Assessing the ecological state of agricultural irrigated fields of the Orenburg gas processing complex with dumping sewage water for crop irrigation

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Abstract. The article is devoted to using wastewater of the Orenburg Gas Chemical Complex in the amount of up to 7.0 million m³ for irrigating agricultural crops with the purpose of additional cleaning of wastewater and increasing the yield of agricultural crops. Analyzing the obtained data, it is shown that in the arid climate with rainfall deficiency, the use of wastewater for irrigation of forage crops is the best variant in providing the necessary measures for preserving the ecological status of the agricultural sewage farms (ASF). As a result of own research over years 1982 – 2015, the influence on the ecological state of ASF soils was detected in the form of deterioration of the water-physical properties and increased content of easily soluble salts in the soil; with that, the content of gross and mobile forms of heavy metals is significantly lower than MPC, but slightly above the background values, which does not affect the quality of sorghum harvest. Pollutants accumulate in the top layer of soil; therefore, the impact on surface water bodies has not been established. The authors suppose that maintaining the ecological state of ASF requires some measures like the introduction of calcium-containing substances and optimization of the irrigation conditions. The practical importance of scientific research is that based on the obtained results, a project of ASF soil rehabilitation has been developed and put into production.

1. Introduction

Extraction and processing of fossil fuels have a significant effect on flora and fauna, agriculture, and landscape aesthetics [1, 2].

Additional treatment of large volumes of wastewater with low concentrations of contaminants to the standards that would allow discharging into water bodies is a problem. The problem of sewage and sediment disposal is also being solved by foreign scientists [3–7]. Therefore, the studies of gas-processing industry sewage disposal are relevant. The relevance of the research studies lies in the fact that extraction and cleaning of associated gas from sulfur-containing components at the Orenburg Gas Chemical Complex (OGCC) requires significant consumption of water, which simultaneously results in an impact on the components of the environment [8–10].
Discharging sewage in the natural-technical system of OGCC is associated with two problems: improving the quality of wastewater based on tertiary treatment in the natural subsystem of the agricultural sewage farm (ASF), and creating safe conditions for their return into the environment and increasing the yield of forage crops upon irrigation.

OGCC ASF was designed as an ecological measure. They have been functioning since 1976, and are an integral part, the last step of the existing post-treatment of wastewater from three enterprises: the Orenburg Gas Processing Plant, the Orenburg Helium Plant, and the Kargalinskaya CHP [9, 10]. After biological treatment, up to 7.0 million m$^3$ of wastewater are sent to the setting pond (SP).

In the technical subsystem, wastewater is discharged by Fregat sprinkling machines. The existing closed type irrigation network is implemented according to the dead-end system and consists of the main and the distribution pipelines.

The scientific novelty of the research is in the fact that it was the first long-term study with the aim of assessing the effect on the environment during the disposal of wastewater from gas processing enterprises.

The object of the research was using sewage from gas processing enterprises for irrigating fodder crops.

The subject of the research was the impact of wastewater irrigation on the environment.

2. Materials and methods

The research methods were planned in accordance with RD 52.18.595-96 "Federal List of Measurement Procedures allowed for environmental pollution monitoring", MU 2.1.7.730-99 "Hygienic assessment of soil quality in residential areas", SP 11-102-97 "Engineering-Ecological Surveys for Construction"; the ecological state of the soils was assessed by the total chemical pollution index. The ecological-geochemical state of the soils was assessed based on the background characteristics and the maximum (approximate) permissible concentrations of harmful substances in the soil. Using the methods of mathematical statistics, the significance of controlled parameters was promptly assessed in the "Statistics" software. Monitoring of the soils chemical contamination was developed according to GOST 27593-88. The chemical composition of the soils, the surface runoff and vegetation was analyzed in certified and accredited laboratories.

The effect in the natural-technical system was studied in laboratory and field experiments. In a field experiment, the formation of the technical parameters of the subsystem was studied with the wetted soil layer depth of 0.5 m. For studying heavy metals behavior in the soil, 30 points were allocated on the territory of the ASF. The total of 120 soil samples were taken annually. The water-physical properties of the soil were determined according to [11].

