A NUMERICAL MODEL STUDY OF CHEMICAL POLLUTION MIGRATION IN GROUNDWATER NEAR INDUSTRIAL WASTE STORAGES LOCATED IN RIVER VALLEYS

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ABSTRACT

The paper deals with the use of the "memory effect" of a groundwater aquifer for the retrospective estimation of the sources of groundwater industrial pollution, and in order to obtain a reliable estimate of their impact on groundwater and surface water. It is shown that combination of the mathematical modelling with the analysis of the age of underground waters during the calibration of the geomigration model makes it possible to significantly refine the parameters of pollution sources, obtain reliable modern aureoles of groundwater contamination, and thereby increase the reliability of predictive calculations.

Key words: Retrospective estimation; sources of groundwater industrial pollution; mathematical modelling; age of groundwater; current and forecast aureoles of groundwater pollution.

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1. INTRODUCTION

1.1. The Relevance of the Problem

The problem of the quantitative estimation and prediction of groundwater pollution spreading from shallow-ground waste repositories is very pressing throughout the world. Virtually every large settlement has waste deposits, industrial or household. Commonly, waste deposits are located in river valleys, which are areas of polluted groundwater final discharge. First of all, this refers to the deposits created dozens of years ago, i.e. in those times when the issue of the deposit’s impact on the environment received almost no attention. Modern challenges require a quantitative estimation of the waste deposits’ impact on the environment, including an estimation of the impact on groundwater and surface water. At that, one of the important issues is the circumstantiation of intensity of the contaminants’ input from the deposits into the groundwater, the natural barrier that detains the flow of contaminants from the deposits to the surface water. The complexity of estimating waste deposits as a source of groundwater contamination is related to the lack of information about the waste deposits’ operation during their life cycle; the duration of which can be dozens of years.

1.2. State of the Art

Despite the apparent urgency of predicting the storage reservoirs’ impact on groundwater and surface water, comparatively little research has been done on the estimation of storage reservoirs as sources of natural waters contamination. The works of domestic and foreign scientists, devoted to this issue, concern the hydrofiltration and geomigration characteristics of ground flows [1–7]. At the same time, much attention is paid to mathematical modelling, geoinformation systems and databases in hydrogeology [6]. Considerable attention is paid to modelling [1,5] and migration of radionuclides [4]. Kletskina and Oschepkova [8], in particular, considered migration of nitrogen compounds in groundwater from storage reservoirs.

Kuvaev and coauthors [9] considered the geomigration model of the area of groundwater discharge into the river, with groundwater formed near the tailings pond and having mineralization up to 55 g/l. The model is implemented using the SEAWAT-2000 program. It is shown that the density effects contribute to the conservation of the contamination source in the aquifer and make the mass flow of toxic pollutants stable for a long period of time.

The study performed by Lyubimova and coauthors [10] deals with infiltration of saturated brine into adjacent groundwater and surface water bodies from the liquid waste storage located in the Verkhnekamsk deposit of potassium and magnesium salts (Perm Krai, Russian Federation). This storage contains a highly concentrated brine of potassium, sodium and magnesium salts. The process of distribution of the brine from an unprotected bottom of the storage in the upper layers of adjacent rocks – due to the violation of waterproofing associated with the destruction of the insulating substance during the long-term operation of the storage facility – was numerically and analytically investigated. The time of the setting up of the stationary concentration profile, the time of the impurity advance to the nearest water reservoir, and the concentration value at the point of entry into the reservoir were estimated, without regard to and with regard to weak adsorption of contamination in the soil. With the help of three-dimensional numerical modelling, the main stages of the impurity distribution have been traced. In the mentioned works, the quantitative assessment of the pollution sources on the basis of monitoring data has not been provided.

Lawrence and Bailey [11] indicate that monitoring of the environment is an important tool for detecting changes in the biosphere. The need for environmental data has led to the establishment of national programs for monitoring atmospheric deposition, composition and
growth of forests, and chemical formulas of lakes and streams in areas prone to acid deposition. However, no effort was made to monitor changes in soils despite their importance for agriculture, forests, wetlands and water quality.

The lack of attention to soil monitoring may be partly related to issues concerning its feasibility. Soil changes are too slow to ensure the necessary monitoring, and territorial variability is too great for detecting changes. However, over the past 15 years, changes in soil chemistry have been measured by repeated sampling of different soil types in eastern North America and in Europe at the sampling interval equal to 5 years. As the number of studies increases, it is also recognized that sampling and analysis methods are not always compatible, and archiving methods are not sufficiently developed.

Seismic interferometry is used to perform continuous seismologic records covering 5 days and more than 2,200 stations in the Valhall seismic unit in the Norwegian North Sea. The main overtone Scholte waves are extracted by mutual correlation. Ambient seismic noise tomography using the vertical component of this dense array gives group velocity maps of the fundamental mode Scholte waves with high reliability in just 24 hours of recording. This reliability allows daily continuous monitoring of the subsurface layer. Such monitoring can detect changes associated with production over a long period of time (from several months to several years), and in short-term scale (from several days to several weeks) can be useful for early detection of such problems as migration gases and liquids. Velocity maps are tested by comparing them with maps representing changes in state and obtained from independent controlled sources [12].

