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MIGRATION OF BIOGENIC SUBSTANCES THROUGH THE AERATION ZONE

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Abstract. The article presents the migration of biogenic substances in the aeration zones of different sedimentary riverbanks. Sand and loam sediments in Lithuanian river basins are studied, and experimental research is carried out under natural conditions by increasing the loads of biogenic substances. The modeling was performed using the modeling program CHMFLO-2000. It was established that the transport of total nitrogen by the river water is formed by the amounts of nitrates, which make up 92–97% of the total transport in individual seasons. Nitrates account for 15–23% of the total nitrogen transport through sediment surface and groundwater runoff. The regularities of vertical and horizontal migration of biogenic substances have been established and defined. The suitability of the modeling program CHEMFLO-2000 for modeling the transport processes of ammonium ions, nitrates and nitrites by underground runoff on the banks of Lithuanian rivers has been confirmed, the applicable constants for modeling have been provided.

Keywords: aeration zone, biogens, modelling, ground water, river pollution.

Introduction

Groundwater communicates with the environment through the aeration zone. Precipitation that replenishes groundwater resources infiltrates through it, pollutants also enter the ground aquifer through it (Huang et al., 2014; Liu et al., 2022; Kirchmann et al. 2002; Hill & Cardaci, 2004). The thickness and conductivity of the aeration zone determine what materials will reach groundwater and when. The chemical composition of groundwater, as well as its quality, are largely dependent on the sediments in which it accumulates. As research has shown, the concentration of nitrogen in groundwater, as well as the amount of leached nitrate nitrogen, is influenced by the balance of precipitation, vegetation and crop rotation, the amount of humus and clay particles in the soil (Wang et al., 2020; Nie et al., 2018; Liu et al., 2022; Lu et al., 2019). The pollution of soil and subsoil sediments and groundwater is conditionally divided into two groups: industrial (including transport) and agricultural. Agriculture-induced pollution can be local and diffuse. Pollution of soils and sediments, unlike air or water, can go unnoticed for a long time. Pollution of soil, and especially subsoil sediments, is noticed much later than that of surface water; moreover, due to the sorption properties of sediments, changes in its properties or composition may not appear immediately (Hill & Cardaci, 2004). Ammonium nitrogen is quickly absorbed by the soil, so this nitrogen is not very mobile. It stays at the place of insertion. Percolating water does not wash it into deeper layers of sediments, it also migrates slightly in the horizontal direction (Lazaratou et al., 2020). Studies of nitrate diffusion migration in immobile structure soil monoliths confirmed the influence of soil moisture on nitrate diffusion (Lu et al., 2019). The results of the mathematical statistical analysis showed that the soil granulometric composition, soil moisture, precipitation, hydrogeological conditions, depth of groundwater subsidence, thickness of the aeration zone, amount of nitrates in the soil solution, soil tillage influence groundwater pollution with nitrates (Chelil et al., 2022; Wang et al., 2019; Kyllmar et al., 2006). The aim of the work is to determine the characteristics of the migration of biogenic substances in the sediments and the surface groundwater layer, taking into account the climatic and geomorphological conditions of the river basin, to evaluate the regularities of changes in the concentrations of biogenic substances in the aeration zones of different sediments on the banks of rivers, affecting the quality of the river water.

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Materials and methods

Natural and experimental studies aim to determine the general characteristics of vertical migration of biogenic substances in the aeration zone in sand and loam sediments by increasing the loads of biogenic substances. The results obtained in the experimental studies were used to calibrate the modeling program. The calibrated model was applied in the basin of natural studies; the results were compared with the results of natural studies.

For studying the migration of biogenic substances, natural research stations have been installed on river banks, multilevel lysimeter wells, installed at a distance of 3, 5, 10 and 20 meters from the shore (Figure 1).

