Impact of emissions from the Orenburg gas chemical complex on the state of forest ecosystems

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Abstract. The article presents the results of a study of the state of forest ecosystems growing in the zone of the Orenburg gas-chemical complex. The authors established a taxation characteristic depending on the degree of remoteness from the source of pollution, the degree of accumulation and the accumulation series of heavy metals in the forest litter, and the horizontal crown density was calculated. All obtained data were analyzed using statistical analysis methods. The data obtained can be used for practical purposes.

1. Introduction
Pollutants enter the atmosphere and are deposited on the surface of the Earth. The spread of pollutants from emission sources is determined by the residence time of impurities in the atmosphere. Gases have little interaction with other components of the atmosphere and therefore their residence time is quite large [1]. However, most of the impurities under the influence of certain reactions turns into aerosols, and the residence time of particles in the atmosphere depends on their size, which as a result determines the rate of removal of impurities from the atmosphere, the smallest aerosols can be in the atmosphere for up to 30 days, but the distribution of emissions is determined by the direction wind, power emission and height of the pipe. The concentration is close to zero at the source itself, then it rises. Thus, given that the average wind speed in the lower kilometer layer is 20 km/h, it can be said that pollutants can be transported long distances from the source of their release [2, 3].

A study of the chemical composition of snow cover gives an idea of the flow of pollutants during the winter period. In winter the mineralization of precipitation and the concentration of impurities are usually high, frequent air inversions and low wind speeds contribute to this. Also, the level of pollution of snow is influenced by the direction of the prevailing wind, the capacity of the enterprise, and the distance from the source of emission [4].

2. Materials and methods
The studies were conducted in forest cultures on the territory of the Orenburg region in the zone of the Orenburg gas chemical complex.

The main research method is the laying of permanent sample plots and temporary test plots according to the requirements and guidelines for laying test plots in forest crops with subsequent long-term or one-time observations on them to obtain versatile and reliable information on the state of forest communities.
and their dynamics. To study the experience of creating artificial plantations, forest management materials, books of forest cultures and other scientific and technical documentation were used.

The plantings under study were characterized by the main forest management and taxation indicators: forest type and type of forest conditions, type of forest plantation area, type of forest crops, method of soil preparation, method of creation, mixing scheme, density and age of tree stands, quantity and quality of applied treatments [5, 6].

Soil samples were collected by genetic horizons on 5 test plots, in layers of 0–5, 5–10, 10–20 cm. To determine the degree of influence of atmospheric emissions of MCC on the state of coniferous species, depending on the degree of soil contamination, 5 zones were identified [7], where 6 RFPs were laid. Landings distant from the source of pollution at a distance of 5 km, 2–10 km, 3–15 km, 4–30 km, 5 – more than 30 km were assigned to zone 1.

The accumulation of pollutants in the snow was studied in 3 test plots and in the control area. An agrochemical analysis of the soil, forest floor and snow water was performed by the atomic absorption method at the Orenburg Chemical Production Center.

To study the radial growth of the test plots cores were selected using an age drill at a height of 1.3 m from the northern side of the trunk. Processing of cores was carried out in the laboratory using a microscope, measured the width of the annual layer with an accuracy of hundredths of a millimeter.

In order to study the formation of a canopy of artificial forest stands under pollution and background conditions at the test plots, in each row, the planting step and the diameter of the crowns along and across the row were measured by the method of A. Makarenko. After that, in laboratory conditions, the crown of each tree of the corresponding row was applied to the calico paper. Then, we separately measured the crowns and voids on the analytical scales of class 2 VLR-200G (GOST 19491-74).

Experimental material collected in field conditions was processed by methods of variation statistics and methods of statistical analysis.