Subsurface approaches to monitoring CO₂ content in the soil are gaining importance for studies of terrestrial carbon. When using subsurface methods in combination with the diffusion model in order to determine CO₂ generation, it is required to estimate the effective diffusion of soil gas. Risk et al. [13] describe a new membrane probe and continuous flow system for measuring soil gas diffusion in situ. Laboratory trials confirm the effectiveness in the entire range of CO₂ diffusion in natural soils. Field tests were conducted over the soil moisture range, 8 soil types were artificially hydrated for 3-7 days. These soils were a number of texture classes from eastern Nova Scotia, Canada. The absolute values of the diffusion coefficient, as well as the rate of the diffusion decrease in the conditions of increasing moisture content in the soil, are usually very different from the predictions of the model. When applied to underground CO₂ monitoring at two sites, the specific diffusion measurements significantly increased the accuracy of CO₂ production estimates. There was a consistent and close correspondence between the calculated CO₂ production profile and the soil CO₂ surface flux (measured independently). The estimates of the subsoil CO₂ production, obtained by in situ diffusion measurements, allow detailed resolution of the vertical profile over a long period of time. Most of CO₂ was formed at shallow depths, but periodic contributions from deeper depths were important, especially at the end of the growing season [13].

As Jandl et al. [14] note that to meet human needs for ecosystem services provided by soil, reliable data on global soil resources are required for sustainable development. The pool of soil organic carbon (SOC) is a key indicator of soil quality, as it influences on the basic biological, chemical and physical functions of the soil, such as the cycling of nutrients, pesticides, and water retention, as well as soil structure maintenance. However, information about the SOC pool and its temporal and spatial dynamics is not balanced. Even in well-studied regions which pay attention to environmental problems, information on soil carbon is incompatible. A number of activities aimed at collecting global soil data are underway. However, different approaches to soil sampling and chemical analysis make regional comparisons highly uncertain. The up-to-date procedures have not provided a reliable estimation of the total SOC pool, partly because the available knowledge is focused on clearly defined upper soil horizons, and the contribution of the subsoil to the SOC reserves is less taken into account. It is even more difficult to quantify
the changes in the SOC pool over time. SOC consists of various amounts of labile and recalcitrant plant molecules, as well as molecules of microbial and animal origin, which are often determined operationally. A comprehensively active community of soil experts should agree on geodetic survey protocols and laboratory procedures for reliable estimate of the SOC pool. The existing long-term environmental research sites, where SOC changes and basic mechanisms are investigated, are potentially the basis for regional, national and international SOC monitoring programs [14].

Kuras et al. [15] carried out a full-scale field experiment using four-dimensional (three-dimensional time lapse) cross-hole electrical resistivity tomography (ERT) to monitor the simulated leakage of the subsurface layer at the legacy nuclear waste site, Sellafield Site, UK. The experiment was the first application of geoelectric monitoring in support of decommissioning at the UK nuclear licensed site. Other studies on radioactive waste have also been carried out [16,17].

Recommended guidelines for monitoring soil changes have been given by McKenzie et al. [18].

An overview of various current monitoring methods for CO\textsubscript{2} storage is given. Methods are divided according to their applicability for monitoring three different areas: atmosphere and surface area; overburden (including faults and wells); reservoir with its seals. Another division can be done with respect to time, that is, the first monitoring during the injection and storage process and subsequent monitoring over a long period of time (after abandoning the field). In this perspective, the importance of characterization and monitoring prior to injection is considered [19].

Radiation monitoring is of particular importance [20–22]. Because of the increased environmental awareness in most countries, each utility that owns a commercial nuclear power plant was supposed to have a response plan both on-site and off-site since the 1980s. A radiation monitoring network, considered as part of an emergency response plan, can provide information on the radiation dose emitted by a nuclear power plant in a regular operating period and/or abnormal measurements in an emergency. Such monitoring information can help field operators and decision-makers to provide accurate responses or make decisions to protect public health and safety. The purpose of this study is to perform complex modelling and optimization analysis, which considers the relocation strategy for a long-term regular off-site network at a nuclear power plant. The aim of planning is to reduce the existing monitoring network but to support its monitoring capabilities as much as possible. The control sensors considered in this study include thermoluminescent dosimetry (TLD) and air probes system (AP) simultaneously. It is designed to detect a constant concentration of radionuclides, frequency of violation, and possible population exposed to long-term influence in the surrounding area, while it can also be used in case of accidental release. With the help of a calibrated model of Industrial Source Complex-Plume Rise Model Enhancements (ISC-PRIME) tracking the possible diffusion, scattering, transfer, and transformation of radionuclides in the atmospheric environment, a multicriterial estimation process can be used to provide screening of the monitoring stations for a nuclear power plant located in the Hengchun Peninsula, southern Taiwan. In order to take into account many goals, Chang and coauthors [21] have calculated the preference weights for a linear combination of objective functions leading to decision-making with an impact evaluation in the context of optimization. The study contains proposals aimed at narrowing the set of scenarios that decision-makers should consider in the relocation process [21].