Samples of water were taken in accordance with GOST R 51592 – 2000 "Water. General requirements to sampling"; chemical analysis of water samples were performed in accordance with RD 52.24.309-92 “Protection of nature. Hydrosphere. Organization and observation of the conditions of surface runoff pollution with the use of the Roshydromet network. St.-Petersburg. 1992”. The accuracy of measurement was according to GOST 27384-82 "Water. Rates of measurement error of characteristics of composition and properties" and GOST 27384-87. Requirements to instruments and devices for taking samples, primary processing and storage of samples were according to GOST 17.1.5.04-81.

The yield was accounted for using the quadrant sampling method by mowings within the boundaries of the affected area and in the reference plot. The number of samples per plot was three. The results were processed by the analysis-of-variance method [12].

3. Results

In the natural subsystem of ASF, the climate of the Orenburg region is characterized by hot summers and frosty winters, and low year-round rainfall [13].

Before wastewater discharge, the soils of ASF were presented by southern black soils with the humus content of about 4 % and the thickness of the humus layer of 35 – 55 cm with the predominance of
physical clay by more than 50%. The natural conditions of the OGCC ASF location are shown in Table 1.

**Table 1. ASF natural conditions**

| Parameters                                      | Orenburg district, the zone affected by OGP                                                                 |
|------------------------------------------------|-------------------------------------------------------------------------------------------------------------|
| Geological structure                            | the area belongs to the Paleozoic group of the Permian system; the composition of the parent rocks includes sandstones, limestones, dolomites, and clays |
| Soil texture                                     | fine- and medium-loamy                                                                                      |
| Soil type                                        | ordinary black soil                                                                                        |
| Zonal type of vegetation                        | fescue-feather grass steppe                                                                               |
| The average depth of soil freezing (end of February), cm | 100 – 120                                                                                                    |
| Wetting area                                    | Arid                                                                                                         |
| Hydrothermal coefficient (HTC)                   | 0.6                                                                                                          |
| The sum of temperatures above +10 °C             | 2,700                                                                                                        |
| Duration of the frost-free period, days          | 136                                                                                                          |
| Heat provision area                              | warm                                                                                                         |
| Snow depth, cm                                   | 30 – 40                                                                                                       |
| Average annual rainfall, mm                      | 350 – 400                                                                                                    |
| Air temperature, °C:                            |                                                                                                              |
| – July                                          | +21                                                                                                          |
| – January                                       | -15                                                                                                          |
| The absolute maximum of temperatures, °C         | +42                                                                                                          |
| The absolute minimum of temperatures, °C         | -43                                                                                                          |
| Snow cover melting                               | April 4                                                                                                       |
| The absolute value of potential water resources, l/s×km² | 0.5 – 1                                                                                                      |
| Ecological state of the natural environment      | unfavorable with three factors, anthropogenically disturbed environment                                     |
| Index of environmental factors                  | 12                                                                                                            |
| Elements concentration in the rocks              | 8 MPC                                                                                                        |
| The thickness of the aeration zone, mm           | 4,000 – 36,000                                                                                                |

The natural environment in the area of the gas processing plant is experiencing significant pressure from technical systems: the environment is anthropogenically affected, the index of ecological factors is 12, and elements concentration in the rocks reaches 8 MPC. Irrigation has a significant effect on the soils of ASF.

For studying the dynamics of changes in the water-physical properties of soil over the many-years period, the authors performed a comparative analysis of their own average data on the ASF and the data for the year 1988 (Table 2).

These data show the pattern of soil compaction on the entire ASF massif, compared to the values of this parameter in 1988. Soil humidity at full and minimum water capacity during ASF operation reduces. The soils in ASF are not only greatly over-compacted, but the water capacity decreases steadily throughout the entire territory of the massif. Soil water capacity in the spring is higher, which clearly indicates their seasonal over-wetting.

