



## Analysis of annual and seasonal total nitrogen pollution in the Mūša catchment

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### Abstract

The quality of water in rivers depends on many hydrological and anthropogenic factors. The Mūša catchment belonging to the northern part of Lithuania was taken for water quality investigation. In this catchment 63% of the territory is under arable land.

A conceptual FYRIS model was chosen to identify the impact of the sources of pollution with total nitrogen (N) in the Mūša river. The modelling encompasses 1997–2011 period. Having preformed calibration the model efficiency coefficient was  $E = 0.46$ , which was fairly good and correlation coefficient was  $r = 0.69$ . Having analysed total nitrogen load into the Mūša catchment from different pollution sources it was established that about 87% of it come from arable land, 10% enter from waste water treatment plants (WWTP), households and urban territories and only 3% of all nitrogen within the catchment come from wooded territories and pastures.

The analysis of the results of simulation shows the seasonal amounts of scoured total nitrogen were different. Their highest amounts got to the rivers during the winter (January, February, December) season – 36% of total nitrogen, when there is no vegetation processes. The highest loads 35–37% from the scattered pollution sources. In spring (March, April), in the period of snow melting, one third, i. e., 31% was scoured because of a higher runoff to the researched subcatchment. And in the summer (May, June, July, August) and autumn (September, October, November) seasons, respectively, 16 and 17% of all nitrogen falling to the subcatchment.

**Keywords:** model; water quality; nitrogen pollution.

### Nomenclature

$E$	model efficiency coefficient
$c_0$	empirical calibration parameter
$kvs$	empirical coefficient
$n$	number of observations (units)
$R$	nitrogen retention coefficient
$T_a$	temperature adjustment factor
$T$	water temperature
$\Theta_{obs}$	average of all observations(units)
$\Theta_{obs,i}$	observed N concentration (mg/l)
$\Theta_{sim,i}$	modelled N concentration (mg/l)

### 1. Introduction

In the Accession to the European Union (EU) Treaty Lithuania has taken the responsibility to follow all requirements of the EU water protection policy. In recent years water quality protection has called for considerable attention and the result is the increase of investments into water sector and the development of management and the legal system.

The quality of water directly depends on many factors: climate, soils, water flora and fauna, hydrological and hydrodynamic processes, however, the main cause of pollution and eutrophication is economic activities of people. [1–5]. Lithuanian rivers receive a huge pollution load from industry and other production enterprises as well as from agriculture and cities. Various pollutants are found in rivers, they enter from numerous pollution sources by different ways and thus surface waters and groundwater's are polluted [6].

The investigations carried out in Sweden and Finland also proves that the variations of river water quality originate both due to the variation of river runoff and meteorological conditions as well as the nature of agricultural production (peculiarities of plant production and animal husbandry) in the rivers catchments [7], [8].

It is stated that area of arable land within a river catchment have a large influence on river water quality. H. Pauliukevičius using AGNPS model to investigate the relationship between the territorial distribution of agricultural land and water quality in the Nevėžis catchment has established that variation of agricultural land area can increase or decrease nitrogen load from 1.5 to 2 times within the river catchment [9], [10]. This was proved by the other scientists who investigated the runoff of biogenic matter into the water courses of the karst region [11–13]. They established that it was important to evaluate the type of agricultural land and suggest that the least amount of nitrate nitrogen is leached from pasture and the largest amount – from arable land.

Nitrogen and phosphorus concentrations in river water increase with an increase of agricultural land area within a river catchment and decrease in the water of wooded and boggy river catchments. Having estimated possible natural background pollution in the Nevėžis catchment it was established that about 84 % of all nitrogen enter into the catchment from agricultural production sources. That happens due to the large area of arable land and mobility of nitrogen as this element is easily leached out of drained soils [14]. However, the concentrations of biogenic matter in the water of wooded and boggy river catchments decrease mainly due to denitrification of nitrate nitrogen.

The use of mathematical models in order to investigate water runoff, quality, to elaborate pollution prevention decisions, to use the water resources in a rational way and to understand the processes taking place in the environment is one of main means for investigation of ecosystems [15], [16].