Avwiri et al. believe that the presence and concentration of radionuclides can be the result of the natural and human activity. In their study [20], the characteristics and differences between soil, sedimentary and water-specific activities of long-lived radioactive elements (LLREs) were
studied. Gamma spectroscopy was used to measure the concentration of LLREs along the Mini Okoro/Oginigba mine, Port Harcourt. Specific activities of three selected LLREs were obtained. A correlation analysis was performed to study associations between specific activities on different substrates. A strong and significant negative correlation was found between the specific activities of water $^{40}$K and the soil $^{232}$Th ($r = -0.721$, $p < 0.05$); water $^{238}$U and soil $^{238}$U ($r = -0.717$, $p < 0.05$), and water $^{40}$K and sediment $^{238}$U ($r = -0.69$, $p < 0.05$). A comparison using the Mann-Whitney U test showed that the soil and sediment were similar in their specific activity with Z-values of -0.408, -1.209 and -1.021 ($p > 0.05$) for $^{40}$K, $^{232}$Th and $^{238}$U, respectively. The concentration of solid samples (soil and sediment) differed from liquid (water) samples. These characteristics can be attributed to some specific underlying factors. To understand these, more research is needed [20].

The paper by Mladenov et al. [22] identifies important components and describes safe methods for implementing radiation protection and radioactive waste programs, as well as their optimization at the Nuclear Scientific Experimental Center with research reactor IRT at INRNE-BAS. It covers facilities and personal protective equipment and organizational issues related to the constant monitoring of the site. The reactor is being reconstructed, and thus, the study also considers the measures used for radiation monitoring of the environment and the work area and aimed at limiting the radiation exposure of personnel as well as compliance with international best practices related to environmental and public radiation safety requirements [22].

Greenhouse gases are not ignored, and they have found their place in the "underground kingdom". Fay and coauthors [23] note that the cost of monitoring greenhouse gas emissions at the landfill sites is a matter of serious concern to the regulatory bodies. The current monitoring procedure is recognized as labor-intensive, requiring agency inspectors to visit the borehole perimeter and manually measure gas concentrations with the help of expensive hand tools. The authors demonstrated a cost-effective and efficient system for remote monitoring of underground methane migration and carbon dioxide concentration. Based solely on the autonomous sounding architecture, the proposed measuring platform was capable to perform complex analytical measurements in situ and successfully transmit the data remotely to the cloud database. A web-based tool was developed to present the data to the party concerned. The authors related their experience in implementing this approach for a period of 16 months.

Gas constituents of the solid municipal waste deposits have acquired special interest in the context of monitoring. Nwaishi [24] notes that garbage dumps are areas where biogenic gases (known as "landfill gases") are produced. They are generated in the subsoil layer during the buried waste decomposition. The gas consists of 60% methane (CH$_4$) and 30% carbon dioxide (CO$_2$), with a small amount of other organic vapors and gases. The share of these compounds, as well as the total quantity and gas production rate, depends on the stage of decomposition, operation conditions, density, composition and age of the buried waste. The author reminds that the release of these gases and their constituents into the atmosphere has certain harmful consequences for human health and the environment, such as carcinogenicity and mutagenicity, air pollution, corrosion of monitoring facilities, fires and explosions. For this reason, integrated monitoring of landfill gas has become a common practice in Europe and North America. Subsurface monitoring of methane production is one of the main components of the integrated landfill gas monitoring programs due to the hazards associated with methane’s subsoil production and migration. Although the integrated approach has succeeded in reducing the dangers associated with explosions, their scale of operation remains a limiting factor. For example, the existing practice of subsoil landfill gases monitoring, which includes the installation of gas monitoring probes or wells, may be ineffective if it is implemented in large disposal areas for the creation of forest vegetation. This limitation is manifested in the
remediation of open pit mines in Alberta, Canada, where residual materials from the extraction of oil sands (overburden), containing fragments of concentrated oil sands (lean oil sands), are used to fill the open quarries. Oil degradation under anaerobic (no oxygen) conditions results in the production of methane gas and other volatile organic compounds (VOCs).

Radon is considered as well. The work by Ulyanov [25] substantiates the use of innovative earthquake warning system at the Bushehr-1 nuclear power plant in the Islamic Republic of Iran. The proposed warning system is based on the comprehensive monitoring of radon in order to improve safety during the nuclear power plant operation. The regulation on the application of this system in the context of subsoil monitoring at Bushehr-1 should be fixed in the official instructions. This system can be used as part of the seismic monitoring of other nuclear power plants sites in zones with increased seismicity.

On-site Subsoil Condition Monitoring (OSCM) at the enterprises of the ROSATOM State Atomic Energy Corporation is the most important issue. OSCM Standard establishes general recommendations for conducting on-site monitoring of the subsurface (to a depth of 100 m) at the stage of engineering survey for the construction of the ROSATOM’s nuclear facilities, as well as for providing services to the organization operating nuclear facilities at all stages of the site’s life cycle, including operation, reconstruction, expansion, decommissioning, and liquidation.