3. Results
A large enterprise, the Orenburg Gas Chemical Complex, which is an enterprise of the first danger category, is located in the study area. The development of the Orenburg gas condensate field began in 1966. The gas composition includes the following components: methane (83.3 %), ethane (4.6 %), propane (1.6 %), butane (0.8 %), pentane (0.6 %), hexane and higher hydrocarbons (1.2 %), nitrogen (4.9 %), carbon dioxide (0.9 % by volume), helium, condensate and hydrogen sulfide (more than 2.0 %) [8, 9].

The complex has been operating since 1974; its main purpose is to clean and process natural gas and liquid unstabilized hydrocarbons and to produce liquefied gas, stable condensate, sulfur gas and odorant. The atmospheric emissions of the OGCC contain Fe, Al, Zn, Mn, Cr, Mg, Ni, B, Cu, Ba, Ti, Pb, Sr, Mo, Cd, Li, and also contain sulfur dioxide, nitrogen dioxide, carbon monoxide , hydrogen sulfide and other impurities.

Protective Sanitary Zone OGHK is located within a radius of 5 km from the extreme sources of emissions. The air pollution index (API) in this area varies from 0.7 to 1.2.

According to the mass characteristics of emissions of pollutants into the atmosphere, the gas industry ranks seventh (47.7 thousand tons or 7.56 %). The main pollutants are carbon monoxide (61.2 %) and sulfur dioxide (36.4 %).

In order to determine the degree of impact of industrial emissions on forest stands, permanent test areas were laid at a distance of 5, 10 and 15 kilometers from the source. The studied stands grow on southern chernozem and belong to protective forests (green zone). The cultures were laid in 1968, the method of preparing the soil is plantation plowing to a depth of 45–50 cm. To identify the effects of industrial emissions, three permanent test areas were laid in the background.

In all cases, planting was carried out by two-year-old seedlings. The initial density in the pine-ash solid type of crops for ash 5.7 thousand pieces/ha, for pine 2.7 thousand pieces/ha; in the second zone in the pine-ash-tree solid type for ash crops 3.3 thousand pieces/ha, in the pine tree 5.7 thousand pieces/ha, in the third zone of ash-birch-pine-larch continuous type, the density was in the ash tree
5.7 thousand pieces/ha, birch 4.7 thousand pieces/ha, pines 6.4 thousand pieces/ha, larch 7.7 thousand pieces/ha. In cultures of considerable remoteness from the source of pollution, the initial density was in the solid pine type – 3.4 thousand units/ha, in the larch continuous type – 1.1 thousand units/ha, in the ash-larch continuous type in larch – 5.7 thousand pcs./ha, green ash – 4.0 thousand units/ha.

Research revealed that ash-tree green has the greatest safety 36–59 %. The low safety of the plants in the third zone is explained by the influence of emissions, where the general sanitary condition of the stands is deteriorating. At the same time, in the conditions of the background as a whole, the safety of plants is higher and ranges from 11.4 to 67.0 %.

In all the cultures studied there are stumps – traces of unauthorized logging. Thus, 9.6 % of pine specimens from the originally planted were cut down in the 5 km zone, 9.5 copies of the pine tree were in the 10 km zone, and 17.7 % birch in the 15 km zone. In cultures more than 30 km distant, in pure larch the percentage of unauthorized logging was 33.0, in pure pine – 14.4, in mixed larch-ash trees – 3.5 in larch. The largest number of dry trees was observed in the 10 km zone and in the crops of the composition 5L5A.

The height and diameter of the trunk in the 5 km zone is more than 10 and 15 km zones. Thus, in the 5 km zone, the average height was 15.0 m in the 10 and 15 km zones, respectively, 13.3 and 9.5 m. The average diameter of the trunk at a distance of 5 kilometers was 20 cm, at 10 and 15 km distance, respectively, 16.7 and 9.2 cm. The development of the crown is uniform both along and across the row in all the zones studied.

The differences in the average heights and diameters of the trunk can be explained by the fact that the main carriers of the mass of heavy metals in the atmosphere are aerosols, which are very easily carried by the wind over long distances, and are deposited at a relative distance from the enterprise. The planting composition has an obvious effect due to the fact that different tree species have different bioecological properties, and in conditions of insufficient atmospheric moistening, the bulk of tree roots are in the upper soil layer and when several species of trees grow together as a result of interspecific competition, overall productivity decreases.

