

# Nutrient Retention in Surface Waters of Lithuania

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## Abstract

The statistical model MESAW was applied to simultaneously estimate export coefficients and retention of nutrients in four Lithuanian river basins (area range: 2,634-6,140 km<sup>2</sup>). The estimated results revealed substantial capabilities to retain nitrogen and phosphorus in river basins: from 67 to 78% of total nitrogen and from 24 to 63% of total phosphorus relative to the input is retained in surface waters. Estimation of retention was found to be larger in lakes: 27-59% for nitrogen and 11-31% for phosphorus. In-stream retention appeared to be much lower and varied from 11 to 15% for total N and from 3 to 12% for total P.

**Keywords:** nutrients, export coefficients, retention, MESAW, river basins

## Introduction

Riverine ecosystems consisting of streams, wetlands, lakes, and reservoirs play an important part in the large-scale sustainable management of surface waters. In Lithuania, different measures were proposed to reduce nutrient inputs into surface waters and to enhance nutrient retention in such systems in order to meet the requirements of the EU Water Framework Directive [1].

When analyzing nutrient exports from river basins, a quantitative knowledge of retention is needed, especially if export from non-monitored diffuse sources of nutrients is to be determined [2]. Nitrogen and phosphorus discharges from anthropogenic and natural sources are affected by temporary and more permanent sinks, as well as by cyclical and removal processes (e.g. denitrification and sedimentation in streams, lakes, and reservoirs, and on flooded riparian areas). These river systems' internal retention processes should be taken into account in order to assess the relative importance of the discharges of nitrogen and phosphorus from different sources. If the retention is not considered in the riverine load apportionment quantification, the initial nitrogen and phosphorus loss from diffuse sources will be underestimated.

In earlier studies, only data on lakes were included in estimations of nutrient retention in river basins [3]. However, various investigators [4, 5] indicate that the assumption that retention process can be neglected in river systems is in general wrong. For nitrogen, it has been shown by many studies that substantial losses of nitrogen occur also in rivers [6-10]. Small streams have recently been recognized as effective nutrient transformers and sinks in the basin because of their advantageous ratio of water volume and sediment surface [11, 12]. Measured denitrification rates in rivers are often higher than in lakes [13], and the sum of phosphorus inputs to a river system is higher than the observed transport. Based on the cited studies, it can be concluded that both lakes and river networks influence nutrient retention, although such information is scarce for the Baltic States.

Simplified models addressing the problem of water quality are proposed in the literature and based on the export-coefficient approach [14-16]. This approach is based on the idea that nutrient load exported from a basin is the sum of the losses from individual sources and on the assumption that specific land use will yield characteristic quantities of nutrients to a receiving water body. However, reports have also indicated large differences in export coefficients for the same land-use categories [17-19] and, in Lithuania, export coefficients have been shown to vary in

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different regions [20, 21]. Hence, it is clear that export coefficients must be estimated for each region on the basis of available measurements.

The objectives of the present study were as follows:

- (i) to estimate export coefficients for different types of land use
- (ii) to assess retention relative to nitrogen and phosphorus inputs at a river basin scale
- (iii) to distinguish between retention in lakes (including reservoirs) and that in the stream network.

To achieve those goals, the statistical model MESAW was used to evaluate nitrogen and phosphorus export coefficients and retentions in surface waters of four basins in Lithuania.

### Study Areas and Data

The study was done in the Merkys (MER), Mūša (MUS), Nevėžis (NEV), and Žeimenė (ZEI) River basins (Fig. 1). The analyzed areas belong to the Baltic Sea basin and cover 28.2% of the total area of Lithuania. The basins represent diverse soil, land use, hydrology, and nutrient load conditions. Characteristics of river basins related to the period of modelling 1995–2006 (2000–06 for ZEI) are summarized in Table 1.

