To the problem of the natural environment quality in the oil storage and transshipment facilities zones of influence

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Abstract. The oil storage and transshipment are usually located outside the boundaries of settlements, often on agricultural lands. Environmental pollution will inevitably have a negative impact on land productivity and products quality. The study deals with the problem of atmospheric air and soil quality in the impact zones of objects of storage and oil reloading. It is established that the quality of atmospheric air and soil in the zones of influence of such facilities does not meet the environmental legislation requirements. The main sources of environmental pollution are: the reservoirs of raw materials and final products, pumping station pumps and place of the final product loading in automotive, rail tank cars and other containers. The priority pollutants include hydrogen sulfide, phenol, benzene, ethylbenzene, toluene, xylenes, mercaptans, saturated hydrocarbons C1-C5 and C6-C10. It is established that the greatest threat of the environment pollution is: the imported product low quality; a legacy hardware design of the petroleum products storage and handling, improper waste management. Economic subjects recommended to organize the incoming quality control of oil confirmation of compliance of its members with supporting documents. In terms of improving the hardware design of the technological process is proposed: application of loopback vapors during road tankers discharge, creating a covered loading with an oil overload from storage tanks to rail tank cars, the use of nitrogen cushions or pontoons in oil storage, the use of modern technologies of storage and/or disposal of oil sludge liquidation and sludge pits recultivation.

1. Introduction
Oil and gas industry is leading in the fuel and energy complex of the Russian Federation. In 2018 Russia produced 555.9 million tons of oil and oil condensate. Enterprises of fuel and energy complex of Russia are a vital component of the state economic and social welfare. However, oil production facilities, including the oil storage and transshipment, are the largest source of environmental pollution, especially air and soils. Despite the fact that facilities for the extraction, primary processing, storage and transshipment of oil, are usually located outside the boundaries of settlements, often on agricultural lands, pollution of the environment inevitably has a negative impact on land productivity and quality of products [1,2]. Emissions of oil and petroleum products vapors are due to the natural evaporation with formation of steam-air mixture of oil during its storage at constant temperature and atmospheric pressure, with discharge and loading operations in warehouses of oil and petroleum products in the so-
called "large and small breaths". Sludge pits are a potential source of pollution of both soil and air due to evaporation and migration of hydrocarbons and their derivatives from the surface from the waste layer [3,4]. In general, light oil fractions - the most mobile components of a natural resource - migrate from air to natural waters, soils, or vice versa, which significantly expands the influence zone of the production facility. The total environmental impact from various sources of pollution leads to the fact that the environmental standards established for the enterprise do not ensure the environmental safety of the population [5]. And if large enterprises try as much as possible to adhere to environmental standards and pursue responsible environmental policies [6], small and medium enterprises are far from always ready to bear the burden of environmental protection costs.

2. Problem statement and research methods

The purpose of the study was to evaluate atmospheric air and soil in the zones of objects of storage and transshipment of crude oil influence owned by small owners. Automobile and rail transport are used to deliver oil to consumers at the facilities. The subject of the study was the parameters of the distribution of chemicals in atmospheric air during short-term single emission and long-term multiple pollution of the atmosphere by oil storage and transshipment objects emissions in the zone of their influence and levels of formed concentrations in air and soils. The study was based on complaints from employees of nearby agricultural enterprises about the persistent smell of petroleum products.

The study area was a territory with several oil storage and transshipment facilities operating on the cycle “tank truck - tank - railway tank”. Region - Perm Territory. In close proximity to them are agricultural land and small villages where about 4.2 thousand people live. The most likely sources of negative impact are Enterprise “A” and Enterprise “B”.