The use of mathematical models provides a possibility to describe the processes of water runoff and water quality, establish the state of a water ecosystem and forecast water quality. It would not be possible to achieve that just analysing the results of water quality monitoring. When using the mathematical models describing water ecosystems cause and result relationship, which conditions the changes taking place in a water body, is established. Knowing this relationship it is possible to make different plans for water quality improvement and management.

Mathematical models are classified also according to the type of processes they describe and systems they assess. They can be models intended to assess and model underwater, river runoff and pollution.

Mathematical modelling and appropriate model selection provide better possibilities to make proper evaluation of the extent and importance of the impact of anthropogenic activities, as well as elaborate the optimum river basin management plan ensuring the improvement of water quality.

Work purpose is to calculate and analyze the sources and extent of annual and seasonal water pollution with total nitrogen in the rivers of Mūša catchment using Fyris mathematical model.

## 2. Research subject and methodology

The Mūša catchment belonging to the northern part of Lithuania was chosen for the investigation (Table 1). Arable land accounts for 63% of the catchment territory. The entire Mūša catchment was divided into seven smaller subcatchments (Fig. 1). State water quality monitoring posts are located at the mouths of all the investigated rivers.

The state monitoring data of 1997–2011 was used to run the model. The data of water discharges were obtained from the Lithuanian Hydrometeorological Service and the water quality data from the Environmental Protection Agency.

To describe meteorological conditions the data of the closest Biržai meteorological station was used. Other data required for FYRIS model was collected using CORINE 2000 land cover map and LTDBK 50000 digital data base of the cosmic view map of Lithuania.

*Model description.* The dynamic FYRIS model [17]. Calculates source apportioned load and transport of nitrogen in rivers. The main scope of the model is to assess the effects of different nutrient reduction measures on the catchment scale. The time step for the model is one month and the area resolution is on the subcatchment level. Retention, i.e. losses of nutrients in rivers and lakes through sedimentation, uptake by plants and denitrification, is calculated as a function of water temperature, potential nitrogen concentration and lake area, and stream area. The model is calibrated with regard to two retention parameters,  $k_{vs}$  (retention parameter, m/year) and  $c_0$  (temperature parameter, dim. less), using time series on measured nitrogen and phosphorus concentrations. Data used for calibrating and running the model can be divided into time dependent data, e.g. time series on observed nitrogen concentration, water temperature, run off and point source discharges, and time independent data, e.g. land use information, lake area and stream length and width (Fig. 2).

Table 1. Characteristics of analysed subcatchments

Post No.	Rivers and observation post	Subcatchment area, km <sup>2</sup>	Land use, km <sup>2</sup> /%				
			Arable	Pastures	Forests	Water bodies	Towns and built up territory
1	Mūša upstream Kulpė	374.45	<u>206.46</u>	<u>15.83</u>	<u>143.56</u>	<u>1.62</u>	<u>8.93</u>
			55.1	4.2	38.3	0.4	2.4
2	Kulpė at mouth	262.96	<u>155.20</u>	<u>16.11</u>	<u>27.96</u>	<u>18.95</u>	<u>38.22</u>
			59.0	6.1	10.6	7.2	14.5
3	Kruoja at mouth	361.34	<u>261.88</u>	<u>27.72</u>	<u>49.54</u>	<u>3.92</u>	<u>20.19</u>
			72.5	7.7	13.7	1.1	5.6
4	Daugyvenė at mouth	487.34	<u>336.53</u>	<u>24.18</u>	<u>108.08</u>	<u>4.74</u>	<u>19.30</u>
			69.1	5.0	22.2	1.0	4.0
5	Lėvuo at mouth	1627.36	<u>914.62</u>	<u>170.97</u>	<u>485.50</u>	<u>19.67</u>	<u>45.42</u>
			56.2	10.5	29.8	1.2	2.8
6	Tatula near Trečionys	453.11	<u>331.83</u>	<u>43.98</u>	<u>67.63</u>	<u>2.01</u>	<u>10.67</u>
			73.2	9.7	14.9	0.4	2.4
7	Mūša downstream Saločiai	1729.9	<u>1152.2</u>	<u>118.72</u>	<u>419.62</u>	<u>9.95</u>	<u>49.91</u>
			66.6	6.9	24.3	0.6	2.9
Total area of Mūša catchment in Lithuanian territory, km <sup>2</sup> / %		5296	<u>3358</u>	<u>417</u>	<u>1301</u>	<u>60</u>	<u>192</u>
			63	8	24	1	4