The mean annual amount of precipitation in the north and middle located river basins (MUS and NEV) is similar, while it is slightly higher in the southeastern basins (MER and ZEI). In addition to the increased precipitation, the

southeastern basins show a spread of highly water-permeable sand and sandy loam soils that absorb snow and rainwater, thus the values for specific runoff and base flow index (ratio of mean annual 30-day minimum runoff to mean annual runoff) are highest at MER and ZEI and much lower at MUS and NEV. The basins also differ in the presence of standing water bodies: there is a large system of interconnected lakes (surface area >0.5 ha) at ZEI (number=479), numerous individual lakes at MER (number=175) and artificial reservoirs (surface area >5 ha) at NEV (number=107). The MUS basin is distinguished for the least number of lakes and reservoirs (38 and 54, respectively). The ZEI basin is one of the largest lake-dominated river basins in the country. Along with runoff characteristics this strongly influences hydraulic load (defined as the annual runoff divided by the water surface area) in the basins.

The land cover in the MUS and NEV river basins is dominated by agricultural land, while the MER and ZEI are largely forested and where intensive farmland varies in between 17 and 21% of the total area. The MUS and NEV basins represent typical fertile lowland areas with river systems of small amplitude in altitude and low flow velocities. In the last century large-scale land reclamation measures were applied there in order to provide areas for agriculture. Consequently, artificially drained areas (mainly tile drained) make up to 63% of the total area in the NEV and 72% in the MUS. The waters in the ZEI and MER basins flow across hilly forested areas that are less affected by human activity. Only the upper and middle reaches of the

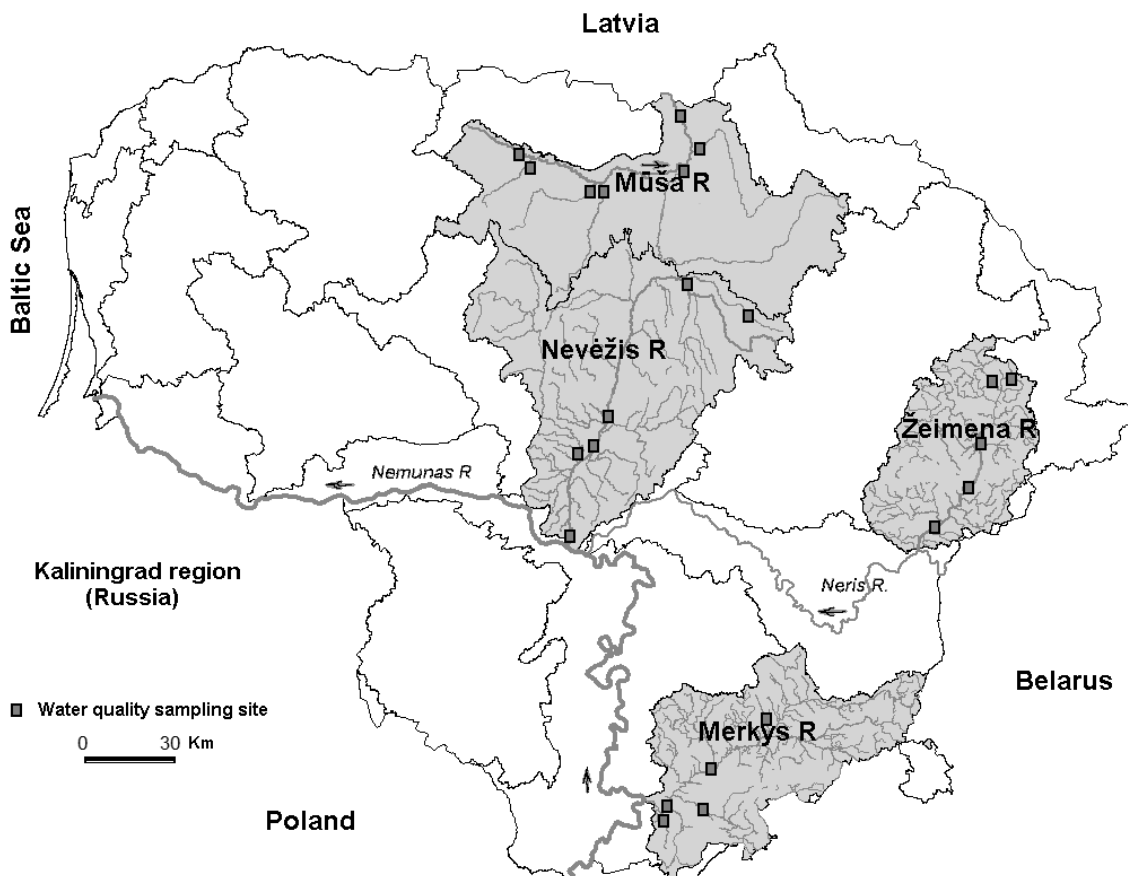


Fig. 1. Location map of river basins within Lithuania.