Pine and Siberian larch are first-class trees of height, fast-growing, light-loving, moderately demanding to soil fertility and moisture.

Birch is hanging and ash is green trees of the second class height, birch is a light-loving breed, and ash belongs to medium-sized light-loving breeds, birch is of little demand, and ash is highly demanding of soil fertility of the breed.

In addition, when determining the horizontal closure of the canopy by research, it was found that this indicator at 15 km distance was 83.6 % (the maximum value of the studied), respectively, the accumulation of pollutants is higher and affects the decrease in taxation indicators.

With the distance from the source of pollution, the fullness of the plantings decreases from 0.91 (in the 5 km zone) to 0.7 (in the 15 km zone), bonitet, stock and average growth, as well as the sanitary condition of the plantings worsens. The quality class at different distances from the complex was in pine ordinary from Ib to II, in ash green II and III, cultures of considerable distance were characterized by I, Ia. The stock is the result of increment, the minimum value of 117.7 m$^3$/ha was recorded in zone 3, in zone 1 and zone 2, respectively 168.2 and 186.0 m$^3$/ha.

Consequently, the impact of industrial emissions adversely affects the plantations, which is manifested in the reduction of taxation indicators, sparseness of crowns, deterioration of sanitation and can be traced at a distance of up to 15 km from the source.

To study the degree of influence of atmospheric emissions of the gas-chemical complex on the soil, as well as the accumulation of pollutants in snow cover and forest litter, samples of soil, snow and litter were taken on four permanent test plots.

Studies have shown that the acidity of snow water at sites is close to neutral (pH 6.6–7.2).

The content in the snow of heavy metals in the studied zones in almost all elements do not have significant differences. However, lead content in snow water in the 5 km zone is two times more than in 10 and 15 km and in cultures of considerable distance. Almost the same distribution can be noted
for cadmium (5km -0.0026ml/l over 30 km -0.0014 ml/l), which indicates that lead and cadmium are the main components of air pollution.

Analysis of the data revealed that with distance from the source, the content of copper and lead in the litter decreases. At a distance of 5 km, respectively, the content is 1.13 mg/l and 8.21 mg/l, 10 km – 1.08 mg/l and 7.39 mg/l, in 15 km – 0.92 mg/l and 7.15 mg/l and at a distance of more than 30 km – 0.49 mg/l and 0.85 mg/l.

The maximum concentration of zinc was at a distance of 15 km (20.0 mg/l), minor differences in the content were in the 5 and 10 km zones, respectively, 11.33 and 12.667 mg/l.

As a result of studying the nickel concentration, the following data were obtained: in the 5 km zone, 1.125 mg/l, in the 10 km zone, 1.056 mg/l, in 15 km, 0.847 mg/l, in cultures of considerable distance, 0.972 mg/l.

The chromium content was almost the same in the 5 km zone and at a considerable distance from the source of emission (0.99 and 0.98 mg/l, respectively), the maximum concentration was in the 10 km zone (1.07 mg/l), the minimum 15 km a zone of 0.87 mg/l.

The rows of accumulation of elements in the forest litter in the symbolic and percentage (to the general level of accumulation) expression are as follows:

- **distance from the source – 5 km**
  - Mn> Zn>Pb> Cu; Ni> Cr> Co> Cd
  - % 77.2> 11.1> 8.1> 1.1> 1.0> 0.3> 0.1
- **remoteness – 10 km**
  - Mn> Zn>Pb> Cu; Cr> Ni> Co> Cd
  - % 66.9> 17.8> 10.4> 1.5> 1.4> 0.3> 0.2
- **remoteness – 15 km**
  - Mn> Zn>Pb> Cu; Cr; Ni> Co> Cd
  - % 73.2> 17.8> 6.4> 0.8> 0.2> 0.1
- **remoteness – more than 30 km**
  - Mn> Zn> Ni; Cr>Pb> Cu> Co> Cd
  - % 92.4> 3.3> 1.2> 1.0> 0.6> 0.2> 0.08

