lithogenic base and mining industry of the region.

4. Conclusion

Based on the analysis of remote sensing data, field research data of past years, a list of modern sites was determined, where comprehensive studies of the potential emission of a substance in the European territory of Russia were carried out. In 2020, observations of surface aerosols were carried out in the background landscapes of the forest-steppe, forest and tundra zones of the ETR.

The research results show that in the submeridional profile, the mass concentration of aerosols decreases regularly from south to north, the minimum concentrations of atmospheric aerosols are observed in the forest zone, in the tundra there was a slight increase due to anthropogenic landscapes and the influence of the sea. Analysis of the chemical composition of aerosols revealed that, among the elements of global importance, aluminosilicates naturally increase to the south of the ETR as elements of clay minerals that are widespread in the Russian Plain. The maximum phosphorus content occurs in the residential area with agricultural landscapes. Sulfur concentrations are confined to the semiarid zone of the ETR, then decrease in the forest zone and increase again in the technogenic regions and the tundra belt of the Kola Peninsula, surrounded by the sea. The concentrations of chemical elements of regional and local distribution in atmospheric aerosols are more differentiated on the ETR and depend on the natural and technogenic features of each region. Thus, heavy metals are more common in the Plain territories of the forest-steppe and forest zones of the ETR and are confined to the bedrock and technogenic sources. High concentrations of calcium and strontium are associated with areas of weathering of carbonate rocks. In general, increased concentrations of atmospheric aerosols with an increased content of anthropogenic elements are observed during the western and southern transport of air masses. At the same time, the amount of rainstorm precipitation increases when these aerosols act as condensation nuclei.

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