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Analysis of the Mūša catchment pollution with total nitrogen

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The quality of water in rivers depends on numerous hydrological and anthropogenic factors. The Mūša catchment, belonging to the Lielupė river basin district (RBD) in the northern part of Lithuania, was taken for water quality investigation. In this catchment, 63% of the territory is under arable land.

The 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 the 1997–2006 period.

After calibration, the model efficiency coefficient was $E = 0.46$, i. e. fairly good, and the correlation coefficient was $r = 0.69$.

While modelling the variation of nitrogen concentrations during the study period (1997–2006), the results did not correspond to the monitored concentrations equally well in all subcatchments. One of the main reasons for the disagreement between the model and monitoring data can be a vast dispersal of the monitoring data. The model represents the monitoring results in the Mūša, Daugyvenė and Tatula rivers quite well. There is a strong linear correlation between the model and the monitoring results. The determination coefficient of the regression equation R^2 varies from 0.48 to 0.56.

Analysis of the total nitrogen load to the Mūša catchment from different pollution sources has shown that about 87% of it comes from arable land, 10% enters from waste water treatment plants (WWTP), households and urban territories, and only 3% of all nitrogen within the catchment comes from wooded territories and pastures.

Key words: water pollution, nitrogen, load, catchment, model

INTRODUCTION

Under conditions of the ongoing global climate change and increasing anthropogenic impact, it is relevant to evaluate the quality of water bodies. The preservation of surface water quality is considered to be the main priority in the Lithuanian Environmental Strategy adopted in 1996 (Lietuvos..., 1996).

In the Accession to the European Union (EU) Treaty, Lithuania has taken up 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 the water sector and the development of its management and the related legal system.

While following the requirements of the Common Water Framework Directive (ES Bendroji..., 2000), water resources are managed by the principle of a hydrological unit – river basin district (RBD). According to this principle, all territory of the Republic of Lithuania is divided into four RBDs (Nemunas, Venta, Dauguva, Lielupė). All these RBDs are cross-border ones.

The quality of water directly depends on numerous factors: climate, soils, water flora and fauna, hydrological and hydrodynamic processes; however, the main cause of pollution and eutrophication is the economic activities of people (Gailiušis, 1996; Pauliukevičius, 1998, 2000; Povilaitis, 2008). Eutrophication of water depends on the agricultural measures. In intensive agriculture, organic and mineral fertilizers are important. Some of them get into water with runoff. Thus, fertilizers washed from the soil increase phosphorus and nitrogen levels in water as well. Increased levels of these compounds lead to eutrophication, which is observed almost in all Lithuanian rivers. Nitrogen compounds promote the growth of algae and macrophytes, thus narrowing the river channel and increasing alluvial water.

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Lithuanian rivers receive a huge pollution load from industrial and other enterprises as well as from agriculture and cities. Various pollutants are found in rivers. They enter from numerous pollution sources by different ways, therefore, surface waters and groundwater are polluted (Idzelis et al., 2006).

An investigations carried out in Sweden and Finland has also proven that the variations of river water quality are due both 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 river catchments (Kyllmar et al., 2006; Vuorenma et al., 2002).

Areas of arable land within a river catchment have a great influence on river water quality. H. Pauliukevičius, using the AGNPS model to investigate the relationship between the territorial distribution of agricultural land and water quality in the Nevėžis catchment, has established that variations of agricultural land area can increase or decrease nitrogen load 1.5 to 2 times within the river catchment (Pauliukevičius, 1998, 2007). This was proved by other scientists who investigated the runoff of biogenic matter into the water courses of the karst region (Rudzianskaitė, 2000; Morkūnas et al., 2005; Tumas, 2003). They established that it was important to evaluate the type of agricultural land and suggested that the least amount of nitrate nitrogen is leached from pastures 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. Analysis of the possible natural background pollution in the Nevėžis catchment has revealed that about 84% of all nitrogen enter into the catchment from agricultural production sources. This happens due to the large area of arable land and the mobility of nitrogen as this element is easily leached out of drained soils (Šileika, 2007). However, the levels of biogenic matter in the water of wooded and boggy river catchments decrease mainly due to denitrification of nitrate nitrogen.