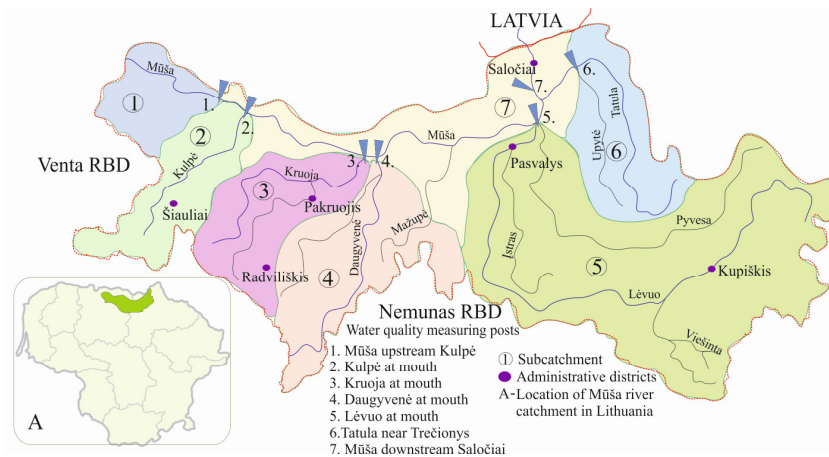


Fig. 1. Subcatchments of Mūša river basin and water quality monitoring posts

Part of nutrients due to processes of sedimentation, uptake by plants and denitrification are retained as it flows from headwater downstream. Removal or retention of nitrogen in rivers or lakes is calculated by the model assessing weather or water temperature, nitrogen concentration in the river, river runoff, lake and river water surface.

Nitrogen retention is in the catchment:

$$R = \frac{T_a \cdot kvs}{q_s + kvs} \quad (1)$$

Temperature adjustment factor given by:

$$T_a = \begin{cases} 0, & T < 0 \\ c_0 + \frac{T(1-c_0)}{20}, & 0 \leq T \leq 20 \\ 1, & T > 20 \end{cases} \quad (2)$$

The parameter  $c_0$  determines how strongly the retention is reduced by temperatures below 20 °C.

In calibration of nitrogen retention two parameters are changed: empirical nitrogen retention coefficient  $kvs$  and coefficient  $c_0$  which assesses how much is the reduction of nitrogen retention when the temperature drops below 20 °C.

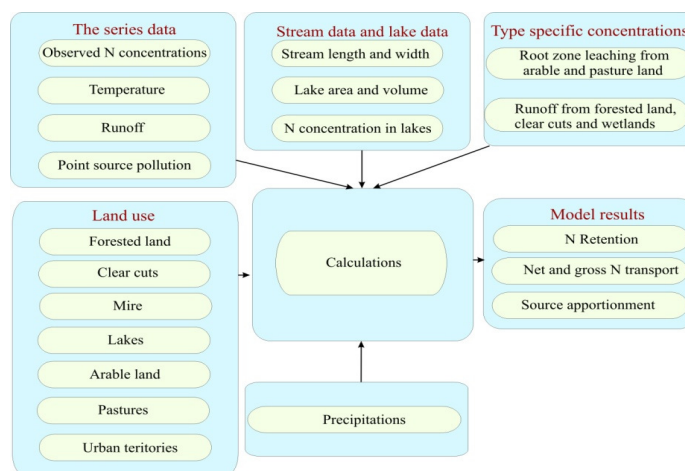


Fig. 2. Structure of FYRIS model inputs and outputs [18]

To assess the correspondence of FYRIS model results to the observed ones two indicators are used: model efficiency  $E$  and determination coefficient  $R^2$  [19]. Model efficiency is expressed by the equation:

$$E = 1 - \frac{\sum_{i=1}^n (\theta_{obs,i} - \theta_{sim,i})^2}{\sum_{i=1}^n (\theta_{obs,i} - \bar{\theta}_{obs})^2} \quad (3)$$

$E = 1$  indicates, that the observed and modelled data coincide ideally.  $E = 0$  indicates, that the modelled data is a straight line coincide with the average of the observed data.