Company "A" performs services for reception, storage and loading of crude oil in rail cars. The enterprise "A" has a maximum admissible discharge (MAD) project coordinated by the authorized supervisory authorities and permission to emission of harmful substances into the atmospheric air. There are approved limits for waste disposal. On the territory of the enterprise "A" there exists 26 sources of emissions of pollutants, including breathing valves of the tanks. From sources of the enterprise "A" the environment stands 21 ingredients, including benzo/a/pyrene, manganese and its compounds, hydrogen sulfide, benzene, iron oxide, nitrogen dioxide, nitrogen oxide, sulfur dioxide, soot, xylene, toluene, inorganic dust SiO\(_2\) 20-70%, inorganic dust up to 20% SiO\(_2\), carbon monoxide, gasoline, hydrocarbons limit C\(_{12}\) - C\(_{19}\), methane, a mixture of hydrocarbons limit C\(_{1}\) - C\(_{5}\), the ultimate mixture of hydrocarbons C\(_{6}\) - C\(_{10}\), kerosene and abrasive dust.

Enterprise “B” collects, temporarily stores and ships oil products to automobile and mobile railway vehicles for subsequent shipment to consumers. On the territory of enterprise “B” there are 6 sources of emissions of pollutants, including receiving tanks for oil discharge, oil storage tanks, a loading rack for railway tanks, a pump station, strapping of technological equipment, and a tank for collecting leaks. Enterprise "B" has a permit for the emission of 12 pollutants into the atmosphere from stationary sources of pollution, including hydrogen sulfide; saturated hydrocarbons C\(_1\) - C\(_{5}\); saturated hydrocarbons C\(_6\) - C\(_{10}\); benzene; xylene; toluene; nitrogen dioxide; nitric oxide.

It has been established that the main environmental hazards are emissions of the industrial region into the atmospheric air, primarily: benzene, xylene, toluene, C\(_6\) - C\(_{10}\) saturated hydrocarbons, C\(_1\) - C\(_{5}\) saturated hydrocarbons, and hydrogen sulfide.

The study included:

- analysis of actual emissions compliance of enterprises with permits and regulatory documents;
- oil quality analysis;
- oil discharge and loading work schedules analysis;
- sources of oil storage and transshipment facilities emissions, settlements (points for monitoring air quality) spatial reference;
• assessment of atmospheric air quality parameters at the border of the sanitary protection zone and at the nearest points of agricultural use during various technological operations at production facilities.

The locations of the sources of emissions, the points of atmospheric air sampling were plotted on an electronic map of the territory.

Calculations of the dispersion of pollutants in the air were carried out by the Federal Scientific Centre for Medical and Preventive Health Risk Management Technologies taking into account actual emissions.

Oil quality analyses were performed based on the protocols and conclusions of the accredited laboratory of PermNIPIneft LLC. The transported and stored oil quality was investigated using chromatography-mass spectrometric analysis. A total of 8 oil samples were examined for 15 indicators.

Air quality assessment was carried out according to field studies by the Centre for Hygiene and Epidemiology in the Perm Territory Federal State Health Institution, Perm Centre for Hydrometeorology and Environmental Monitoring, Federal Scientific Centre for Medical and Preventive Health Risk Management Technologies.

In total, more than 50 atmospheric air samples were taken during the study period. Samples were taken during the process of oil discharge and loading. The sampling program included the determination of one-time and daily average concentrations of impurities in the atmosphere.

In periods when there was no oil overload, air samples were taken, which were qualified as “background”.

Air samples were examined for components that are characteristic of emissions from oil production and primary oil refining facilities and have the most pronounced negative effects on public health: hydrogen sulfide, phenol, benzene, toluene, ethylbenzene. At the time of the study, none of the laboratories had accreditation and the method used to determine mercaptans in the air, which did not allow to obtain quantitative characteristics of atmospheric pollution with these impurities. At the same time, the presence levels of aromatic hydrocarbons, hydrogen sulfide and phenol were considered as indicators of oil pollution.

The content of pollutants in atmospheric air was determined using gas and high performance liquid chromatography methods approved in through the established procedure and included in the register of measurement methods of the Russian Federation.

3. The main results
Analysis of the technological process, storage, and reloading of the oil showed that the main sources of polluting substances hit in atmospheric air are: reservoirs of raw materials and final products (the release is carried out through the breathing valves), pumps pumping station (emission is through looseness of joints), and the final product place of loading in automotive, rail tank cars and other containers.