A. Bučienė investigated nutrients leaching from traditional and ecological farms and has found that the level of nitrogen and total phosphorus increases with an increase in farming intensity. For example, in 2007 from the traditional farming area leached 23 times more nitrogen than from the ecological farming system in Lithuania (Bučienė, 2009).

Relatively numerous investigations of river water quality are carried out; however, the majority of them are limited to the analysis of the State Water Quality Monitoring data. The analysis of the peculiarities of water quality variation remains relevant, especially now when there is a need to elaborate the programme and management plan to achieve the water protection goals.

Mathematical models are becoming more and more popular for analysing water quality variations. So far, there is no distinct description of a model imitating natural processes in a water body. Some authors think that a model is software specially calibrated for a certain river or other water body; others believe that a model is a system of mathematical equations, which approximates the behaviour of a natural system or a phenomenon (Vincevičienė, 1998).

The use of mathematical models in order to investigate water runoff, quality, to elaborate pollution prevention decisions, to use water resources in a rational way and to understand the processes taking place in the environment is one of main means for investigating ecosystems (Grason et al., 1992; Taylor et al., 1999).

The use of mathematical models provides a possibility to describe the processes of water runoff and water quality, to establish the state of a water ecosystem and to forecast water quality. This is impossible to achieve by just analysing the results of water quality monitoring. Using the mathematical models describing the cause and result relationship in water ecosystems, changes taking place in a water body are 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.

Nitrogen leaching models can be divided into two main types: semi-empirical conceptual models and physical dynamic models.

Semi-empirical conceptual models (N-LESS, AGNPS, EVENFLOW, MONERIS) are distinguished for simpler empirical or statistical relationship functions, having a physical background or using only empirical coefficients. Their possibilities to describe the processes of water flow or nitrogen leaching are limited. For this reason these models are mostly used to solve the basic problems of water quality management.

Physical dynamic models (ANIMO, DAISY, EPIC, SOILNDB, SWAT) are used mainly to small-scale objects, or a catchment is divided into subcatchments, each of them being modelled separately. Nitrogen leaching from soil is simulated by separately modelling water flow in soil and the nitrogen cycle in soil and plants.

Mathematical modelling and selection of an appropriate model alleviate a proper evaluation of the extent and importance of the impact of anthropogenic activities and elaborating the optimum river basin management plan to improve water quality.

The objective of our work was to adapt a mathematical method in analysing nitrogen pollution sources and proportions within the Mūša river catchment. The conceptual FYRIS model was chosen to identify the impact of the sources of pollution with total nitrogen in the Mūša river. This model was proposed in 1996 by H. Kvarnas for the Swedish river Fyris (Kvarnas, 2000). Later on it was developed and in 2004 adapted to quantify nitrogen load from various pollution sources, as well as its retention in streams and lakes in medium and large river catchments.

MODEL DESCRIPTION

The dynamic FYRIS model calculates the 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, up-take 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, *kvs* (retention parameter, m / year) and c_0 (temperature parameter, dimention 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, runoff and point source discharges, and time-independent data, e. g. land-use information, lake area and stream length and width (Fig. 1).

Part of nutrients due to sedimentation, uptake by plants and denitrification are retained as they flow 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 expressed by the coefficient R of nitrogen retention in the catchment:

$$R = \frac{T_a \cdot kvs}{q_s + kvs}, \tag{1}$$

where kvs is an empirical coefficient and T_a is a temperature adjustment factor given by:

$$T_a = \begin{cases} 0, & T < 0 \\ c_0 + \dfrac{T(1 - c_0)}{20}, & 0 \le T \le 20 \\ 1, & T > 20 \end{cases} \tag{2}$$

where T is water temperature and c_0 is an empirical calibration parameter. The parameter c_0 determines how strongly the retention is reduced by temperatures below 20 °C.

Furthermore, the hydraulic load, q_s, is given by

$$q_s = \frac{Q}{A_{lake} - A_{LM} + A_{stream}}, \tag{3}$$

where A_{lake} is the total surface area of all lakes in the subcatchment, A_{LM} is the area of the lake treated in a separate lake module (in case it exists in the subcatchment), and A_{stream} is the surface area of all streams in the subcatchment.