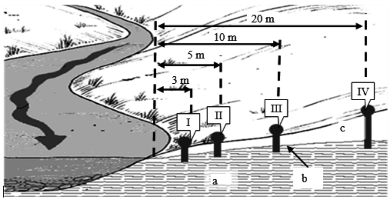

Figure 1. The scheme of multilevel lysimeters places: a – groundwater zone, b – groundwater table, c – aeration zone, I, II, III, IV – multistage lysimetric boreholes

Multistage lysimeter well – a well in which reservoirs are installed for collecting samples of deeply percolating water. To determine the background, the reservoir is installed in the upper part of the soil at a depth of 10 cm and every 0.5–1.0 m deep in the groundwater. A reservoir is installed to collect groundwater samples in the deepest place, an additional reservoir is installed 0.5 m above. The multistage lysimeter well used in the research differs from the traditional lysimeter well in that in the traditional lysimeter well, the trap is installed in the deepest part of the well and the water filtered through the entire borehole enters the reservoir. Meanwhile, in the multistage lysimeter, vertical water filtration in the well is limited and the water percolating through the still sediments enters the reservoirs (Litvinaitis, 2013).

In evaluating the water balance of the river basin, the following was done: a database of air temperature, evaporation and precipitation of the studied period, distribution of Quaternary sediments of the basin, and morphometric data were compiled. The quaternary geological map (M 1: 50 000) was used to evaluate the structure in the sediments of the investigated river basins. According to sediment filtration coefficients, three classes of sediments are distinguished: sand, loam, and clay. Sediment dispersion is estimated as a percentage of the basin, basin segment, or tributary area. For a more detailed distribution of sediments in the basin and in the selected segment of the basin, parallel sections 0–50 m, 50–200 m, 200–500 m, 500–800 m, 800–1100 m and >1100 m wide were distinguished from the riverbed using ArcGIS software. When precipitation falls on the surface of the watershed analyzed by parallel sections, part of the water evaporates, the rest filters into sediments and enters the riverbed through underground runoff. The water balance equation was used to estimate this process:

$$R = \sum_{i=1}^{f}\left[\left(K_f - E_f\right)\cdot A_f \cdot \left(\frac{1}{2}\cdot\frac{L_f}{v_f} + \sum_{i=1}^{f+1}\frac{L_{f+1}}{v_{f+1}}\right)\right], \qquad (1)$$

where R is the height of the leak (mm); f – parallel section, counting from the furthest >1100 m to the river; K_f – amount of precipitation per parallel section (mm/d); E_f – total evaporation in the parallel section (mm/d); A_f – area of the inlet section (km^2); L_f – section width (m); L_{f+1} – width of the parallel section closer to the river (m); v_f – water filtration rate in the parallel section (m/d); v_{f+1} – water filtration rate in the parallel section closer to the river (m/d).

Mathematical modeling was performed with the CHEMFLO^{TM}-2000 modeling software package. The software allows users to determine the systems of movement of water and chemical substances in sediments, solves the mathematical models of these systems, and presents the results graphically and in the form of convenient export to other programs (Nofziger & Wu, 2003). The computational differential equation systems used in the modeling program are suitable for studying and predicting the migration of water and chemicals. Richards' differential equations are used for water filtration through sediments:

$$C(h)\frac{\partial Q}{\partial t} = \frac{\partial}{\partial_x}\left[K(h)\left(\frac{\partial h}{\partial x} - \sin(A)\right)\right], \qquad (2)$$

where $Q = Q(h)$ is the flowrate, $h = h\,(x, t)$ is the thickness of the sediments through which the coordinate of water flows, x is the position parallel to the direction of flow, t is the time; $sin(A)$ is the sine of the angle A between the direction of flow and the horizontal direction; $K(h)$ is the hydraulic conductivity of the soil at the matric potential h, $C(h)$ is the specific water capacity.