Table 1. River basin characteristics.

Characteristic	MER	MUS	NEV	ZEI
Total area, km <sup>2</sup>	4416	5462	6140	2793
Artificially drained area %	14.4	71.3	62.5	12.6
Area above the lowest downstream water quality sampling site, km <sup>2</sup>	4259	5296	6140	2634
Mean annual precipitation, mm	720	630	640	730
Mean specific runoff, l/s km <sup>2</sup>	7.2	3.6	4.8	7.9
Hydraulic load of surface waters, m·yr <sup>-1</sup>	24.3	14.7	27.0	3.7
Baseflow index	0.658	0.125	0.046	0.628
Land cover %				
Arable land	17.0	66.5	59.9	20.5
Forest	56.9	21.7	28.6	54.2
Wetlands	8.3	0.61	0.64	1.31
Pastures and meadows	13.7	5.4	7.3	15.4
Lakes and reservoirs/streams	0.82/0.21	0.94/0.20	0.43/0.20	6.8/0.19
Population density, inhabitants/km <sup>2</sup>	16	36	25	20
Soils %				
Sand	60.1	12.8	11.1	49.4
Loam	8.8	7.9	16.6	28.6
Clay	0.00	12.8	0.54	0.42
Peat	11.4	3.6	3.6	8.7
Mean slope of the main watercourse/mean watercourse slope of tributaries, m·km <sup>-1</sup>	0.67/1.86	0.48/1.08	0.35/1.14	0.62/1.43
Flow-weighted concentrations at the lowest sampling site:				
N <sub>tot</sub> , mg·l <sup>-1</sup>	1.525	4.471	4.211	0.962
P <sub>tot</sub> , mg·l <sup>-1</sup>	0.101	0.134	0.196	0.053

basins experience influence from agriculture and urbanization. In all the basins discharges from municipal wastewater treatment facilities are the largest point source contributors of nutrients.

Monthly water quality sampling data of total nitrogen (N<sub>tot</sub>) and total phosphorus (P<sub>tot</sub>) from 23 sites for the period mentioned above were used in this study. The sampling and chemical analyses were done by the Lithuanian Environment Protection Agency. The same institution also provided with digital information for delineation of sub-basins and a database on atmospheric deposition and the point source emissions from 368 sites (32, 124, 167, and 45 in MER, MUS, NEV, and ZEI basins, respectively). The load from atmospheric deposition was set to 9.5-10.0 kg·ha<sup>-1</sup> for N and 1.0-1.2 kg·ha<sup>-1</sup> for P. The digital CORINE land cover map was used to derive land use statistics for each of the 23 subbasins where the water quality data was collected.

The load of each water quality constituent was calculated as a function of daily concentration of the constituent and stream discharge. Daily concentrations were estimated by

linear interpolation between the values measured at two sampling events. Annual loads were obtained by accumulating the daily load values. Average annual loads for the period 1995-2006 were further used in the MESAW model.

Daily data on precipitation and continuous measurements of water discharge were provided by the Lithuanian Hydrometeorological Service. Daily discharge at the sites that lacked measurements was obtained from linear regression using the data from the most adjacent sites with flow measurements.

The mean annual N<sub>tot</sub> and P<sub>tot</sub> concentrations at the lowest sampling sites showed different relations to runoff (Fig. 2). Significant decreasing trends (p<0.05) for P<sub>tot</sub> at the MUS and ZEI basins suggest an decreasing importance of point sources with increasing flow, while scattered values with no significant trends in the other cases indicate the complexity of processes included in nutrient losses from the basins. The flow-weighted riverine concentrations (Table 1) also reveal that the load of nutrients entering the waters in the MUS and NEV basins is much higher compared to the others.