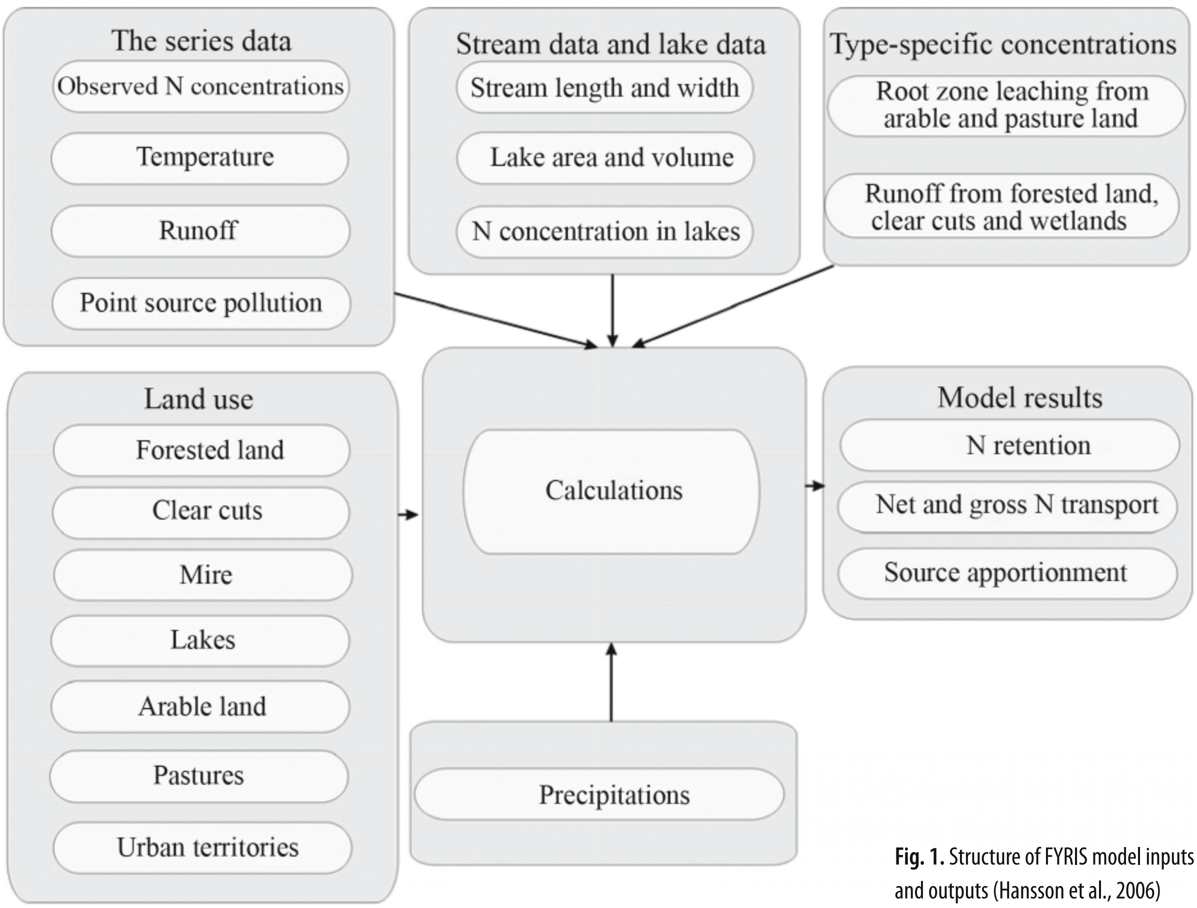

Fig. 1. Structure of FYRIS model inputs and outputs (Hansson et al., 2006)

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

To assess the correspondence of the FYRIS model results to the observed ones, two indicators are used: the model efficiency E and the determination coefficient R^2 (Nash, Sutcliffe, 1970). The model efficiency is expressed by the equation:

$$E = 1 - \frac{\sum_{i=1}^{n} \left(\theta_{obs,i} - \theta_{sim,i}\right)^2}{\sum_{i=1}^{n} \left(\theta_{obs,i} - \overline{\theta}_{obs}\right)^2}, \tag{4}$$

where n is the number of observations, $\overline{\theta}_{obs}$ is the mean of all observations, and $\theta_{obs,\,i}$ and $\theta_{sim,\,i}$ are the observed and the modelled N concentrations, mg l^{-1}.