The analysis of permits showed that the Company "A" emits substances that do not have a MAC and approximate safe level of impact (ASLI): hydrocarbons C1-C5, hydrocarbons C6-C10. Development of MAC or ASLI for hydrocarbons C1-C5 hydrocarbons C6-C10 by the enterprise is not carried out. The company has not developed a draft justification of the sanitary protection zone. The nearest company residential building is located at a distance of 450 m and falls within the boundaries of the regulatory sanitary protection zone of 500 m.

According to the statistical reporting form 2-TP air pollutant emission enterprise "B" for 2017 was exceeded by 2.4 times. The main contribution in excess of maximum-permissible emissions contribute: hydrogen sulfide, hydrocarbons limit C1-C5, hydrocarbons limit C6-C10, benzene, xylene, toluene, (excess 2.3-2.6 times). If when it is not possible to achieve maximum admissible discharge (MAD) the company has not provided measures and specific time frames to reduce or eliminate this pollution by process changes, the capacity reduction or conversion of the enterprise, as well as not informed the local authorities and (or) state authorities of the violation of regulations in the field of environmental protection due to the impact of the enterprise's activity and proposals on elimination of such violations.
An analysis of the quality of oil established that a sample of oil taken from a tanker transporting oil for Enterprise “B”, being a marketable oil, belongs to the class of sulfur oils of the 1st type, 1st group, and 3rd fuel. The content of mercaptans in oil is 89.97 ppm (with a declared level of less than 0.02 ppm), the concentration is more than 40 times the content of hydrogen sulfide. Mercaptans are not included in the design of maximum permissible emissions and emission permits. It has been proved that the calculated zone of atmospheric air pollution by mercaptans captured part of the residential area, unregulated emissions of mercaptans, substances with a low threshold for smell (the threshold for smell for methyl mercaptan is $2 \times 10^{-5}$ mg / m$^3$, for ethyl mercaptan - $1.6 \times 10^{-4}$ mg / m$^3$), could lead to the appearance of an unpleasant odour in the nearest residential development and complaints of residents.

The calculations made taking into account the actual emissions carried out established:

- the atmospheric air pollution zone by mercaptans (the options for the ratio in the methyl mercaptan-ethyl mercaptan mixture 1:1 and 7:3 are considered) significantly exceeds the size of the established sanitary protection zone of Enterprise “B”. Ground concentrations in agricultural areas and in the nearest residential buildings during technological operations for oil discharge and loading exceed permissible standards from 2 to 10 times;
- with winds of the south-west, north and north-west direction, agricultural territories and agricultural workers, as well as residents of one of the villages (about 3.5 thousand people) can be negatively affected;
- an area with a radius of more than 600 m around objects is negatively affected under calm conditions, when dispersion of impurities in the atmosphere is minimal and pollution forms in the surface layer of the atmosphere.

By instrumental studies, it was proved that the procedure for discharging and loading oil products was accompanied by an increase in the level of air pollution even with the normative quality of refuelling oil and in compliance with the approved MAD standards. In the absence of oil refuelling in the industrial district, air pollution was minimal: concentrations of hydrogen sulfide, phenol, benzene, ethylbenzene, toluene and xylenes were recorded below the threshold for determination or not higher than 0.3 MAC. When performing oil transshipment operations (up to 35 minutes) and within 25-30 minutes after their completion, concentrations of pollutants were recorded at different points on the border of the sanitary zone and in the territory of nearby agricultural land:

- phenol - an excess of the MAC in 45.4% of samples to 5 MAC o. t.;
- hydrogen sulfide - excess of MAC in 2% of samples to 1.1 MAC;
- benzene (at one of the points) - an excess of 21.4% of the samples to 2.4 MAC o. t.;
- ethylbenzene - excess of MAC in 42.9% of samples to 4.4 MAC o. t.

Xylene excesses were also observed in 0.4% of samples up to 4.4 MACo.t.; according to formaldehyde in 50% of samples up to 1.5 MAC o. t.