OSCM is an integral part of the environmental monitoring carried out during engineering and environmental surveys, as well as during the nuclear facilities operation. It is established by the Standard [26] and is implemented at the ROSATOM State Corporation [27,28].

2. OBJECT, PURPOSE AND OBJECTIVES OF THE STUDY

The objects of the study are industrial storage reservoirs located in the valley of the Vyatka River in the outskirts of the Kirovo-Chepetsk city, Russia (Figure 1).
The distance from the waste storage facilities to the riverbed of the Vyatka River, which is a drinking water supply source, is 2-3 km.

The climate of the region is continental with a relatively hot summer and a long harsh winter. The average annual air temperature is 1.8 °C. The study area is in the zone of excessive moistening – the average annual precipitation during a multi-year period is about 530 mm and prevails over the total evaporation (about 300 mm).

Groundwater is confined to alluvial deposits of the Vyatka River – to the floodplain and terrace above the floodplain (Figure 2). The hydrogeologic section of alluvial deposits of the Vyatka River valley within the floodplain development, as well as the first terrace above the floodplain, is characterized by a two-layered structure (Figure 3). The upper layer is formed mainly by fine- and medium-grained occasionally clayey sands with interlayers of loam with a total thickness of 5-7 m. The lower layer is medium- and coarse-grained sands with the inclusion of gravel-pebble deposits with a total thickness of 3-5 m. The regional relatively waterproof layer is the stratum of heavy plastic clays of Permian age underlying the alluvial deposits.

Figure 2. Schematic hydrogeological map of the studied territory
The formation of the groundwater flow occurs mainly due to infiltration of atmospheric precipitation. Groundwater receives additional technogenic recharge in the areas of the water storage reservoirs. Groundwater discharges into rivers, oxbow depressions (seasonal hydraulic connection with rivers), as well as by means of evaporation from the groundwater table and transpiration.

The operation of storage facilities started in 1956, but information about the operating mode and the content of chemical substances in the storage facilities that determine the pollution of groundwater is episodic. Monitoring of groundwater at the facility to obtain a quantitative assessment of the groundwater pollution spread has been carried out since 2009. Thus, monitoring data characterize only the current state of groundwater pollution.

The hydrogeochemical conditions of the studied territory are determined by a complex of natural and technogenic factors. Outside the zone of anthropogenic impact, the groundwater of Quaternary sediments is fresh, transparent, colorless and odorless, the mineralization varies from 0.01 to 0.5 g/l, pH 5.3-8, the main cations are Ca$^{2+}$, Na$^+$, Mg$^{2+}$, the main anion is HCO$_3^-$.

The main sources of groundwater pollution in the territory under consideration are storage reservoirs: three sections of the sludge collector (Nos. 1, 2, 3), and two sections of the tailings pond for chalk (Nos. 5, 6). Sludge storage sections are used for cleaning of the enterprise’s neutralized sewage waters from slimes and suspended solids before discharging them into the Yelkhovka River. The tailings sections for chalk serve for the storage of chalk formed during the processing of apatite; the chalk enters the tailing pond by hydrotransport along with technological waters. As a result of the imperfection of the sludge collector’s and tailing pond’s waterproofing, pollutants enter the underground water.

These pollution sources are characterized by different chemical composition of the liquid phase. In the sections 1-3 of the sludge collector, the main chemical components are ions Cl$^-$, SO$_4^{2-}$, Ca$^{2+}$, Na$^+$, and in sections 5-6 of the tailing pond for chalk – NO$_3^-$ and NH$_4^+$. The concentrations of pollutants in sections 5-6 of the chalk tailing ponds were determined on
irregular basis, at that, during their operation, the content of pollutants in these sections varied greatly (Table 1).

**Table 1.** The main pollutants content in the groundwater pollution sources (monitoring data)

<table>
<thead>
<tr>
<th>Sludge storage</th>
<th>Tailings pond for chalk</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Section 1</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>400</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>3,800</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>2,000</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>3,900</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>n/a</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>n/a</td>
</tr>
</tbody>
</table>

In the groundwater of the area adjacent to the sludge storage, concentrations of Cl$^-$, SO$_4^{2-}$, Ca$^{2+}$ ions, significantly exceeding the standards for drinking water, were found. In the area adjacent to the tailings pond, high concentrations of NO$_3^-$ and NH$_4^+$ ions were found.

Pollutants from various sources spread with the flow of groundwater, and they mix at the mouth of the Yelkhovka River (near its influx into the Prosnol Lake); as a result, downstream groundwater contains all of the above contaminants.