Accumulation of sulfur-containing compounds may be considered as the main negative process in the soils of ASF, despite the fact that the overall mineralization of wastewater does not exceed 1 g/l. The concentration of sulfate ions in the top soil layer in the autumn is notably higher than in the spring,
their coefficient of local concentrations is in the range between 1.89 and 2.50. The content of hydrosulphide ion across the entire massif exceeds the background value by 5 – 10 %.

Table 2. The dynamics of changes in the water-physical properties of ASF soil (average for the wetted soil layer)

| Indicator | Date and location of taking soil samples | Humidity, % | Bulk density, g/cm³ | Humidity at the lowest water holding capacity, % | Humidity at full water holding capacity, % |
|-----------|----------------------------------------|-------------|----------------------|-----------------------------------------------|------------------------------------------|
| Background | autumn 1988                            | 21.50       | 1.17                 | 35.29                                         | 54.80                                    |
| Average values for ASF | autumn 2014                           | 26.20       | 1.22                 | 21.53                                         | 46.51                                    |
| Average values for ASF | spring 1988                           | 26.90       | 1.36                 | 32.78                                         | 51.85                                    |
| Average values for ASF | spring 2015                           | -           | -                    | -                                             | -                                        |

Comparative analysis of changes in the soil chemical composition in the years 1982 through 2015 is shown in Table 3. In 1982, the concentration of chlorides and sulfates in the soil exceeded the background values only 1.2 times, in 2015 — 2.18 times.

Table 3. The content of chemicals in the arable soil layer, the average for the ASF, 1982 through 2014, mg/kg

| Period of time | pH | Cl⁻ | HCO₃⁻ | Ca²⁺ | Mg²⁺ | HS⁻ | NH₄⁺ | SO₄²⁻ | Zn²⁺ |
|----------------|----|-----|-------|------|------|-----|------|-------|------|
| Background     | 7.5 | 69.90 | 742.90 | 64.50 | 32.70 | 38.50 | 35.60 | 41.00 | 0.046 |
| 1982 – 1984    | 8.2 | 84.007 | 279.76 | 56.14 | 26.99 | -    | -    | 51.307 | -    |
| 2014 (autumn)  | 7.3 | 95.35 | 441.38 | 104.02 | 25.49 | 39.55 | 57.08 | 89.24 | 0.106 |

The content of mobile forms of heavy metals in ASF soils is much less than MPC, Table 4. Compared to the background, the content of mobile forms of manganese, chromium, nickel, lead, and cadmium is elevated.

The highest concentration of heavy metals and the indicator of their total pollution are observed in the vicinity of hydrant No. 7 where the amount of discharged water is greater than in other analyzed areas. Here, the content of mobile forms of manganese is three times higher than the background value, of lead — 2.5 times higher, and of cadmium — 2.2 times higher than the background value.

Table 4. The content of mobile forms of heavy metals in ASF soil (0.1 – 0.25 m horizon depth), mg/kg, October 2014

| Location of taking soil samples | The content of mobile forms of heavy metals | Chemical Pollution Indicator |
|--------------------------------|-------------------------------------------|-------------------------------|
| Background, mg/kg              | Mn | Cr  | Ni  | Pb | Cd |            |
| Hydrant No. 7                  | 4.40 | 0.58 | 0.61 | 0.44 | 0.05 | 9.68 |
| Hydrant No. 11                 | 11.90 | 0.51 | 0.80 | 1.14 | 0.11 | 5.26 |
| Hydrant No. 15                 | 5.00 | 0.37 | 0.67 | 0.43 | 0.07 | 7.84 |
| Average for ASF                | 8.73 | 0.46 | 0.69 | 0.80 | 0.09 | 7.59 |
| MPC                           | 140.0 | 6.00 | 4.00 | 6.00 | 1.00 |        |
The Chernaya River nearby is the area of groundwater discharge. Therefore, the chemical composition of the waters in the river upstream and downstream of the ASF was studied, Table 5.

The excess of MPC upstream of the ASF was noted for copper — 8.5 times, for iron — 7.1 times, for chlorides — 1.44 times, for sulfates — 2.7 times, for COD — 3.3 times, for BOD₅ — 2.14 times, and for suspended solids — two times. In the water downstream of the ASF, the concentration of these substances exceeds the MPC, but the content is much lower than at the cross-section close to the tributary.