The movement and degradation of chemicals in this model is described by the convection-dispersion equation.

$$\frac{\partial}{\partial t}\left(Q_c + \rho S_c\right) = \frac{\partial}{\partial x}\left(QD\frac{\partial c}{\partial x} - q_\rho c\right) - \alpha Qc - \rho\beta A + \gamma Q, \qquad (3)$$

where $c = c(x, t)$ is the concentration of chemical in the liquid phase, $S = S(x, t)$ is the concentration of chemical in the solid phase, $D = D(x, t)$ is the dispersion coefficient, $Q = Q(x, t)$ is the flowrate, $q = q(x, t)$ is the flux of water, $\rho = \rho(x)$ is the soil bulk density, $\alpha = \alpha(x)$ is the first-order degradation rate constant in the liquid phase, $\beta = \beta(x)$ is the first-order degradation rate constant in the solid phase, and $\gamma = \gamma(x)$ is the zero-order production rate constant in the liquid phase. Here α, β, and γ are zero or greater

From Richards Eqs (2) we get:

$$\left(QR_R c\right) = \frac{\partial}{\partial x}\left(QD\frac{\partial c}{\partial x} - q_\rho c\right) - \left(\alpha Qc - \rho\beta k\right)c + \gamma Q, \quad (4)$$

where R_R is the retardation factor for the chemical in the soil and is given by

$$R_R = 1 + \frac{\rho k}{Q}. \quad (5)$$

In this model, the concentration of a chemical substance in the liquid phase and the movement of water at any place and time are determined by solving Eq. (4). Eq. (5) is used to calculate the absorption of chemicals in the solid phase.

Since each of the seasons has specific conditions, the simulation is performed in three scenarios corresponding to the spring, summer, and autumn seasons. The spring season will be dominated by frost remnants and the predominance of surface runoff, the beginning of plant vegetation. Possible increased inflow of biogenic substances from agricultural fields into water. The summer season will be dominated by intense plant vegetation, field fertilization in agricultural regions, and limited surface runoff. The fall season is characterized by the decline of plant vegetation and more intense release of biogenic substances from decaying plants, surface runoff.

To evaluate the prediction accuracy of the implemented model, statistical indicators were used: Nash–Sutcliffe (Nash & Sutcliffe, 1970; Knoben et al., 2019) efficiency (E_m), correlation (r) and error (p).

Results and discussion

Parts (segments) of the basin of river Ūla (dominated by sand deposits) and the basin of river Lėvuo (dominated by loam deposits) basins were selected for natural research. The studied 379 km^2 segment of the Ūla basin (up to the Zervynos water measuring station) includes the middle and lower reaches of the Ūla river on the territory of Lithuania (Figure 2). Here, sandy deposits cover 69.4% of the area of the segment of the basin and vary consistently from 52.6% to 73.2% in the section from 0–50 to 500–800 m. The load covers 17.3% of the basin area of the segment and 21.3% in sections 200–500 m wide. Swamps settled mostly on sand deposits in the upper and middle reaches, covering 33.6% of the area in the 0–50 m section.

The loamy upper reaches of the Lėvuo basin were chosen for the study – up to the Kupiškis water measuring station (Figure 3). There, the loam covers 68.2% of the segment area. In all coastal stretches of the upper

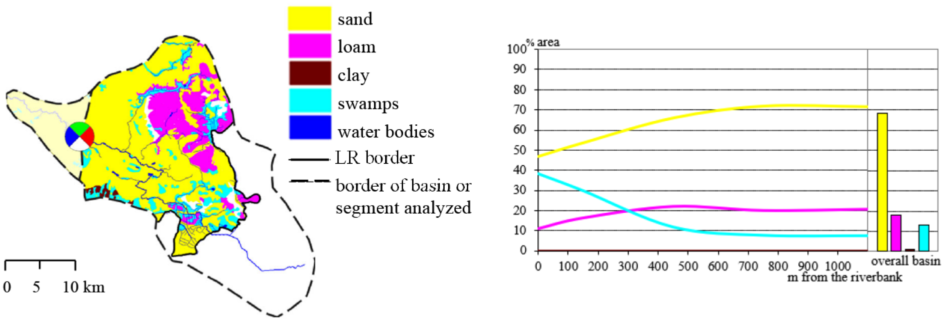

Figure 2. Sediment dispersion of Ūla basin. Bright part – investigated segment of the basin, – hydrological, hydrochemical and inkind research stations; and dispersion of segment, m from riverbank