## Methodology

### Mesaw Model

The MESAW model is a statistical model for source apportionment of the riverine transport of pollutants [22]. The model uses non-linear regression for simultaneous estimation of source strength (i.e. export coefficients to surface waters) for the different land use or soil categories and retention coefficients for pollutants in a river basin. The basic principles and major steps in the procedure are as follows:

- (1) estimation of riverine loads at each water quality monitoring site
- (2) subdivision of the entire drainage basin into subbasins, defined by the monitoring sites for water quality and their upstream-downstream relationships (describing the river system)
- (3) derivation of statistics on e.g. land use, lake area, point source emissions, and other relevant data for each subbasin
- (4) using a general non-linear regression expression with loads at each subbasin as the dependent/response variable and subbasin characteristics as covariates/explanatory variables.

Load at the outlet of an arbitrary subbasin is estimated from the following general expression [23]:

$$L_i = \sum_{j=1}^n (1-R_{i,j})L_j + (1-R)S_i + (1-R)P_i + (1-R)D_i + \varepsilon_i \quad (1)$$

...where:

$L_i$  – load at outlet of subbasin  $i$

$L_j$  – load at outlet of nearest upstream subbasin  $j$

$R_{i,j}$  – retention on the way from outlet of subbasin  $j$  until outlet of subbasin  $i$

$n$  – number of subbasins located nearest upstream

$S_i$  – total losses from soil to water in subbasin  $i$

$P_i$  – point source discharges to waters in subbasin  $i$

$D_i$  – atmospheric deposition on surface waters in subbasin  $i$

$R$  – retention in subbasin  $i$

$\varepsilon_i$  – statistical error term

The load at each subbasin is decomposed into contributions from sources located in subbasins further upstream (the first term in Equation 1) and contributions from sources located within the subbasin under consideration (the  $S_i$ ,  $P_i$ , and  $D_i$  terms). The parameterization of the model is flexible and can be study-area specific. The model is fitted by minimizing the sum of squares for the difference in observed and estimated loads. In this study,  $P_i$  and  $D_i$  were assumed to be known and  $S_i$  was assumed to be a simple function of land use according to:

$$S_i = \beta_1 a_{1i} + \beta_2 a_{2i} + \beta_3 a_{3i} \quad (2)$$

...where  $a_{1i}$ ,  $a_{2i}$ , and  $a_{3i}$ , respectively, denote the area of arable land, forests, and wetlands (combined area due to the fact that wetlands are mainly located in forested land) and pastures and meadows (combined) in the subbasin  $i$ ; and  $\beta_{1,3}$  are unknown emission/export coefficients for the land use categories. The point source emission,  $P_i$ , and atmospheric deposition,  $D_i$ , were allocated to the respective subbasin.

Nutrients are normally retained temporally or permanently in watercourses. Therefore, retention in the model is expressed as a summary expression for all hydrological and biogeochemical processes that may decrease the transport