Based on the data of hydrogeochemical monitoring of groundwater and surface waters, a schematic map has been generated. It characterizes the groundwater contamination in the vicinity of the industrial waste storage facilities (Figure 4). As can be seen from the presented data, considering the total mineralization as the main indicator of groundwater pollution, it can be concluded that the main source of groundwater pollution is the tailings pond for chalk, near which the salinity of underground water reaches 78 g/l.
Figure 4. The map of the chemical composition of groundwater in the study area (according to the data of the trials in 2009-2012)

The ratio of the ammonium ion and nitrate ion contents is shown in Figure 5. In wells located near the tailings pond and in the liquid phase of the tailings pond (sections 5 and 6), the content of ammonium and nitrate nitrogen is practically the same.
In wells near the sludge collector (sections 2 and 3), the content of both forms of nitrogen is two orders of magnitude lower, hence, the tailings pond for chalk is currently the main source of nitrate-ammonium pollution.

In the mixing zone, the content of nitrate nitrogen is higher than that of ammonium. Together with the sodium ion observed in groundwater of this zone, this can testify to a possible source of nitrate-sodium contamination that existed in the past.

A good correlation between the concentration of NO$_3^-$ and the salinity level (Figure 6) is observed for wells located near the tailings, the liquid phase in the tailings and mixing zone wells. This fact suggests that the main source of pollution of underground water is filtration of tailings chalk.
Figure 6. The ratio of the nitrate ion concentration and total mineralization in the tailings pond for chalk and in water of wells (according to the 2010-2012 test data)

Taking into account the good correlation between the mineralization and the main indicators of chemical contamination of groundwater, in the future, the groundwater total mineralization can be considered as a generalized indicator of groundwater pollution.

Waters of sections 1-3 of the sludge collector are characterized quite well by the test data. As noted above, at present, sections 1-3 are not the sources of nitrate-ammonium pollution of groundwater. At the same time, the waters of sections 5-6 of the tailings pond for chalk, which are the main sources of pollution of groundwater by nitrogen compounds, are characterized by insufficient monitoring data.

On the basis of the monitoring of groundwater levels and the content of the pollution’s main indicators in groundwater, it is necessary to obtain a reliable estimate of the sections 5 and 6 of the tailings pond as the sources of groundwater contamination with nitrogen compounds, as well as to estimate the current groundwater pollution aureoles and forecast the discharge of pollution into the Vyatka River for the near and distant future.

3. THEORETICAL ANALYSIS

Geofiltration and geomigration modelling was performed to quantify the monitoring data, assess the sources of groundwater pollution and predict the distribution of the pollution aureole.

The main mechanism that determines the migration of chemicals within the aquifers of the zone of active water exchange is portage with a filtration flow [5]. The differential equation of filtration with allowance for dense convection has the following form [4]:

$$\nabla \cdot \left[ \rho_0 \mu K_0 \left( \nabla h_0 + \frac{\rho - \rho_0}{\rho_0} \nabla z \right) \right] = \rho S_{z,0} \frac{\partial h_0}{\partial t} + \theta \frac{\partial p}{\partial t} \frac{\partial C}{\partial t} - \rho_s q_s$$

(1)

$$h_0 = \frac{p}{\rho_0 g} + z$$

(2)

where

$p$ is the hydrostatic pressure [ML$^{-2}$ T$^{-1}$];
\( \rho_0 \) is the water density \([\text{ML}^{-3}]\) at the reference concentration of dissolved substances and reference temperature (hereinafter, 1000 kg/m\(^3\) was used in calculations);

- \( g \) is the gravitational acceleration \([\text{LT}^{-2}]\);
- \( z \) is the height of the point above the plane of reference \([\text{L}]\);
- \( \mu \) is the dynamic viscosity \([\text{ML}^{-1} \text{T}^{-1}]\);
- \( K_0 \) is the tensor of the filtration coefficient \([\text{ML}^{-1}]\);
- \( h_0 \) is the equivalent head \([\text{M}]\) of fresh water;
- \( S_{s,0} \) is the elastic capacity \([\text{M}^{-1}]\) of fresh water;
- \( t \) is the time \([\text{T}]\);
- \( \theta \) is the porosity \([-]\);
- \( C \) is the concentration of the solution \([\text{ML}^{-3}]\);
- \( q_s' \) is the source or sink \([\text{T}^{-1}]\) with fluid density \( \rho_s \).

The differential equation for the migration of dissolved substances with allowance for dense convection has the following form [4]:

\[
\left( 1 + \frac{\rho_b K_d^k}{\theta} \right) \frac{d(\theta C^k)}{dt} = \nabla \cdot (\theta D \cdot \nabla C^k) - \nabla \cdot (q C^k) - q_s' C_s^k \tag{3}
\]

where

- \( \rho_b \) is the density of the soil skeleton \([\text{ML}^{-3}]\);
- \( K_d^k \) is the distribution coefficient of the species \( k \) \([\text{L}^3 \text{M}^{-1}]\);
- \( C^k \) is the concentration of the species \( k \) \([\text{ML}^{-3}]\);
- \( D \) is the tensor of the hydrodynamic dispersion coefficient \([\text{L}^2 \text{M}^{-1}]\);
- \( q \) is the filtration velocity vector \([\text{LT}^{-1}]\);
- \( t \) is the time \([\text{T}]\);
- \( \theta \) is the porosity \([-]\);
- \( C \) is the concentration of the solution \([\text{ML}^{-3}]\);
- \( C_s^k \) is the source or sink \([\text{ML}^{-3}]\) of the concentration of the species \( k \).