### 3. Results of research

*Reliability of modelling results.* Having systemized model entry data a model of the Mūša catchment was made. The modelling includes a period 1997–2011 years. Calibration of FYRIS model is carried out by changing empiric calibration coefficients  $c_0$  and  $kvs$ . During the calibration process it was established that the most appropriate  $c_0$  value is  $c_0 = 0.34$  and coefficient  $kvs = 2.92$ . After calibration the model efficiency coefficient was  $E = 0.46$ , i.e., it was more than substantially good and correlation coefficient  $r = 0.69$ .

*Annual distribution of total nitrogen loads.* Modeling results show that average loads of scattered pollution determined by total nitrogen all over Mūša catchment (within the period of 1997–2011) vary from 0.54 to 2.23 t/km<sup>2</sup>, whereas of point pollution – from 0.05 to 0.13 t/km<sup>2</sup> per year. The highest alternation of total nitrogen loads from the scattered pollution sources is found in Daugyvenė subcatchment, where total nitrogen load fluctuated from 0.59 to 2.50 t/km<sup>2</sup> per year and in Tatula subcatchment at Trečionys, where the load changed from 0.58 to 2.35 t/km<sup>2</sup> per year. The areas of these subcatchments do not amount 500 km<sup>2</sup>, whereas the areas of arable lands there make about 70%, so there large fluctuations of loads are determined by intensive arable farming and high potential of pollutant washout. The alternation of the average loads of point pollution caused by total nitrogen was not so pronounced, the highest alternation boundaries were found in Kulpė and Kruoja subcatchments, where total nitrogen loads changed correspondingly from 0.23 to 1.45 t/km<sup>2</sup> per year and from 0.06 to 0.20 t/km<sup>2</sup> per year. Higher fluctuations of point pollution loads than in other rivers are determined by the fact that these rivers flow through Šiauliai, Radviliškis and Pakruojis administrative regions where the water discharged from water treatment plants gets into the abovementioned Kulpė and Kruoja rivers.

The highest load of total nitrogen from all pollution sources in the Mūša catchment was recorded in 1998 and it was 9874 t/year or 1.85 t/km<sup>2</sup> per year. Later the extent of pollution decreased somewhat and in 2003 the lowest load during the research period was recorded 2117 t/year or 0.40 t/km<sup>2</sup> per year. The estimated average multi total nitrogen pollution load reached 5181 tons/year, or 0.97 t/km<sup>2</sup> per year.

It was established that the highest load of total nitrogen from WWTP in the Mūša catchment was observed in 1997 and it was 450 tons, i.e., more than 106 tons higher compared with the long term mean (average = 340 t). Later, in 1998 and 1999 loads from WWTP decreased by more than 70 tons, however, in 2000 and 2001 they increased again approaching to the level of 1997. Since 2003 nitrogen loads in the catchments deceased considerably and they did not exceed 300 t margin. Although point source pollution make considerable influence on water quality, however, the majority of pollutants, especially nitrogen, comes into rivers and streams from nonpoint pollution sources. The modelling results showed that the greatest nitrogen pollution source in the Mūša catchment was arable land – during the study period 58670 t of nitrogen leached out to surface waters. Meanwhile, only 4612 t of total nitrogen passed from concentrated pollution sources and urban territories.

When analysing total nitrogen pathways to the Mūša catchment from different pollution sources it was established that on average about 87% of it came from arable land, 10% of it came from WWTP, households and urban territories and only just above 3% of all nitrogen in the catchment came from wooded territories and pastures (Table 2).