$E = 1$ indicates that the observed and the modelled data coincide ideally. $E = 0$ implies that the modelled data are a straight line and coincide with the mean value of the observed data.

OBJECT

The Mūša catchment, belonging to the Lielupė RBD in the northern part of Lithuania, was chosen for the investigation. Agricultural land prevails in this catchment (Table 1). Arable land accounts for 63% of the catchment territory. The entire Mūša catchment was divided into seven smaller subcatchments (Fig. 2). State water quality monitoring posts are located at the mouths of all the rivers studied.

The state monitoring data of 1997–2006 were used to run the model. Data on water discharge were obtained from the

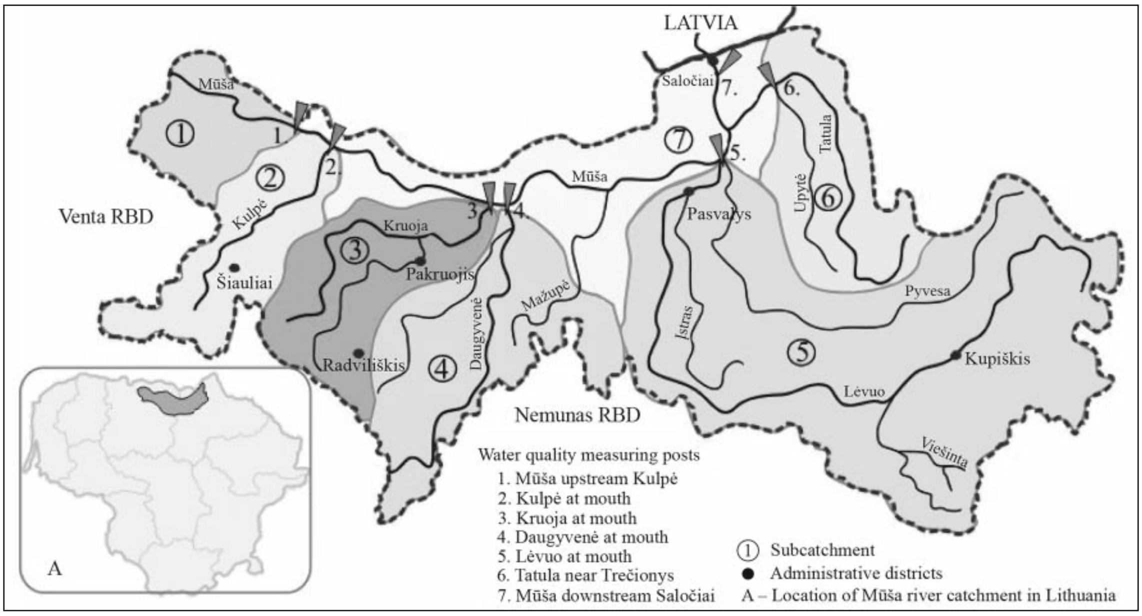

Fig. 2. Subcatchments of the Mūša river basin and water quality monitoring posts

Table 1. **Characteristics of analysed subcatchments**

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

Lithuanian Hydrometeorological Service and water quality data from the Environmental Protection Agency.

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

RESULTS AND DISCUSSION

Reliability of modelling results. Upon systemizing the entry data, a model of the Mūša catchment was made. The modelling included a period of ten years (1997–2006). The calibration of FYRIS model was carried out by changing the empiric calibration coefficients c_0 and *kvs*. During the calibration process, it was established that the most appropriate c_0 value was $c_0 = 0.34$ and the coefficient $kvs = 2.92$. After calibration, the model efficiency coefficient was $E = 0.46$, i. e. more than substantially good, and the correlation coefficient $r = 0.69$.

Having completed the calibration of FYRIS model for the Mūša river basin the time series and observed versus simulated charts for all subcatchments were drawn (Figs. 3, 4).

The simulated versus the measured nitrogen concentrations during the study period (1997–2006) did not correspond equally well in all subcatchments. In the beginning of the study period (1997), the modelled concentrations were higher compared to the observed ones in five out of seven subcatchments (except the Mūša upstream the Kulpė and the Kulpė). Besides, nitrogen concentrations higher than the observed ones were simulated in all rivers except the Kulpė in the second half of the study period, i. e. in 2003 and 2006. In the whole ten-year study period, an exceptional year was 2000, when the observed nitrogen concentrations were among the highest (Fig. 3). The observed nitrogen concentrations were much higher compared with the levels achieved by modelling in this particular year.