There has been an assumption that the groundwater density depended only on the mineralization and was determined by a simplified expression:

\[
\rho = \rho_0 [1 + \beta_{TDS} TDS] \tag{4}
\]

where \( \beta_{TDS} \) \([\text{L}^3 \text{M}^{-1}]\) is the empirical coefficient accepted, upon the literature data, as \( 6.4 \times 10^{-4} \text{ m}^3/\text{kg} \) [7]; \( TDS \) is the total dissolved solids, or groundwater total mineralization \([\text{ML}^{-3}]\). The value \( \rho_0 \) is assumed to be 998 kg/m\(^3\) (as for fresh water). In modelling, the influence of pressure and temperature variations on groundwater density and viscosity has not been taken into account.

The geofiltration flow mode was assumed to be stationary during the simulation. It was assumed that the groundwater mean annual levels and level gradients correspond to the average values of the levels and gradients of the levels obtained from the data of regime observations that have been performed at the research site since 1968.

The spatial structure of the geofiltration flow was assumed to be a three-dimensional one.

The substantiation of the hydrogeological stratification of the section, as well as the geofiltration and geomigration parameters of the water-bearing sediments, is given in [4–6].

The calculated model of the aquifer is represented by 6 calculated strata. Strata 1-3 represent...
surface clay deposits of the floodplain facies and the strata 4-6 represent sandy-gravel deposits of the alluvia channel facies of the Vyatka River (Figure 7). The thickness of the surface deposits and the water-bearing deposits of the channel facies were taken in accordance with the geological model of the groundwater aquifer developed earlier [4–6].

For calculations, a regular grid with cell sizes of 25×25 m was adopted.

![Figure 7. Model stratification of the hydrogeological section of Quaternary sediments](image)

The filtration properties of the water-bearing sediments are characterized by the data of experimental pumping and express-fillings performed in 2009-2010, and of a complex hydrogeological survey (1:50000 scale) performed in 1968.

Possible variations in the change in the module of infiltration recharge and evapotranspiration for zones 1 and 2 were previously estimated on the basis of the modelling of moisture transfer in the aeration zone [2]. For all zones, the infiltration recharge module was selected during the calibration of the geofiltration model.

The calibration of the geofiltration model is described in works of Kuvaev and coauthors [5,6]. Based on the model results, a map of hydroisohyposes of the groundwater flow is shown in Figure 8. On the map, the local area of anthropogenic groundwater feeding in the vicinity of waste storage facilities is clearly distinguished.
According to the model data, the total rate of the geofiltration flow within the studied area is 7,568 m$^3$/day. The main source of the geofiltration flow supply is the infiltration of atmospheric precipitation (6,534 m$^3$/day). Filtration losses from water bodies and streams amount to 1,034 m$^3$/day. The evapotranspiration of groundwater is estimated to be 1,551 m$^3$/day. The subaqueous discharge of groundwater into rivers and reservoirs of the Vyatka River floodplain, as well as directly into the Vyatka River, in total amounts to 6,016 m$^3$/day.

The total supply of water from the waste storages located at the floodplain of the Vyatka River is 1,317 m$^3$/day, which is about 17% of the total rate of the geofiltration flow.

**Figure 8.** Hydrodynamic scheme of groundwater flow (based on model results)
The porosity of the water-bearing sediments was determined from the data of geomigration observations and was 0.2 for the surface and water-bearing strata. Geomigration observations have also shown that the distribution coefficients for the chloride ion, nitrate ion and ammonium ion can be taken equal to zero, i.e. the migration of chemical pollution, in this case, occurs almost at the rate of groundwater. For the ammonium ion, this circumstance is explained by the relatively high mineralization of the contamination aureole.

In the modelling, as sources of the groundwater chemical pollution, sections 1-3 of the sludge collector and sections 5-6 (containing highly concentrated nitrogen compounds) are further considered. As noted above, a feature of the research object is the lack of data on regularly measured content of the main pollution indicators in sections 5-6 of the tailings pond for chalk since the beginning of operation.

It is well known that groundwater pollution aureoles are formed relatively slowly [2,7]. In the studied case, the aureole of groundwater mineralization near the sections 5 and 6 has been formed since 1987; for more than 30 years. Thus, the aureole contains information about the natural-technogenic conditions of its formation including the mode of the pollution sources’ operation. It can be concluded that the aureole of groundwater contamination has a kind of the "memory effect" that can be used for a retrospective assessment of pollution sources.

The correction of mineralization in sections 5 and 6 of the tailings pond for chalk was carried out in the following sequence.

1. The calculation of the age of groundwater contained in the sandy-gravel deposits of the channel facies was carried out for the entire studied area. The age of the groundwater was taken as the time for the migration of the liquid particle from the feeding region to a specific point of the geofiltration flow with the coordinates x, y, z. Taking into account that at a distance from the sources, the filtration and migration flows were formed mainly within the lower part of the aquifer represented by sandy-gravel sediments, the calculation of the groundwater age and the groundwater age map were made for a stratum of sandy-gravel deposits (Figure 7). Figure 9 shows a schematic map of the age of groundwater in the studied area. It can be seen that the age of groundwater naturally increases with distance from pollution sources.