Table 2. Total nitrogen (%) load from different sources during study period

Post No.	River	Arable	Pastures	Forests	Urban territory	Concentrated pollution
1	Mūša upstream Kulpė	94.6	1.2	2.8	1.0	0.3
2	Kulpė	50.9	0.9	0.4	0.8	47.0
3	Kruoja	86.9	1.7	0.8	2.7	8.0
4	Daugyvenė	95.0	1.7	1.3	1.5	0.5
5	Lėvuo	90.5	4.2	2.1	2.1	1.1
6	Tatula near Trečionys	93.1	2.2	0.9	1.7	2.1
7	Mūša downstream Saločiai	94.4	1.6	1.5	2.2	0.2
Average in all catchment, %		86.5	1.9	1.4	1.7	8.5

The Kulpė subcatchment is one of the exclusive ones in the Mūša catchment. The parts of total nitrogen load from arable land territories and from point source pollution are more or less equal. A supposition could be made that the part of total nitrogen from point source pollution entering the Kulpė is much greater than in other rivers because both sewage from smaller Šiauliai enterprises and from Šiauliai WWTP are emitted into it. A major part of the nitrogen coming into the Kulpė from arable land can be explained by the fact that about 60% of the catchment area includes arable land territory, in which intensive agricultural takes place.

The reduction of nitrogen load from arable territories could be most probably expected having applied Good Agricultural Practice and appropriate environmental measures.

The model distinguish the main pollution sources, calculates their loads and retention in rivers catchments. Efficient preventive measures can be elaborated after appropriate assessment of these results. It is relevant to construct various model scenarios for reduction of nitrogen losses to the river Mūša. One of scenarios can be increasing pasture areas for account of arable land. It is also relevant to establish how much nitrogen pollution would decrease having reduced emission from WWTP.

*Seasonal distribution of total nitrogen loads.* The analysis of modeling results shows that washed out seasonal amounts of total nitrogen within the period of 1997–2011 were different. During winter season the largest amounts of total nitrogen were washed out. Over this period 36% of all nitrogen which falls on the catchment (Table 3) got into Mūša catchment from all the selected subcatchments. The largest amounts of nitrogen got into from arable land, grazing land and forest lands 35–37%. It can be explained by the fact that during winter season vegetation processes do not take place, there are no plants which would keep and absorb nitrogen. Within this period organic substances accumulated during summer decompose, so the nitrogen excess is formed which gets into water bodies.

Most nitrogen is washed out when more water gets into soil with precipitation than evaporate, and then intensive water movement takes place in the soil. It has been established that in spring during snow melting, when the runoff into the catchment under examination is bigger the third, i.e. 31% of all nitrogen which falls on the catchment (Table 3), was washed out. Together with surface runoff from arable lands bigger nitrogen amounts (32%) were washed out from grazing lands than formed from point pollution sources (17–18%).

Table 3. Obtained by modeling the seasonal total nitrogen leaching into Mūša catchment, % of the amount over the modeled period

Season	Arable land	Pastures	Forests	Waste water treatment plants and urban territories	Concentrated pollution	From the basin during the season
Summer	14.03	14.34	15.18	32.93	33.66	15.87
Winter	36.95	36.86	35.18	24.01	24.03	35.94
Spring	32.90	32.26	32.07	18.46	16.99	31.22
Autumn	16.12	16.54	17.57	24.60	25.32	16.97
Sum	100	100	100	100	100	100

During warm season when vegetation processes take place and plants intensively assimilate biogenic substances nitrogen washout from scattered pollution sources into water bodies noticeably reduces (Table 3). Besides, smaller amounts of washed out nitrogen are determined by the fact that during summer season spontaneous water purification process picks up speed. In summer, when more precipitation evaporates than falls, less amounts of total nitrogen are washed out.

Modeling results also showed that during autumn season 17% of all nitrogen which falls on the catchment get into Mūša catchment. Within this season the highest amounts of nitrogen (25%) get into from point pollution sources (Table 3).