One of the main reasons for such a mismatch between model and monitoring data can be extensive outliers of the monitoring data. This happens due to the fact that momentary monitoring samples taken once a month for analyses are considered a monthly mean. The momentary samples taken once a month cause accidental mistakes. In order to achieve an accurate mean value of monthly concentration and to avoid mistakes, water samples must be taken much more often.

To assess the reliability of results and to establish a statistical relationship between the variables, the determination and correlation coefficients were calculated (Table 2). Statistical calculations revealed a strong relationship between the observed and the modelled nitrogen concentrations. When comparing the results of modelling and monitoring, more extensive data distribution and mismatch were found only in the Kulpė river (Table 2). In this river catchment, the determination coefficient of the relationship equation $R^2 = 0.34$ was one of the lowest and the established correlation depend-

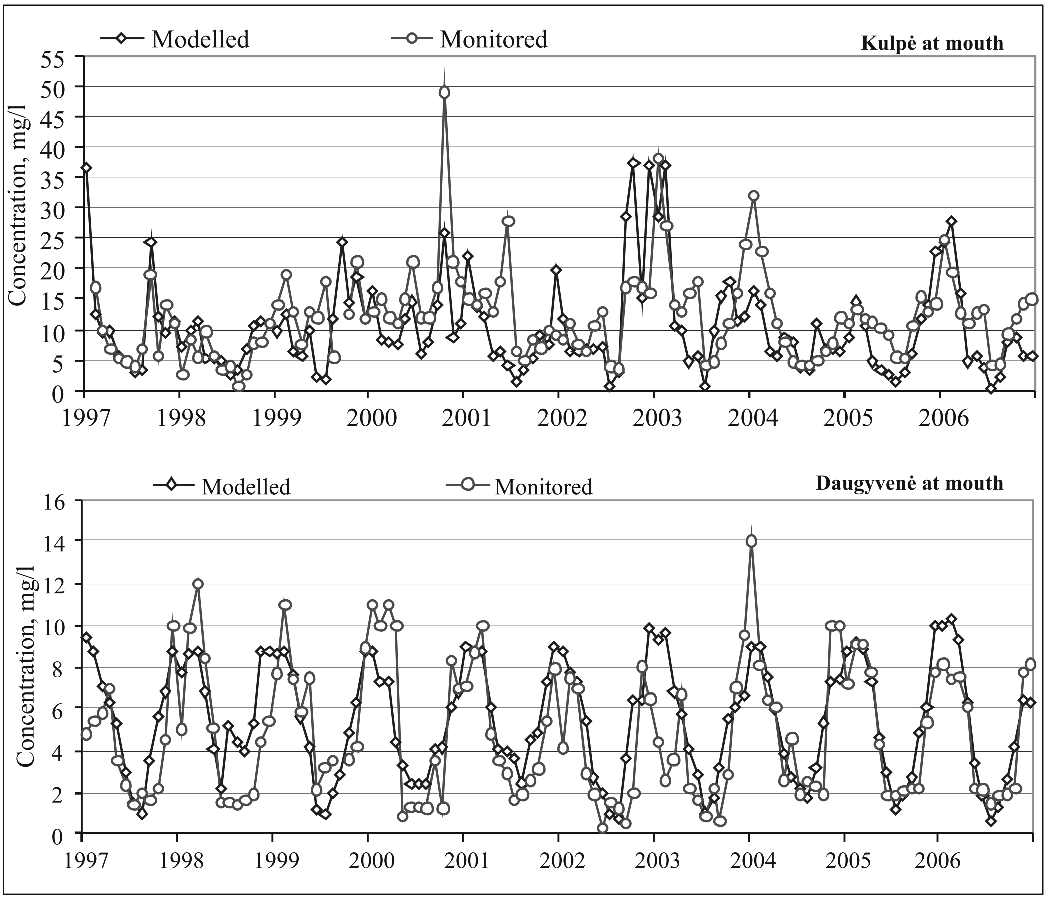

Fig. 3. Time series simulation of nitrogen concentration in the Mūša river subcatchments