**Figure 9.** Schematic map of the groundwater age and estimated zones of the sections 5 and 6 influence on the underflow
2. The influence area of the pollution source has been calculated for the entire period of its operation. For this purpose, the trajectories of geomigration flow from the considered storage facilities were developed for the entire period of their operation using the standard PMPATH software module integrated into the PMWIN-8 software package [1]. Further, the boundaries of the source influence area were determined by connecting the outermost (most distant from the storage) points of the trajectories. Figure 8, in particular, shows the areas of storage 6 influence.

3. The aureole of the groundwater mineralization was calculated using the developed geomigration model and the mineralization values obtained from direct measurements in the storage facilities. When modelling the mass transfer, the code SEWAT Version 4 [4] integrated into the PMWIN 8 software package was applied [1].

4. For each well in the influence area of the relevant storage, a stress period corresponding to the sample was determined, and the ratio of the in situ and model mineralization values was calculated:

\[ \alpha_{i,k} = \frac{c_{i,k}^{obs}}{c_{i,k}^{mod}} \]

where \( \alpha_{i,k} \) was the correction factor for the \( i \)-th well at the \( k \)-th stress period of the storage operation, \( c_{i,k}^{obs} \) and \( c_{i,k}^{mod} \) were the observed and model values of groundwater mineralization, respectively. The correction factors were averaged for the corresponding stress period and storage facility. As a result, the generalized correction factors \( \bar{\alpha}_k \) were obtained.

5. The corrected mineralization values in the sources were calculated for 19 stress periods:

\[ \hat{c}_k^{corr} = \bar{\alpha}_k \hat{c}_k^{obs} \]

where \( \hat{c}_k^{corr} \) was the corrected value of mineralization in the source at the \( k \)-th stress period of the storage operation, \( \hat{c}_k^{obs} \) was the mineralization.

6. Taking into account the corrected mineralization values in sections 5 and 6, the calculation of the current and predicted aureoles of groundwater mineralization was performed. It should be noted that the approach described above and used to refine the concentrations in the sources is most effective if the wells characterize only one source of contamination. As can be seen from Figure 9, the area of the section 6 influence partially overlaps the area of the section 5 influence. Taking this fact into consideration, the analysis of the data on section 6 included the wells located in the immediate vicinity of it. Thus, the section 5 influence on these wells was minimized.

4. RESULTS AND DISCUSSIONS

To assess the quality of water mineralization correction for sections 5 and 6, we used the local error of the model at the subsection \( \sigma_L \), which was calculated by the formula:

\[ \sigma_L = \frac{S_L}{\Delta M_L} \times 100\% \]

where \( S_L \) was the standard deviation of the model heads from the actual ones in the subsection of the corresponding section; \( \Delta M_L \) was the maximum change in the groundwater mineralization in the subsection.

As follows from Table 2, the local errors of the model in subsections of sections 5 and 6 after correction of mineralization, taking into account the age of groundwater, decreased by almost 2 times.
Table 2. Initial data and results of correction of model groundwater mineralization in wells near sections 5 and 6 of the tailings pond for chalk

<table>
<thead>
<tr>
<th>Section of the tailings pond for chalk</th>
<th>Well No.</th>
<th>Mineralization of groundwater, mg/l</th>
<th>Age of groundwater, years</th>
<th>Model Before correction</th>
<th>Model After correction*</th>
<th>Local relative error of the model σ (%)</th>
</tr>
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<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Before correction</td>
<td>After correction*</td>
<td></td>
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<td>77,400</td>
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<td>64,079</td>
<td>32,826</td>
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<tr>
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<td>32,047</td>
<td>58,399</td>
<td>32,047</td>
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<td>40,495</td>
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<td>51,850</td>
<td>37,134</td>
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<td>0.8</td>
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<tr>
<td>Local relative error of the model σ (%)</td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>23</td>
<td>12</td>
<td></td>
</tr>
</tbody>
</table>