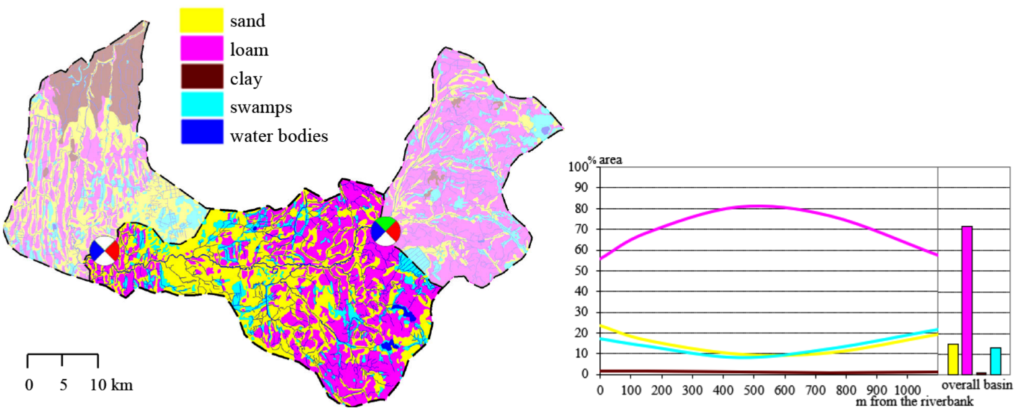

Figure 3. Sediment dispersion of Lėvuo basin. Bright part – investigated segment, – hydrological, hydrochemical and – hydrological, hydrochemical and in-kind research stations; and dispersion of the investigated segment, *m* from riverbank

reaches of the Lėvuo, loam covers most of it, and in the 200–800 m stretch – up to 77.8–73.3%. Sand covers 13.5% of the area of the segment, and larger amounts of up to 21.2% are found closer to the river. The swamps cover 14.3% of the area, the largest part (41.9%) is in a section wider than 1100 m.

The transfer of biogenic substances from cultivated fields to river water is characterized by seasonality (Liu et al., 2022; Lu et al., 2019; Wang et al., 2020). This was also evident in the results of the study. The transport of total nitrogen through surface runoff is shaped by the transport of nitrates. Nitrate was the predominant (more 96%) in drainage water (Norris et al., 2023). According to the results of the study, in contrast to surface runoff, the transfer of total nitrogen through underground runoff is formed by the amount of nitrites, which make up 75% of the total transfer in spring and summer, and 84% in autumn (Figure 4). However, the results of some field experiments have suggested that nitrate leaching responds exponentially rather than linearly to increasing nitrogen input (Wang et al., 2019). The results indicated that the wet season is the hot moment of DON loss, and the average cumulative load reaches 14.1 t, accounting for 72.5% of the annual load (Xu et al., 2023). In the spring season, the transport of the studied materials in all sediments is dominated by surface runoff.

The transfer of ammonium ions by river water is 6.3 times, nitrates 8.3 times higher than the transfer by groundwater or surface runoff, while the transfer of nitrites is 183 times lower. Nitrate concentrations decrease from the surface to the depth in loam sediments in all seasons. The most intense decrease was found at a depth of up to 1 m, in some cases up to 1.5 m deep – in the plant root zone. Here, compared to the surface, nitrates decrease by an average of 2.5 times, and deeper concentration changes are distributed seasonally: nitrification processes prevail in the autumn season, and denitrification processes in the summer.

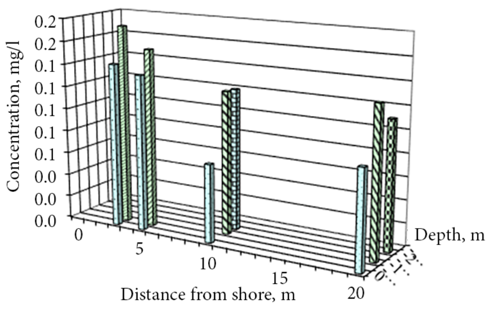

Figure 4. Changes in ammonium ions in the loam sediments in spring

Nitrate leaching processes prevail in sand sediments. The amount of nitrates is 53% higher at a depth of 1 m in the spring season. It is higher by about 36% in the summer and autumn seasons, when vegetation absorbs more biogenic substances. Nitrification processes prevail in summer and autumn, and denitrification processes prevail in spring and summer in the deeper layers.