Nitrogen can get into water bodies with meteorological water – rain, melted snow and ice as well as in consequence of human economic activities. In all subcatchments selected during modeling strong seasonal alternation of total nitrogen is observed. The highest amounts of nitrogen were washed out from arable lands within winter season (Fig. 3a). Analyzing the obtained results it is necessary to take into consideration that a certain tendency of nitrogen loads distribution is partially determined by different conditions of pollutant washout. Heavier precipitation and large area of the subcatchment determined the fact that the largest nitrogen amounts were washed out from Mūša subcatchment below Saločiai. The amounts of total nitrogen getting into Mūša catchment varied over a wide range depending on season and the area of the selected subcatchments. The highest nitrogen load within the modeled period was established in winter and spring. In the selected Mūša subcatchment below Saločiai correspondingly 7410 t in winter and 6480 t in spring were washed out from arable lands. Meanwhile in summer total nitrogen load from arable lands in Mūša subcatchment below Saločiai reduced by 4560 tons or 2,6 times in comparison to winter season.

Total nitrogen load distribution is influenced by the big cities. The simulation results showed that the maximum load of the subcatchments in the point sources, despite the change of seasons, set in the Kulpė subcatchment (Fig. 3b).

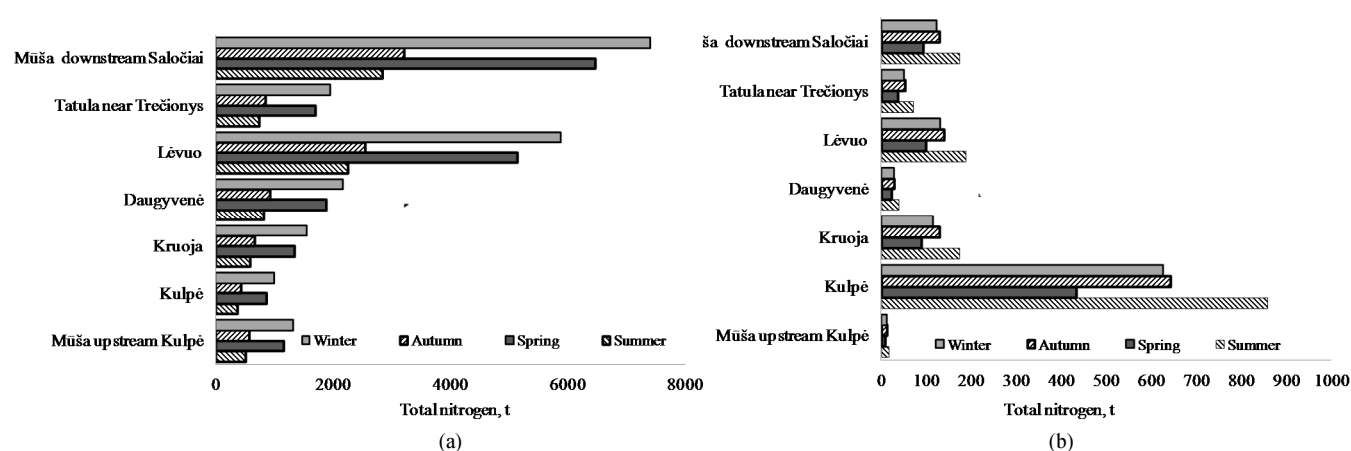


Fig. 3. Seasonal total nitrogen load from arable land areas (a) from point sources (b)

Simulation results show that in Mūša basin average total nitrogen load was 0.19 in summer, 0.21 – Autumn in Spring – 0.39, and in Winter – 0.44 t/km<sup>2</sup>/year.

#### 4. Conclusions

After FYRIS model calibration the model efficiency was sufficiently good  $E = 0.46$  and correlation coefficient was  $r = 0.69$

The highest load of total nitrogen from all pollution sources in the Mūša catchment was recorded in 1998 and it was 9874 t/year. Later the extent of pollution decreased somewhat and in 2003 the lowest load during the research period was recorded (2117 t/year).

On average about 87% of total nitrogen in the catchment comes from arable land, 10% from WWTP, households and urban territories. Only just above 3% of total nitrogen comes from wooded territories and pastures.

Washed out amounts of total nitrogen during the seasons within the period of 1997–2011 were different. In winter in the absence of vegetation processes 36% of all nitrogen which falls on the catchment got into Mūša catchment, of which 35–37% from scattered pollution sources. In spring during snow melting 31% was washed out, from which 32% from scattered pollution sources, whereas in summer and autumn 16–17% of all nitrogen which falls on the catchment got into Mūša catchment, from which the larger half from point pollution sources.

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