| 5                                     | 906      | 33,250                              | 23,861                   | 26,556                 | 23,861                 | 22.3                                   |
|                                       | 939      | 30,600                              | 20,719                   | 27,684                 | 20,719                 | 21.2                                   |
|                                       | 940      | 21,300                              | 19,457                   | 27,263                 | 19,457                 | 21.4                                   |
|                                       | 941      | 20,400                              | 19,249                   | 27,489                 | 19,249                 | 21.2                                   |
|                                       | 942      | 17,400                              | 16,928                   | 26,439                 | 16,928                 | 21.3                                   |
|                                       | 955      | 27,200                              | 25,016                   | 25,837                 | 25,016                 | 23.3                                   |
|                                       | 956      | 23,800                              | 22,552                   | 24,851                 | 22,552                 | 24.5                                   |
|                                       | 957      | 21,900                              | 21,431                   | 24,499                 | 21,431                 | 24.4                                   |
|                                       | 958      | 25,867                              | 20,648                   | 24,199                 | 20,648                 | 22.9                                   |
|                                       | 15018    | 38,870                              | 25,440                   | 50,100                 | 25,440                 | 12.7                                   |
|                                       | 15050    | 78,400                              | 32,029                   | 69,315                 | 32,029                 | 23.2                                   |
|                                       | 15057    | 47,165                              | 33,300                   | 41,661                 | 33,300                 | 15.7                                   |
|                                       | 15088    | 42,000                              | 15,209                   | 30,874                 | 15,209                 | 23.8                                   |
|                                       | 15127    | 33,240                              | 23,310                   | 21,322                 | 23,310                 | 20.2                                   |
|                                       | 15133    | 183                                 | 12,569                   | 14,059                 | 12,569                 | 25.0                                   |
|                                       | 15135    | 15,555                              | 24,528                   | 20,334                 | 24,528                 | 20.3                                   |
| 5-I-4RS                               | 59,000   | 25,846                              | 56,507                   | 25,846                 | 56,507                 | 4.3                                     |
| Local relative error of the model σ (%)|          |                                     |                          | 31                     | 16                     |                                        |

Note: * Taking into account the age of the groundwater

The results of the mineralization correction for sections 5 and 6 of the tailings pond are shown in the graphs in Figure 10. For both sections, the correction was made toward a significant increase in concentrations for the period after 2000; and for section 6, the correction was more than twofold.
Figure 10. Results of correction of mineralization in sections 5 and 6 of the tailing

The model aureole of groundwater mineralization for 2012, calculated taking into account the corrected mineralization values for sections 5 and 6 of the tailings pond, is shown in Figure 11. The model results indicate that groundwater contaminated with nitrogen compounds is not currently discharged in the Vyatka River.
Using the calibrated geomigration model, a forecast was given for the development of the contamination aureole and its spreading to the Vyatka River. When performing forecast calculation, it was assumed that the pollution sources operated at a constant intensity corresponding to the corrected values at the end of 2012 (Figure 10). Figure 12 shows the forecast aureole of the groundwater mineralization in 2017 calculated with the corrected mineralization values for the storage facilities. According to the forecast, the discharge of pollution occurs mainly in the oxbow lakes and in the Yelkhovka River, from which pollution enters the Vyatka River.

Figure 12. Forecast model aureole of groundwater mineralization for 2017 calculated with corrected mineralization values for storage facilities
presented in Figures 5 and 6. In particular, the transition from the mineralization to the content of the nitrate ion $C_{NO_3^-}$ and the ammonium ion was carried out according to the dependences:

$$C_{NO_3^-} = 0.770M$$  \hspace{1cm} (9)

$$C_{NH_4^+} = \frac{C_{NO_3^-}}{3.7147}$$  \hspace{1cm} (10)

Where $M$ was the mineralization, $C_{NO_3^-}$ was the concentration of the nitrate ion, $C_{NH_4^+}$ was the concentration of the ammonium ion, mg/l.

**Figure 13.** Chemical pollution discharge into the Vyatka River (model results)

It follows from Figure 13 that the predicted discharge of ammonium ion into the Vyatka River has practically stabilized. Its average annual value will reach about 11 tons per day in the next 10-20 years.

An estimated conservative calculation of the predicted concentrations of ammonium ions in the Vyatka River for its minimum discharge under condition of complete mixing can be made by the formula:

$$C_{NH_4^+}^p = \frac{Q_{NH_4^+}}{Q_p}$$  \hspace{1cm} (11)

where $C_{NH_4^+}^p$ is the concentration of ammonium ion in the Vyatka River, $Q_{NH_4^+}$ is the mass flow of the ammonium ion entering the Vyatka River with the underflow and waters of the Yelkhovka River; $Q_p$ is the Vyatka River discharge, 95% of the supply, which is 46 m$^3$/s.
Substituting the values of the parameters in the formula (11) and taking into account the dimensions, we obtained $C_{NH_4}^p = 2.8 \text{ mg/l}$.

Thus, it can be expected that the ammonium ion content exceeds MAC (1.5 mg/l) during the low-water period in the coastal current at the left bank of the Vyatka River, where the discharge of pollution is predicted. Since the water intake from the Vyatka River for the Kirov city is carried out on the left bank of the river, it is necessary to carry out a hydrological forecast estimate of the ammonium ion content in the water drawn for water supply.

5. CONCLUSION

When assessing the impact of industrial waste storage facilities on groundwater based on monitoring data in combination with geofiltration and geomigration modelling in the current operating mode of storage facilities, it is advisable to interpret the monitoring data taking into account the age of groundwater. In this case, when interpreting the monitoring data, the "memory effect" of the geomigration flow is used, which allows correcting the parameters of groundwater pollution sources, and therefore, increasing the reliability of forecast calculations.

The experimental data has confirmed the validity of the proposed method of "memory effect" of the geomigration flow.

REFERENCES