A clear decrease is visible in all analyzed indicators in the river below the ASF, compared to the indicators in the midstream. This is explained by the fact that in the aeration zone, a complete final treatment of sewage occurs.

Table 5. Chemical composition of the waters in the Chernaya River upstream and downstream of the ASF

| Indicator                  | Date and location of taking samples | Unit of meas. | MPC (fishery) | Source | 05.2015 Upstream of the ASF (close to the tributary) | Downstream of the ASF | MPC (potable) |
|----------------------------|-------------------------------------|---------------|---------------|--------|-----------------------------------------------------|----------------------|---------------|
|                            |                                     |               |               |        | Concentration | MPC multiplicity | Concentration | MPC multiplicity | Concentration | MPC multiplicity |                  |                      |
| Cl⁻                       | mg/l                                | 300.00        | 353.90        | 1.18   | 432.20      | 1.44            | 197.30        | 0.66            | 350.00        |                   |                  |                      |
| HCO₃⁻                     | mg/l                                | not rated     | 826.60        | -      | 732.00      | -               | 594.70        | -               | 1,000.00      |                   |                  |                      |
| SO₄²⁻                     | mg/l                                | 100.00        | 230.40        | 2.30   | 268.80      | 2.69            | 153.60        | 1.54            | 500.00        |                   |                  |                      |
| HS                        | mg/l                                | absent        | 0.16          | -      | 0.15        | -               | 0.16          | -               | 3.00          |                   |                  |                      |
| Ca²⁺                     | mg/l                                | 180.00        | 119.60        | 0.66   | 102.20      | 0.57            | 100.80        | 0.56            | 200.00        |                   |                  |                      |
| Mg²⁺                     | mg/l                                | 40.00         | 60.00         | 1.50   | 53.60       | 1.34            | 85.00         | 2.13            | 100.00        |                   |                  |                      |
| Total hardness            | mg/l                                | not rated     | 10.98         | -      | 9.58        | -               | 8.60          | -               | 7.00          |                   |                  |                      |
| Zn²⁺                     | mg/l                                | 0.01          | 0.008         | 0.80   | 0.005       | 0.50            | 0.004         | 0.40            | 1.00          |                   |                  |                      |
| Cu                        | mg/l                                | 0.10          | 0.19          | 1.90   | 0.71        | 7.10            | 0.34          | 3.40            | 0.30          |                   |                  |                      |
| Ammonium nitrogen         | mg N/l                              | 0.40          | not found     | -      | 0.20        | 0.50            | not found     | -               | 2.00          |                   |                  |                      |
| Suspended matter          | mg/l                                | 10.00         | 23.50         | 2.35   | 20.00       | 2.00            | 5.26          | 0.53            | 40.00        |                   |                  |                      |
| COD                       | mg O₂/l                             | 15.00         | 33.30         | 2.22   | 50.00       | 3.33            | 25.00         | 1.67            | 30.00        |                   |                  |                      |
| BOD₅                      | mg O₂/l                             | 2.00          | not lower than 4.00 | 4.28 | 2.14 | 4.04 | 2.02 | 4.00 |                   |                  |                      |
| Dissolved O₂              | mg/l                                | 0.05          | 5.00          | 100.00 | not found | - | not found | - | 0.10 |                   |                  |                      |
| Oil products              | mg/l                                | not rated     | 6.5 – 8.5     | -      | 7.6        | -               | 8.1           | 6.5 – 8.5       | 1000.00      |                   |                  |                      |
| pH                        | mg/l                                | 8.0           | 7.6           | -      | 8.1        | -               | 6.5 – 8.5       | 1000.00      |                   |                  |                      |
| Dry residue               | mg/l                                | not rated     | 820.00        | -      | 1140.0      | 0               | 600.00        | -               | 1000.00      |                   |                  |                      |
| Settling substances       | cm³/l                               | not rated     | 0.20          | -      | 0.20       | -               | 0.20           | -               | not rated      |                   |                  |                      |
Being an indicator of the ecological status of the agroecosystem, the quality of the obtained products is of great importance. Therefore, the authors determined the mineral content and crude protein in sorghum cultivated in the ASF, and compared the results to similar indicators in the non-irrigated reference plot (Agricultural Farm Kolkhoz Imeni Lenina in the Orenburg district). The results are shown in Table 6.