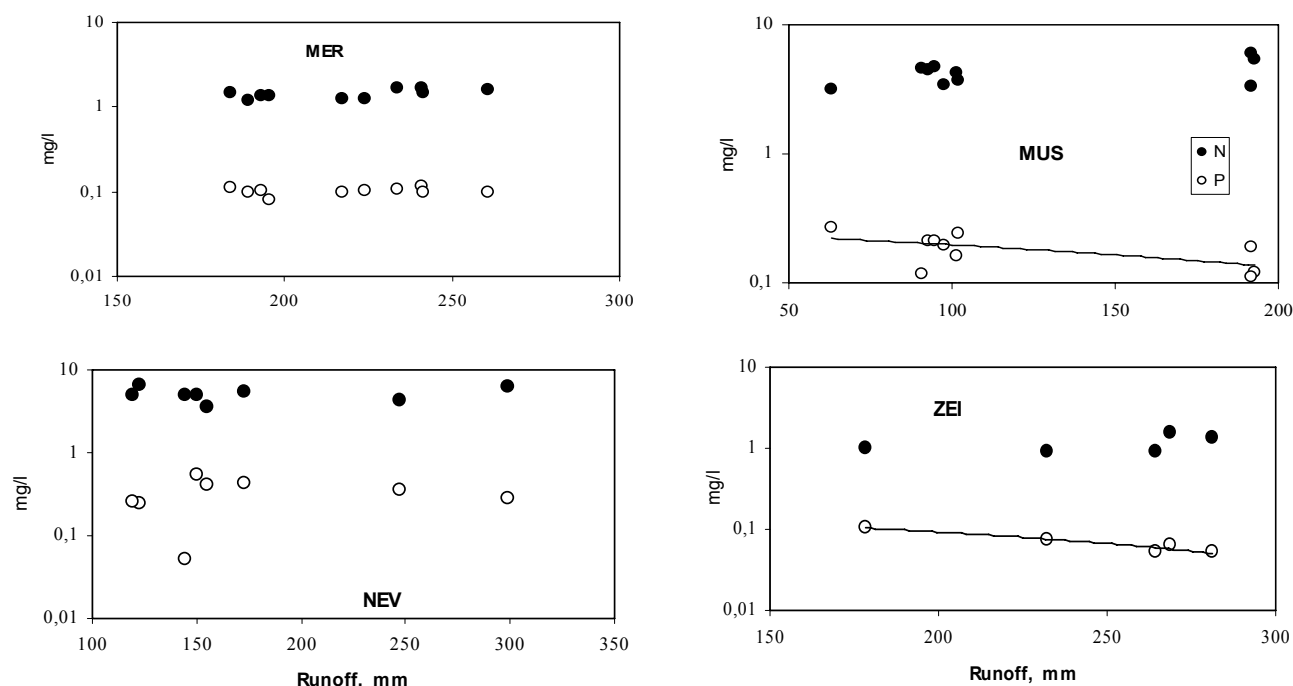


Fig. 2. Scatter plots of measured mean annual  $N_{tot}$  and  $P_{tot}$  concentrations (log scale) against runoff depth at the lowest sampling points of the Merkys (MER), Mūša (MUS), Nevėžis (NEV), and Žeimena (ZEI) basins. Trend lines show significant ( $p < 0.05$ ) relationships.

Table 2. Covariates\* used to estimate nutrient retention.

Type of hydrographic network	Constituent	River basin			
		MER	MUS	NEV	ZEI
Lakes and reservoirs	N <sub>tot</sub>	LS	HL	HL	WA
	P <sub>tot</sub>	LS/WA	LS	HL	A
Rivers and streams (river network)	N <sub>tot</sub>	A	RS	RS	RS/WA
	P <sub>tot</sub>	HL	HL	WS	WS

\*LS/WA – lake and reservoir surface area divided by the total water surface area, RS/WA – river and stream surface area divided by the total water surface area, HL – hydraulic load, LS – lake and reservoir surface area, RS – river and stream surface area, WA – water surface area

or losses of nutrients. It can be parameterized by any empirical function. In this study, the retention was best estimated according to the equation:

$$R = 1 - \frac{1}{1 + (PAR \cdot X)} \quad (3)$$

...where *PAR* is the unknown parameter estimated by the model and *X* is a suitable covariate (i.e. explanatory variable); for example: water surface area, lake surface area, specific runoff, hydraulic load, drainage area of subbasin and etc.

The water surface area (*A<sub>s</sub>*, km<sup>2</sup>) in a river basin can be calculated using the total area of all lakes and reservoirs (*A<sub>Lake</sub>*, km<sup>2</sup>) shown in the CORINE land cover map, and the stream (river network) surface area obtained by applying the equation proposed by Behrendt and Opitz [7]. The mentioned equation was slightly modified under Lithuania's conditions and subsequently adopted to estimate water surface areas in the form:

$$A_s = A_{Lake} + 0.001 \cdot A^{1.10} \quad (4)$$

...where *A* is the total area of the basin (km<sup>2</sup>).

In the MESAW, retention in lakes and river networks can be parameterized separately according to Eq. (3). Therefore, the user can select up to two covariates for retention in this model. In addition to distribution of different land use classes, these covariates serve to explain the observed riverine loads. Table 2 shows the covariates that most suitable to distinguish between the retention in lakes and reservoirs and in river networks. The *PAR* values corresponding to appropriate cases were determined to vary from  $6.80 \cdot 10^{-4}$  to  $1.98 \cdot 10^{-1}$  ( $p < 0.05$ ).

Retention from an arbitrary subbasin *m* to the river mouth *R<sub>m, mouth</sub>* is derived from:

$$R_{m, mouth} = 1 - \prod_{j=1}^k (1 - R_j) \quad (5)$$

...where *R<sub>m, mouth</sub>* is retention from the outlet of the subbasin *m* on the way to the mouth of the whole river; *k* is the number of subbasins downstream sub-basin *m*; and *R<sub>j</sub>* is the values of retention within the different subbasin downstream from subbasin *m*.