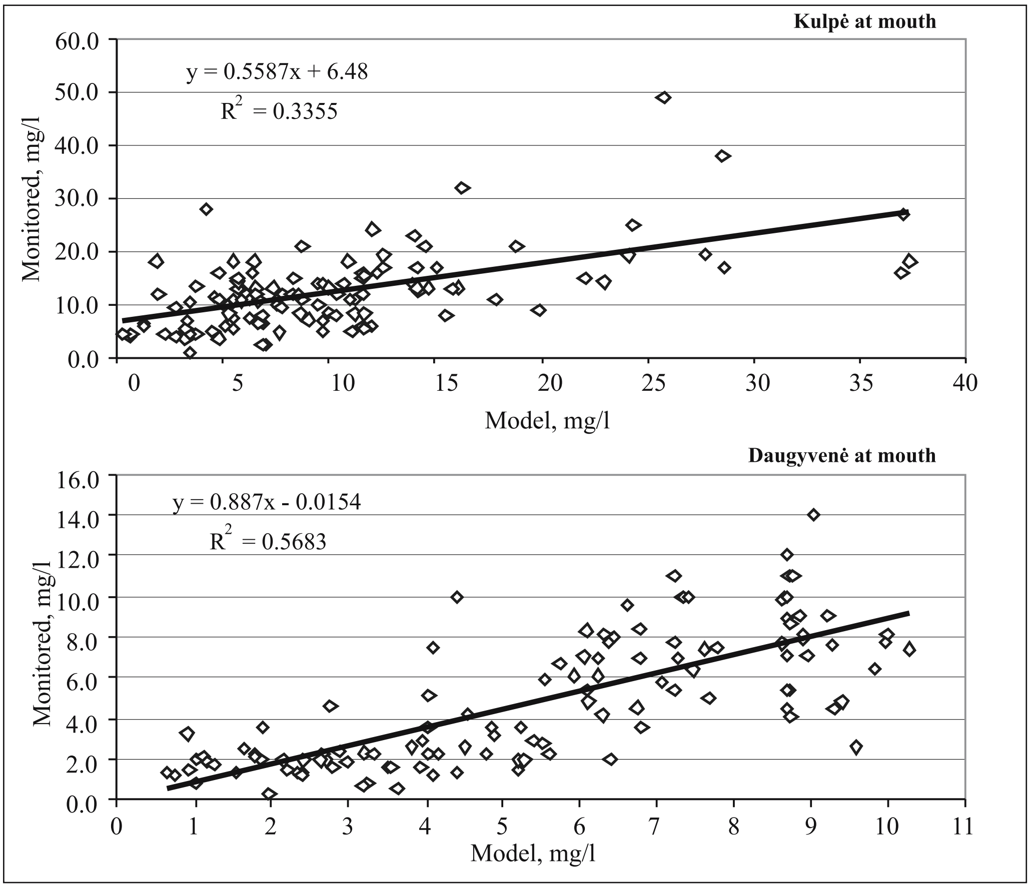

Fig. 4. Simulated versus observed nitrogen concentrations for the Mūša river subcatchments

Table 2. **Regression equations of observed versus modelled nitrogen concentrations and correlation coefficients (mg/l)**

Post No.	River	Equation	Determination coefficient, R^2	Correlation coefficient, r
1	Mūša upstream Kulpė	y = 1.19x – 0.45	0.47	0.69
2	Kulpė	y = 0.56x + 6.48	0.34	0.58
3	Kruoja	y = 0.81x + 0.33	0.43	0.65
4	Daugyvenė	y = 0.89x – 0.02	0.56	0.75
5	Lėvuo	y = 0.71x + 1.61	0.41	0.64
6	Tatula near Trečionys	y = 0.94x – 0.86	0.48	0.69
7	Musa downstream Saločiai	y = 0.95x – 0.54	0.54	0.73

ence $r = 0.58$ was of an average strength. During the ten-year period, the fluctuation amplitude of the observed nitrogen concentrations varied within a broad range – from 0.7 to 49.0 mg/l. Higher fluctuations of concentrations were determined in the small Kulpė catchment (262.96 km^2) because small catchments are very sensitive to the impact of natural and anthropogenic factors. Also, during the study period, the reconstruction and modernization of the sewage treatment plant were carried out in the Šiauliai city. As a result, sewage was started to treat biologically, with an additional removal of nitrogen and phosphorus.