The content of sulfur, sodium, calcium, nitrogen, and protein in the ASF massif was lower than in the reference plot; with that, irrigation provides insufficient yield increase. Lower sulfur content in the sorghum cultivated in the ASF, compared to the plants cultivated in the reference plot, showed that the soil wastewater treatment in the studied massif had been efficient.

Table 6. Chemical composition of sorghum green mass

| Indicators     | OGCC ASF | Agricultural Farm Kolkhoz imeni Lenina (reference) |
|----------------|----------|--------------------------------------------------|
| Yield, t/ha    | 156.00   | 148.00                                           |
| Content, %:    |          |                                                  |
| – nitrogen     | 1.68     | 3.00                                             |
| – crude protein| 10.50    | 18.70                                            |
| – sodium       | 0.05     | 0.07                                             |
| – calcium      | 0.54     | 0.62                                             |
| – sulphur      | 0.49     | 0.50                                             |
| – lead         | 0.11     | 0.12                                             |
| – cadmium      | 0.013    | 0.014                                            |
| – copper       | 35.9     | 40.0                                             |
| – zinc         | 13.5     | 15.0                                             |

4. Discussion
As a result of the authors' own studies, it has been found that over the years of wastewater irrigation, soils were significantly dispersed (the percentage of annealed residue increased, the fraction of silt increased, bulk density increased, and porosity decreased). Relative predominance of sodium over calcium is observed; with that, the content of mineral forms of carbonates has been steadily declining, being contributed to by the process of sodium chloride content reduction [1].

An increased concentration of soluble salts was noted in the soil as a result of wastewater discharge, compared to the indicators for the period between 1982 and 1984. The maximum value of this indicator was observed in the autumn of 2014. The content of gross and mobile forms of heavy metals is significantly below the MPC, but slightly above the background values.

The content of nitrogen (56 %) and crude protein (56.15 %) is below the background values, which confirms the scarcity of nutrients in the wastewater and, consequently, in the soil, and almost complete absence of measures aimed at increasing ASF soil fertility; therefore, mineral and organic fertilizers are to be introduced into the ASF soil. The sorghum yield increase in the ASF, compared to the non-irrigated reference plot, is explained by three mowings as a result of irrigation, vs. single irrigation at the agricultural farm Kolkhoz Imeni Lenina.

Wastewater from OGCC does not contain nutrients in the amounts sufficient for fertilizing plants, thus, the discharge conditions are determined by water consumption by the cultivated crops. Due to the fact that in the recent years, only sorghum has been cultivated for green fodder, it is necessary to present new requirements to the quality of wastewater, and to the design of ASF and watering conditions. The level of technogeneous load on the existing natural-technical system with the seasonal discharge of wastewater is determined from the prerequisites for creating optimal conditions for growth and development of the plants in the agrocoenosis [14].

5. Conclusion
OGCC wastewater has unstable chemical composition, is represented by large volumes, has low concentrations of pollutants; it is, therefore, expedient to discharge it to ASF for irrigating fodder crops in a natural-technical system with the aim of returning into the environment after additional purification in the natural subsystem and obtaining high yields. The wastewater discharge conditions are determined by water consumption by the crops. As a result of years of research studies, it has been found that wastewater irrigation deteriorates the water-physical properties of soils; therefore, additional agrotechnical measures are needed for their stabilization. Easily soluble salts, including sulfates, accumulate in the soil during the period of irrigation. It is, therefore, necessary to perform salt flushing from the soil in the autumn. This prevents the accumulation of heavy metals in the soil. The effect of wastewater on the groundwater and surface water has not been established. In order to increase sorghum yields in the ASF, the introduction of organic and mineral fertilizers is required.

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