Lastly, the estimated export coefficients  $\beta_{1-3}$  and the retention parameters are used to calculate the contribution from each source and sub-basin to the riverine load at the outlet. The advantage of the MESAW model is that the export coefficients and retention are evaluated simultaneously.

### Nutrient Retention Descriptors

Three variables were used to describe N and P retention in surface waters:

- (i) relative retention ( $R_N^r, R_P^r, \%$ ), i.e. the percentage of nutrients retained in surface waters from all basin sources
- (ii) specific retention per area of surface waters in the basin ( $R_N^{Sp}, R_P^{Sp}, \text{kg} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$ ), which expresses the intensity of retention processes in water bodies in relation to hydraulic conditions and nutrient loss processes
- (iii) allocated relative retention in lakes and reservoirs ( $R_N^{LR}, R_P^{LR}, \%$ ) and river network ( $R_N^{RR}, R_P^{RR}, \%$ ) from all basin sources. The latter variable was presented as a covariate-weighted average for each river basin derived from retention in sub-basins under covariates.

## Results

### Estimation of Riverine Loads

Riverine nutrient load during the study period at sampling sites was changing depending on the inputs from the basins and runoff volumes. Fig. 3 presents the comparison between observed and calculated mean annual loads of N<sub>tot</sub> and P<sub>tot</sub> at 23 sampling sites (outlets of subbasins).

The lowest riverine loads of nitrogen were observed in the Žeimena (ZEI) and Merkys (MER) subbasins (from  $30 \cdot 10^3$  to  $630 \cdot 10^3$  and from  $50 \cdot 10^3$  to  $1,450 \cdot 10^3$  kg·yr<sup>-1</sup>, respectively) and the highest ones in the Mūša (MUS) subbasins (from  $360 \cdot 10^3$  to  $5,600 \cdot 10^3$  kg·yr<sup>-1</sup>). The highest transport of phosphorus was determined at the outlets of Merkys (MER) and Nevėžis (NEV) subbasins (from  $2 \cdot 10^3$  to  $100 \cdot 10^3$  and from  $2 \cdot 10^3$  to  $150 \cdot 10^3$  kg·yr<sup>-1</sup>, respectively), while the lowest riverine P<sub>tot</sub> load was measured at the outlets of the Žeimena subbasins (from  $2 \cdot 10^3$  to  $35 \cdot 10^3$  kg·yr<sup>-1</sup>).

Table 3. Export coefficient estimates ( $\text{kg}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$ ).

Land use class	Constituent	River basin			
		MER	MUS	NEV	ZEI
Arable	$N_{\text{tot}}$	13.7	19.2	19.9	10.9
	$P_{\text{tot}}$	0.30	0.14	0.22	0.17
Forest and wetland	$N_{\text{tot}}$	2.53	2.85	3.1	1.9
	$P_{\text{tot}}$	0.20	0.13	0.14	0.13
Pasture and meadow	$N_{\text{tot}}$	3.00	4.9	5.1	2.1
	$P_{\text{tot}}$	0.18	0.14	0.19	0.17

The MESAW model performed well in estimating the loadings. Absolute values of deviation between observed and calculated loads varied from 1 to 15% from the line of equivalence (Fig. 3). The Nash-Sutcliffe coefficient showed 98-99% of modelling efficiency. In turn, the loads of each water quality constituent from each subbasin were set as dependent variables to derive source strength (i.e. export coefficients) and retention.

### Export Coefficients

To estimate the loading contribution for each land use type multiple regression analysis described in the MESAW methodology was applied. The dependent variables were the annual loads of constituents and the independent variable was the land use proportion in each subbasin. The results of the analysis are summarized in Table 3. They represent estimated export coefficients from diffuse sources for the average conditions of three land use classes within the basins. All the coefficients are significant at  $p < 0.05$ . This indicates that the land use categories used as independent variables explained a large proportion of the variability in loadings.