In certain years, the model reflected the data obtained in the Mūša, Daugyvenė and Tatula rivers rather precisely. The determination coefficients of the regression equation varied from $R^2 = 0.48$ to $R^2 = 0.56$. A linear correlation between the modelled and the observed results was about 1.5 times higher in these rivers compared to the Kulpė.

Transport and retention of nitrogen. The qualitative part of the FYRIS model allows a rather accurate assessment of the transport and retention of pollutants in the Mūša catchment. The concentrations of pollutants show the level of pollutants, nitrogen in this case, and the load assesses the extent of pollution. As the load is a product of chemical concentrations and river discharge, its value is immediately related with the variation of river discharge.

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

The highest load of total nitrogen from the WWTP in the Mūša catchment (Fig. 5) was observed in 1997 (450 tons, i. e. by 106 tons higher compared with the long-term mean level (344 t).

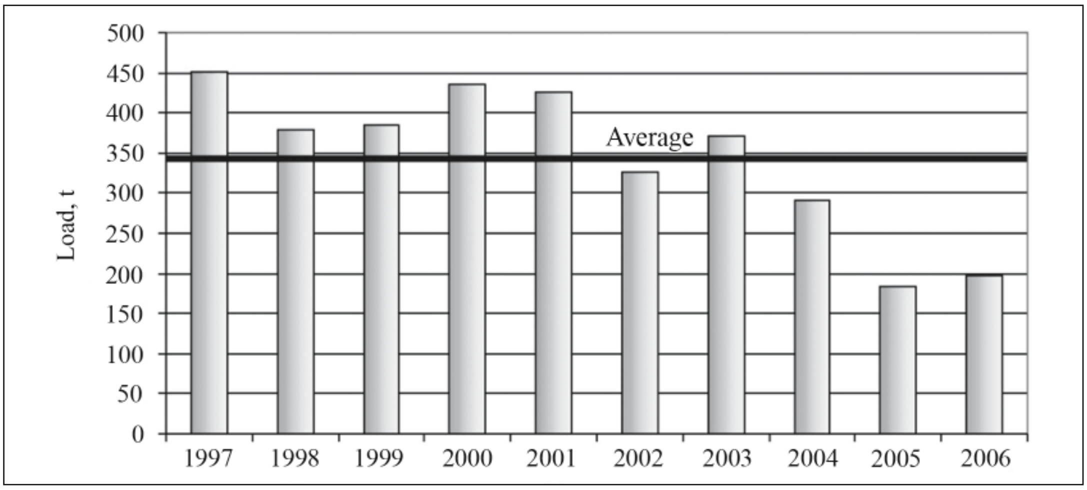

Fig. 5. Dynamics of nitrogen loads from waste water treatment plants and urban territories

Later, in 1998 and 1999, loads from the WWTP decreased by more than 70 tons. However, in 2000 and 2001 they increased again and approached the level of 1997. Since 2003, nitrogen loads in the catchments deceased considerably and did not exceed 300 t. Although point source pollution makes a considerable influence on water quality, the majority of pollutants, especially nitrogen, come 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 58665 t of nitrogen leached to surface waters. Meanwhile, only 4597 t of total nitrogen passed from concentrated pollution sources and urban territories. Analysis of total nitrogen pathways to the Mūša catchment from different pollution sources showed that on average 87% of it came from arable land, 10% from the WWTP, households and urban territories, and only about 3% of all nitrogen in the catchment came from wooded territories and pastures (Table 3). Agricultural land takes up more than a half of the Musa catchment territory, accordingly, water pollution depends on farming culture and land use. As mentioned before, the modelling performed showed that the largest amount of nitrogen came to all subcatchments from arable land (Table 3).

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, implying that the portion of total nitrogen from point source pollution entering the Kulpė is much greater than in other rivers because sewage from both smaller Šiauliai enterprises and the 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 territories in which intensive agricultural activities take place.

A reduction of nitrogen load from arable territories could be most probably expected upon applying Good Agricultural Practice and appropriate environmental measures.