In these series, the dominant participation of manganese is noted, its maximum content (92.4 %) in plantations – more than 30 km distant. The accumulation of zinc, lead and copper in cultures of 1, 2 and 3 zones, primarily due to man-made pollution. In the accumulation of heavy metals, a certain regularity can be traced, so in the litter of cultures growing in zones 1, 2 and 3, the association of elements is as follows: Mn> Zn>Pb> Cu> Cr> Ni> Co> Cd, in plantations 4 zones of position elements and their contents are:

- Mn> Zn> Ni> Cr>Pb> Cu> Co> Cd.

The main pollutant metals that make up the association in the emissions of Zn, Mn, Pb, Cr, Ni, Cu, Cd are also characteristic of the objects where the work was carried out, which confirms the influence of the gas chemical complex on tree plantings.

Research Kaliyev A.Zh. [1999] detected the presence of pollution by atmospheric emissions of OGKH within a radius of 20 km. Associations of elements with elevated concentrations in snow cover, soils and plants are as follows:

- **Snow Zn, Ti, Mn, Sr, Pb, Cu, Ni, Ba, Cr, Sn, Cd**
- **Soils Ti, Mn, Cr, Sr, Zn, Cu, Ni, Pb, Co**
- **Plants Ti, Mn, Zn, Sr, Cu, Ni, Cr, Pb, Co**

Comparing the associations of elements obtained by A.Zh. Kaliyev with the results of our research, it can be found that the accumulation of some heavy metals in a certain substrate has similar positions, which may indicate that heavy metals in the atmosphere are still aerosols, which can remain in it for a certain time and is carried by the wind over fairly long distances.

The results of studies to determine the degree of accumulation of heavy metals in the forest litter indicate that it is a biogeochemical barrier and effectively binds metals, preventing them from further penetrating along the profile. However, accumulating them, it gradually reduces its protective functions, and this is reflected in the condition of both woody plants and the soil.
The percentage of horizontal crown density calculated by us according to the method of A. Makarenko is presented in Table 1.

| Composition, distance, km | Forest canopy closeness, % |
|--------------------------|----------------------------|
| 6P4A 5km                 | 61.3                       |
| 7P3A10 km                | 78.4                       |
| 4A3B2L1P 15 km           | 83.6                       |
| 10P more than 30 km      | 58.9                       |
| 10L more than 30 km      | 59.0                       |
| 5L5A more than 30 km     | 87.0                       |

The horizontal closure of the canopy in percentage terms is characterized by the maximum value in cultures of the composition 4A3B2L1P (distance from the source is 15 km) and the composition of 5L5A (distance of more than 30 km). The minimum values turned out to be in pure pine and pure larch stands (respectively 58.9 and 59.0 %). The data in Table 1 indicate that a mixture of rocks had an obvious effect. Thus, in the 15 km zone, 4 rocks are involved in the composition of the rocks, having a horizontal canopy closure of 83.6 % and it is likely that a significant amount of emissions accumulates in the canopy of this planting, compared with cultures remote from the gas chemical complex at 5, 10 and 15 km that could not but affect taxation indicators. The percentage of closeness of the canopy in cultures located in the 5 km zone is 61.3 %; this is the minimum figure in the zoned area. Accordingly, following this assumption, fewer pollutants precipitate in the canopy of these crops and they are characterized by better taxation indicators.

In general, it can be noted that in mixed cultures the horizontal closure of the canopy is higher than in pure ones and they are preferable as a green filter.