The results showed that the losses of  $N_{\text{tot}}$  from arable land were from 4 to 6 times higher than the corresponding losses from forested land and pastures and meadows. The losses of  $P_{\text{tot}}$  did not reveal the same comparable pattern. The export of phosphorus from arable land was slightly higher compared to the losses from pastures and meadows and

from forested land. Forested areas with an average loss of  $2.6 \text{ kg}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$  of total nitrogen and  $0.15 \text{ kg}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$  of total phosphorus were the least diffuse source contributors of nutrients. The results also showed that the  $P_{\text{tot}}$  export coefficients for all land use classes were significantly below the atmospheric deposition rate. This is likely caused by high phosphorus adsorption capacity, plant uptake, and small phosphorus release from the soil. Significantly higher export values of  $N_{\text{tot}}$  for arable land compared to the atmospheric deposition rates reflect the effect of fertilization.

The highest emission rates of  $N_{\text{tot}}$  from arable land ( $19\text{--}20 \text{ kg}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$ ) and from pastures and meadows ( $4.9\text{--}5.1 \text{ kg}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$ ) were estimated in the the NEV and MUS river basins, where crop and cattle farming is intense and where nitrogen retention processes in the soil are likely reduced due to relatively large tile drainage areas.

In the MER and ZEI river basins the estimated emission rates of total nitrogen from arable land and from perennial grass areas were much lower (40% on average) compared to those in the NEV and MUS. Although mean annual amounts of precipitation are higher in the MER and ZEI, these basins have been significantly less affected by artificial drainage because they lie over the sandy aquifer outcrops. Therefore, higher amount of precipitation can infiltrate and consequently larger quantities of nitrate-nitrogen can be temporary stored or removed by denitrification in these basins.

Comparatively higher (1.4-2.0 times) emission rates of total phosphorus from arable land in the MER basin can be

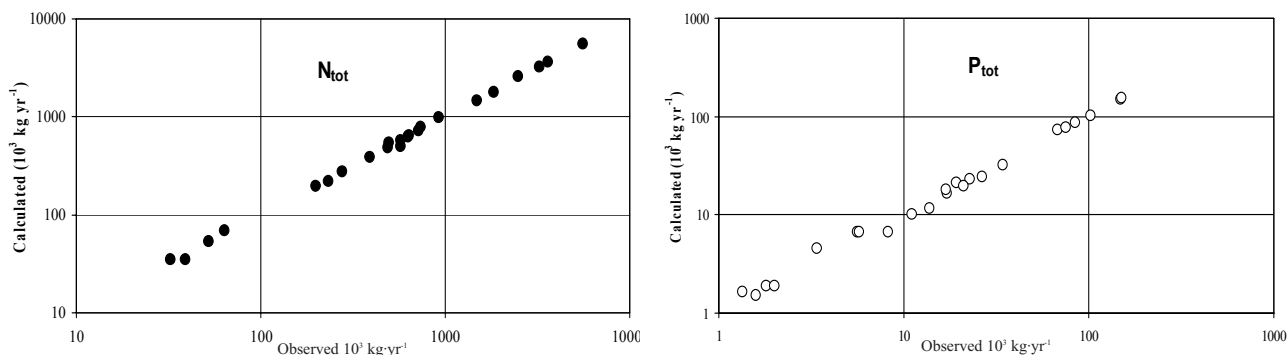


Fig. 3. Observed load of total nitrogen and total phosphorus against calculated values (log scale).

Table 4. Values of  $k_{EC}$  used in Equation 6.

Constituent	Arable land	Forest and wetland	Pasture and meadow
Nitrogen	0.0729	0.0176	0.0160
Phosphorus	0.0014	0.000781	0.00077

Table 5. Estimated nutrient retention values.

Variable	River basin			
	MER	MUS	NEV	ZEI
$R_N^r$ , %	77.8	72.2	66.7	72.9
$R_P^r$ , %	23.5	40.9	44.1	62.8
$R_N^{Sp}$ , kg·ha <sup>-1</sup> ·yr <sup>-1</sup>	1174	1249	1885	92
$R_P^{Sp}$ , kg·ha <sup>-1</sup> ·yr <sup>-1</sup>	7.2	8.8	31.8	3.0
$R_N^{LR}$ , %	59.0	27.6	27.2	48.6
$R_P^{LR}$ , %	11.3	27.2	12.5	31.1
$R_N^{RR}$ , %	14.6	11.8	14.5	11.3
$R_P^{RR}$ , %	3.3	11.5	10.9	9.8

explained by the steeper slopes and higher precipitation amount that increases the washout of soil particles and loss of phosphorus in particulate form by erosion.