The modelling results showed that during the study period the largest part of nitrogen (0.41) was retained in the river Kulpė catchment (Table 4). This catchment is distinguished from the others because it includes a lot of water bodies, a dense hydrographical network and Lake Rekyva which is the biggest one in the entire catchment. The least part of nitrogen was retained in the Mūša catchment downstream Saločiai.

The model distinguishes the main pollution sources, calculates their loads and retention in river catchments. Efficient preventive measures can be elaborated after an appropriate assessment of these results. It is relevant to construct various model scenarios of reducing nitrogen discharge to the river

Table 3. **Total nitrogen (%) load from different sources during the 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 catchments	86.5	1.9	1.4	1.7	8.5

Table 4. **Calculated nitrogen load and its retained part in each subcatchment**

River	Load at sources, t	Load at river mouth, t	Retained part
Mūša upstream Kulpė	3898	3306	0.15
Kulpė	5756	3373	0.41
Kruoja	4973	3774	0.24
Daugyvenė	6367	4992	0.22
Lėvuo	18283	13967	0.24
Tatula near Trečionys	5830	4908	0.16
Mūša downstream Saločiai	21819	20137	0.08

Mūša. One of the scenarios can be increasing pasture areas at the expense of arable land. It is also relevant to establish how much nitrogen pollution would decrease upon reducing its emission from the WWTP.

CONCLUSIONS

1. After calibration, the FYRIS model efficiency was sufficiently good (E = 0.46) and the correlation coefficient was r = 0.69.

2. The modelled nitrogen concentration rather precisely reflects the data observed in the Mūša, Daugyvenė and Tatula rivers. The determination coefficient R^2 of the regression equations varied from 0.48 to 0.56.

3. The mismatch of the simulated and the observed results was more extensive only in the Kulpė river. There, the determination coefficient of regression equation R^2 = 0.34 was one of the lowest, and the established correlation dependence r = 0.58 was of average strength.

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

5. The highest load of total nitrogen from the WWTP was observed in 1997 (450 tons), i. e. by more than 106 tons higher compared with the calculated long-term mean value (344 t). Since 2003, nitrogen loads in the catchment decreased considerably and did not exceed 300 t.

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

7. Increased nitrogen concentrations lead to eutrophication, encouraging the growth of algae and higher plants and thus leading to narrowing the river channel and increasing alluvial water.

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MŪŠOS BASEINO UPIŲ VANDENS TARŠOS BENDRUOJU AZOTU ANALIZĖ

Santrauka

Upių vandens kokybė priklauso nuo daugelio hidrologinių ir antropogeninių veiksnių. Vandens kokybės tyrimams pasirinktas šiaurinėje Lietuvos dalyje esantis, Lielupės upių baseinų rajonui priklausantis Mūšos baseinas. Dirbama žemė užima 63 % baseino teritorijos.

Mūšos upės taršos bendruoju azotu šaltinių poveikiui nustatyti pasirinktas konceptualusis FYRIS modelis. Modeliavimas apima 1997–2006 m.

Atlikus kalibravimą, modelio efektyvumo koeficientas $E = 0,46$ ir buvo daugiau nei pakankamai geras, o koreliacijos koeficientas $r = 0,69$.

Modeliuojant azoto koncentracijų kaitą tiriamuoju (1997–2006 m.) laikotarpiu ne visuose pabaseiniuose modeliavimo rezultatai vienodai gerai atitiko stebėtas koncentracijas. Viena pagrindinių modelio ir stebėjimo duomenų nesutapimo priežastis gali būti didelis stebėjimo duomenų išsibarstymas. Modelis palyginti gerai atspindi Mūšos, Daugyvenės ir Tatulos upių stebėjimų rezultatus. Egzistuoja stiprus modelio ir stebėjimų rezultatų tiesinis koreliacinis ryšys. Ryšio lygties determinacijos koeficientas R^2 kinta nuo 0,48 iki 0,56.

Išanalizavus bendrojo azoto patekimą iš įvairių taršos šaltinių į Mūšos baseiną nustatyta, jog iš žemės ūkio naudmenų į baseiną patenka apie 87 %, iš valymo įrenginių, namų valdų ir užstatytų teritorijų – 10 %, o iš miškingos teritorijos ir ganyklų – vos daugiau kaip 3 % viso baseinui tenkančio azoto.

Raktažodžiai: vandens tarša, azotas, apkrova, upės baseinas, modelis