4. Conclusion
In the zone of technogenic pollution, forest cultures develop with deviations and loss of quality of stands of up to 25 %. Research has shown that green ash has the greatest safety, which was 36-59 %. The low safety of the plants in the third zone is explained by the influence of emissions, where the general sanitary condition of the stands is deteriorating. At the same time, in the conditions of the background as a whole, the safety of plants is higher and ranges from 11.4 to 67.0 %.

The established differences in average heights and trunk diameters are explained by the fact that the main carriers of the mass of heavy metals in the atmosphere are aerosols, which are very easily transported by wind over long distances, and are deposited at relative distance from the enterprise. The planting composition has an obvious effect due to the fact that different tree species have different bioecological properties, and in conditions of insufficient atmospheric moistening, the bulk of tree roots are in the upper soil layer and when several species of trees grow together as a result of interspecific competition, overall productivity decreases.

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The forest canopy, an aggregate of crowns of closed trees, is of significant ecological and silvicultural importance. The amount of precipitation reaching the soil, total evaporation, the amount of light penetrating the planting, temperature and humidity, wind speed, and more depends on the structure of the canopy, a set of tree species and the degree of closure of the canopy.

Mixed forest cultures should be used as a green filter, since they have a higher horizontal density than clean ones.
Acknowledgment
The studies were performed in accordance with the plan of research works of Federal Research Centre of Biological Systems and Agrotechnologies of the Russian Academy of Sciences (No. 0761-2019-0004).

References
[1] Aksyutin O E 2019 Scientific and Technical Problems in Natural Gas Recovery, Transport, and Processing. Her. Russ. Acad. Sci. 89 91–5 Retrieved from: https://doi.org/10.1134/S1019331619020011
[2] Korotkova A M, Sizova E A, Lebedev S V and Zyazin N N 2015 Influence of NPs Ni° on the induction of oxidative damage in Triticum vulgare Oriental J. of Chem. 31 137–45
[3] Korotkova A M, Lebedev S V, Kayumov F G and Sizova E A 2017 The influence metal nanoparticles (Fe, Cu, Ni) and their oxides (Fe₃O₄, CuO, NiO) Sel'skokhozyaistvennaya Biol. 52(1) 172–82
[4] Kalyakina R G, Ryabukhina M V and Maiski R A 2018 Influence of Orenburg gas condensate field development on ecological and biological condition of landscape-botanical complexes IOP Conf. Ser. Mater. Sci. and Engineer. Electr. edition. 451(1) 012194 Retrieved from: https://doi.org/10.1088/1742-6596/451/1/012194
[5] Maiski R A, Ryabukhina M V and Kalyakina R G 2018 Ecological and technological aspects of increasing sustainability of vegetation cover of Caspian oil and gas provinces IOP Conf. Ser. Mater. Sci. and Engineer. Electr. edition. 451(1) 012193. Retrieved from: https://doi.org/10.1088/1742-6596/451/1/012193
[6] Chibilev A A, Sokolov A A and Rudneva O S 2012 The fuel and energy complex of the Russia-Kazakhstan transboundary region: Present state and development prospects Geogr. Nat. Resour. 33 270–6 Retrieved from: https://doi.org/10.1134/S1875372812040026
[7] Kaliyev A Z 1998 Environmental Conditions in the Areas Exposed to Emission from the Gas Processing Industry in South Ural. In: Linkov I, Wilson R (ed) Air Pollution in the Ural Mountains. NATO ASI Series (Series 2: Environment) 40 112–7 Retrieved from: https://doi.org/10.1007/978-94-011-5208-2_12
[8] Vinogradova A A 2015 Distant evaluation of the influence of air pollution on remote areas Izv. Atmos. Ocean Phys. 51 712–22 Retrieved from: https://doi.org/10.1134/S0001433815070099
[9] Yausheva E, Sizova E, Lebedev S et al 2016 Influence of zinc nanoparticles on survival of worms Eisenia fetida and taxonomic diversity of the gut microflora Environ. SciPollut. Res. 23(13) 13245–54 Retrieved from: https://doi.org/10.1007/s11356-016-6474-y