Horizontal migration, when approaching the river. Sand sediments: nitrate concentrations decrease most intensively – 3.9%/m on the surface and 3.0%/m in groundwater in autumn. It decreases by 1.2 and 1.7%/m, respectively in summer. And increases by 2.6 and 0.3%/m in spring (Figure 5). Loam sediments: nitrate concentrations change oppositely on the surface and in groundwater in spring and summer. It increases on the surface by 0.8%/m, in groundwater it decreases by 0.8%/m in spring. And it decreases by 1.0%/m on the surface, and in groundwater it increases by 2.7%/m in summer. Concentrations increase at all depths by 0.9 and 1.5%/m in autumn. Xiaoxin et al. (2021) established soil nitrate was distributed and accumulated in the vadose zone, mainly at a depth of 0–6 m, before being leached into underground water, and crop production contributed, on average, 78.3% to the storage of nitrate in the regional vadose zone.

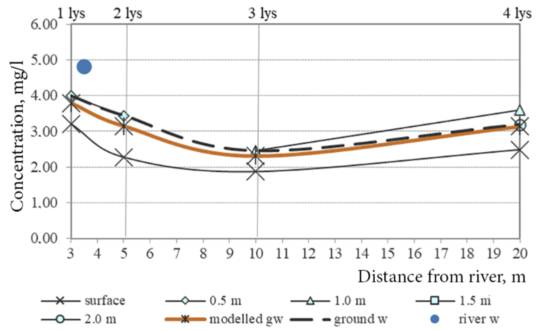

Figure 5. Results of natural research and modeling of nitrates migration in sand sediments profile in spring

Ammonium ion concentrations decrease from the surface to depth in the spring and summer seasons in sandy sediments (Figure 6). It decreases most intensively in the root zone and is 35–42% lower than the surface at a depth of 1 m. Ammonium ions increase by 40% in the spring season in loam sediments at a depth of 1 m. Considering that nitrate concentrations decrease accordingly, it can be said that denitrification processes take place at a depth of up to 1 m during this period. The amount of ammonium ions increases by approximately 85% (at a depth of 1 m), probably due to the beginning processes of vegetation decay in autumn.

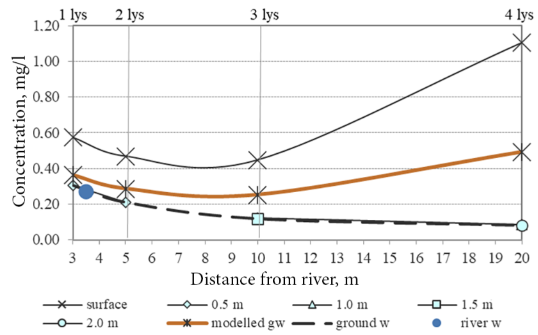

Figure 6. Results of natural research and modeling of ammonium ions migration in loam sediments profile in summer

Studies of the changing anthropogenic load were carried out by checking the assumption that the amount of chemical substances, not absorbed by the vegetation, will be washed deep into the sediments. Every 20 days, the anthropogenic load was increased by an additional load of 10 kg/ha. To allow the analyzed biogenic substances to be intensively transported deep, additional watering was organized in the field every 10 days. Meadow vegetation of *Arrhenatherum elatius*, *Dactylis glomerata* and *Deschampsia* are dominated in the research fields.

Higher surface concentrations of 15 to 32% (average 23%) of ammonium ions and 19 to 29% (average 21%) of nitrate were found each time with increasing anthropogenic load on the predicted schedule in the loam field. At a depth of 0.5 m and deeper, the patterns were divided into 1, 2, and 3–5 experimental samples (Figure 7).