In the course of the analysis of the mode of technological operations for oil discharge and loading, it was found that when receiving tanks from 8 to 18 times a day, on average, the discharge and loading procedure is carried out 11 times a day. Thus, the supposedly short-term rise in pollution during the day is repeated several times. Even with the observance of the standards (maximum permissible concentration) during one technological procedure (20-30 minutes), the actual frequency of “discharge-loading” operations (from 8 to 18 times per day) leads to atmospheric pollution of 5-6 hours per day with a number of impurities at a level that does not meet the MAC d.a. At an average frequency of 12 operations / day, in the air at the border of the sanitary protection zone of the enterprise, concentrations were formed: benzene up to 1.2 MAC d.a., phenol up to 2.4 MAC d.a., formaldehyde up to 2.8 MAC d.a. The data confirmed that the establishment of permissible emissions for the facility according to the MAC o.d. It did not ensure the safety of the population under prolonged exposure.
There were no violations of the quality of natural waters and soils outside the sanitary protection zone.

The research allowed to prove that the greatest threat to the environment when the transfer and storage of oil are: quality of the imported product at the technological operations "delivery of the product to the place of storage"; hardware design procedures for storage and handling of petroleum products (lack of system tightness draining-filling), the frequency of the operation "drain-loading of petroleum products".

As effective measures are proposed for the application of best achievable technologies in the transfer and storage of oil. To minimize the release of hydrogen sulfide, aromatic hydrocarbons, phenol, etc. is achieved by using a system of connection of vapor during the execution of technological procedures discharge from road tankers (the effectiveness of the event – up to 85-90%), creating a covered loading with an oil overload from storage tanks to rail tank cars (the effectiveness of the event – up to 80%) and nitric pillows, equipping tanks with pontoons, floating roofs (a measure of efficiency in reduction of losses - 80-95%), colouring the outer surface of the tank coatings with low emissivity (reduction of losses up to 27-45%); sealing reservoirs and pressurized cups (reduction of losses up to 30-50%); sealing the loading in the vehicle using the capture and vapor recovery of oil from reservoirs (reduction of losses up to 80-90%) [7].

The implementation of enterprise continuous incoming quality control of oil imported from the field and confirmation of the conformity of its composition accompanying documents results in the elimination of an overload of oil with a high content of hydrogen sulfide and mercaptans.

4. Conclusion
Analysis of the situation in the area of placing of storage objects and oil reloading showed that the oil storage and transhipment have a negative impact on atmospheric air, to a lesser extent, on natural water and soil.

Violation of the safety standards are recorded at the border of sanitary-protective zones of the investigated facilities for the storage and reloading of petroleum, including agricultural lands and in nearby settlements.

The main sources of hit of polluting substances in atmospheric air are: reservoirs of raw materials and final products (the release is carried out through the respiration valves), pumps pumping station (emission is through looseness of joints), and the place of loading of the final product in automotive, rail tank cars and other tanks, slurry pits.

The priority factors of air pollution in the zone of objects of storage influence and oil loading include hydrogen sulfide, phenol, benzene, ethylbenzene, toluene, xylenes, mercaptans, aliphatic hydrocarbons $C_1-C_5$ and $C_6-C_{10}$.

MACd.a. on the border of sanitary-protective zone is not reached even when compliance with the criterion MACo.d. values of MAD. The reason is the high frequency of technological operations at the oil loading-unloading. The greatest danger to air quality and human health represent the quality of the imported product (high content of sulfur compounds), hardware design procedures for storage and handling of petroleum products (low degree of system tightness draining-filling), the frequency of execution of the technological operation "drain-loading of petroleum products".

Reducing the negative impact of oil storage and transshipment facilities on atmospheric air and, consequently, improving its quality is achieved by a system of measures aimed at applying the best achievable technologies at the stages of the technological process and tightening the input control of oil.

Minimization of environmental risks arising from the oil storage and handling is possible with the improvement of the hardware design of tanks: the use of a vapor loop system when performing the technological procedure for discharging from car tanks, the creation of covered loading racks when loading oil from tanks to railway tanks, the use of nitrogen pillows, tank equipment pontoons floating roofs; sealing reservoirs and pressure vent valves, sealing filling vehicles with the use of a trapping and recovery unit for oil vapor from reservoirs.
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