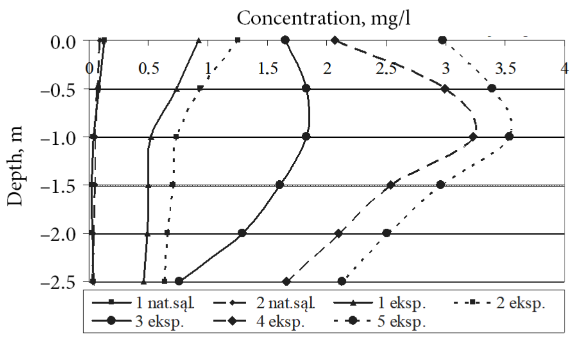

Figure 7. Experimental bench of loam. Ammonium ion concentrations transitions

The patterns split into experimental samples 1, 2 and 3–5, with increasing anthropogenic load in the Sand field, as in the loam field. During experimental samples 1 and 2, the concentrations of ammonium ions of 1.18–1.62 mg/l on the surface were 5 times higher than the concentrations obtained in samples under natural conditions. The concentration of 2.67 mg/l of nitrates determined in experimental samples 1 on the surface was 10.3 times higher than the concentrations of samples under natural conditions. 2 samples had concentrations of 3.46 mg/l, which is 30% higher than 1 (Figure 8).

Deeper, at a depth of 1 m, the average concentrations of ammonium ions are 9% lower; nitrates are 59% lower than at the surface. This was caused by the uptake during the vegetation period, and compared to the results obtained in the loam field, the water velocity in the sand sediments is approximately 5 times higher. In the deeper root zone, which was 1.1–1.4 m in the fields, under the influence of nitrification processes, nitrate concentrations were determined at 2.56–2.69 mg/l at a depth of 2.5 m, but 16% lower than at the surface. The amount of ammonium ions deeper in the root zone was reduced by nitrification processes, the concentrations of ammonium ions reached 0.87–1.22 mg/l, 33% lower than those found on the surface.

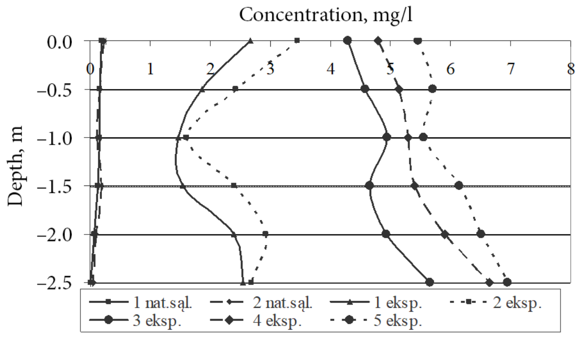

Figure 8. Experimental bench of sand. Nitrate concentrations transitions

The CHEMFLO™-2000 software package was used to model the migration of biogenic substances. Gardner, Brooks, Corey, and van Genuchten water conductivity functions and Simons, Brooks and Corey and van Genuchten water balance functions are used to describe water movement in sediments. When selecting functions for modeling work, water balance modeling was performed for the conditions of natural research stations. The simulation results are compared with the water balance calculations performed using the water balance formula (1), applying the filtration coefficients for sediment types: sand 6.2, loam 1.3 and clay 0.1 m/d. The most accurate simulation results were obtained using van Genechten functions, applying empirical constants α, n: $\alpha = 0.151$, $n = 2.61$ for sand; $\alpha = 0.039$, $n = 1.57$ for loam; $\alpha = 0.017$, $n = 1.29$ for clay. The efficiency coefficient of the software package was obtained in the calculation of the water balance $E_m = 0.95$, when $r = 0.96$, $p = 0.01$.

The model has been calibrated in two ways:

1. Vertical migration was performed according to the results of the natural conditions of experimental study 1 and experimental samples 1 and 5. Calibration was performed by changing the empirical degradation coefficients of the chemicals until the best agreement was achieved between the measured and modeled concentrations of the respective chemicals. The following degradation coefficients were obtained during calibration: 0.098 for ammonium ions and 0.074 for nitrates. The results obtained during calibration were mathematically processed, the efficiency coefficient of the model reached $E_m = 0.67$, $r = 0.78$, $p = 0.01$.
2. Calibration for horizontal migration resulted in degradation coefficients for horizontal migration of 0.012 for ammonium ions and 0.009 for nitrates. Efficiency coefficient of the model $E_m = 0.72$, $r = 0.73$, $p = 0.03$.

When the model for the vertical migration of biogenic substances was verified, the task was to verify the effectiveness of the model using data from experimental fields. The model is verified with values from 2 natural conditions and 2–4 experimental samples. Analyzing ammonium ions in the loam field resulted in an average error of 6%, sand – 11%. The largest errors were found in 3–4 experimental samples at a depth of 2.5 m, where they reached up to 33%. When the model for nitrate migration in the loam field, an average error of 5% was obtained in sand – 9%. The largest errors were found in the root zone at a depth of 0.5 m, where they accounted for up to 25%. The results and the efficiency of the model were close to the simulation results in the fields of France and China (Chelil et al., 2022; Fu et al., 2021). When verifying the model with experimental field data, the efficiency coefficient of the model $E_m = 0.61$, the correlation coefficient $r = 0.68$, and the reliability $p = 0.02$.

The analysis of the simulation results showed that the efficiency of the model and other parameters are: for the summer period, $E_m = 0.65$, $r = 0.75$, when $p = 0.05$; for the autumn period $E_m = 0.67$, $r = 0.77$ with $p = 0.07$. The overall efficiency of the simulation software package CHEMFLO-2000 $E_m = 0.64$, $r = 0.77$ with $p = 0.06$.

Conclusions

Analyzing the results of analytical and natural studies, it shows that the transport of total nitrogen by river water is formed by the amount of nitrates, which in individual seasons constitute 92–97% of total transport. Nitrates account for 15–23% of total nitrogen transport from surface and groundwater runoff.

In vertical migration, nitrate concentrations in sand sediments at a depth of 1 m are, on average, 53% higher than the surface, and in loam and clay sediments, purification processes are taking place and the concentrations are 46% lower than the surface in all considered seasons. The regularities of decreasing concentrations of ammonium ions were determined: in the summer season, the concentrations in the sand sediments are 33%, the loam – 62% lower than the surface, and in the autumn season, an increasing trend was established: in the sand sediments 85%, the loam 13% higher than the surface.

In horizontal migration, nitrate concentrations in surface and groundwater near the riverbank increase by 0.3 and 2.6%/m in spring, decrease by 1.7 and 1.2%/m in summer, and decrease by 3.0 and 3.9%/m in autumn. Ammonium ion concentrations decrease by 0.3 and 0.9%/m in spring, 2.2 and 3.3%/m in summer, and increase by 1.4 and 8.1%/m in autumn.

In horizontal migration, the concentration of ammonium ions in loam sediments near the river decreases by 1.7%/m in summer and 0.9%/m in autumn, and increases by 1.1%/m in spring. In groundwater, it increases by 1.3%/m in spring, 7.3%/m in summer, and 20.9%/m in autumn. Nitrate concentrations on the surface increase by 0.8 and 0.9%/m in spring and autumn, respectively, and decrease by 1.0%/m in summer. Ground water decreases by 0.8%/m in spring, and increases by 2.7 and 1.5%/m in summer and autumn, respectively.

Natural studies and experimental studies have shown that sand sediments are the most sensitive to the vertical migration of biogenic substances. Nitrates that cannot be absorbed by vegetation are washed deep and, compared to those on the surface, the nitrate concentration is on average 53% higher at a depth of 1 m. Ammonium ion concentrations vary seasonally, being on average 33% lower in summer and 85% higher than surface concentrations in autumn.

The assumption that the amount of biogenic substances not absorbed by the vegetation will be washed deep into the sediments with water was confirmed: in experimental sample 3, when the amount of ammonium was increased to the equivalent of 30 kg/ha, nitrate concentrations began to increase deep into the sediments in both research fields.

The chemical transport module of the CHEMFLO-2000 simulation software package is suitable for simulating the transport processes of ammonium ions, nitrates, and nitrites through underground runoff on the banks of Lithuanian rivers. In modeling, it is recommended to use van Genuchten functions, applying empirical constants α, n: $\alpha = 0.151$, $n = 2.61$ for sand; $\alpha = 0.039$, $n = 1.57$ for loam.

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