Although average annual export values are presented in Table 3, analysis of the data showed that nutrient losses depend on the runoff. Therefore, the relationship between the export coefficients of nutrients and the runoff was explored according to the following:

$$EC = EC_{ave} + k_{EC} \cdot (H_{runoff} - H_{ave-runoff}) \quad (6)$$

...where  $EC$  is the export coefficient for runoff depth  $H_{runoff}$ , kg·ha<sup>-1</sup>·yr<sup>-1</sup>,  $EC_{ave}$  is the average annual export coefficient (Table 3),  $H_{ave-runoff}$ =181 mm is the average annual runoff depth, and  $k_{EC}$  is the empirical coefficient (Table 4).

Equation 6 can be applied within the limits of 63-299 mm.

### Nutrient Retention

The estimated  $N_{tot}$  and  $P_{tot}$  retention values in the study basins are presented in Table 5. The relative retention of nitrogen,  $R_N^r$ , did not show any significant difference among the basins and varied within the range 67-78%. This indicates substantial capabilities to retain nitrogen in a hydrographic network. In contrast, the relative retention of phosphorus,  $R_P^r$ , differed significantly among the basins (9-64%). The highest  $R_P^r$  was at ZEI, apparently due to the presence of large area of lakes and reservoirs. The lowest  $R_P^r$  was estimated at MER, likely because of higher (compared

to the other basins) decreases in streambed altitudes along the river network in MER (Table 1), which results in higher flow velocities and, subsequently, weaker possibilities to retain sediment and phosphorus. It is believed that estimated  $R_P^r$  in the NEV and MUS represents typical P retention values in Lithuanian lowland river basins.

Specific retention of nitrogen,  $R_N^{Sp}$  was much higher in the MUS and NEV basins with less lake and reservoir area than in the basins with a large area of lakes (for example ZEI). To a lesser extent the same comparable pattern was repeated for the  $R_P^{Sp}$  values – the highest specific retention of phosphorus was estimated in the NEV. It is believed that these regularities were caused by relatively small water surface area and low flow velocity conditions prevalent in the NEV.

As mentioned above, an attempt was made to distinguish between retention in lakes and reservoirs and in stream networks in each basin. Thus, the results indicated that retention in lakes and reservoirs expressed as  $R_N^{LR}$  and  $R_P^{LR}$  was substantial for both nitrogen and phosphorus. From 27 to 59% of nitrogen and from 11 to 31% of phosphorus were retained in lakes and reservoirs. In-stream retention,  $R_N^{RR}$  and  $R_P^{RR}$ , appeared to be much lower and varied from 11 to 15% for total N and from 3 to 12% for total P, accordingly.

As expected, the highest  $R_N^{LR}$  retention was estimated in the ZEI (high lake and reservoir percentage) and in the MER (large number of small scattered lakes), where N input is relatively small. The  $R_P^{LR}$  value was also highest in the ZEI. This indicates that lake and reservoir percentage clearly had an impact on N and P retention in this basin. The  $R_P^{LR}$  values among other basins were much more variable (from 11.3% in the MER and 12.5 % in the NEV to 27.2% in the MUS) due to variability in the input of P sources and lake (including reservoirs) fraction. Relatively high  $R_P^{LR}$  in the MUS was likely caused by the ability to retain point source phosphorus in Rėkyva (11.8 km<sup>2</sup>), Talkša (0.56 km<sup>2</sup>), and Ginkūnai (0.175 km<sup>2</sup>) lakes surrounding the large urbanized Šiauliai area with a population of 126,000 inhabitants.

The relative retention of nitrogen and phosphorus in river networks  $R_N^{RR}$  and  $R_P^{RR}$ , respectively, did not show any significant differences among the basins, except comparatively low  $R_P^{RR}$ =3.3% for the MER. This, once again, confirmed low capabilities to retain phosphorus in the MER. Low in-stream P retention is expected to be related to the specific hydraulic conditions mentioned above.

### Discussion

The MESAW model based on multiple regression methodology was adopted in this study to estimate nutrient export coefficients and retention in four Lithuanian river basins.

The estimated export coefficients of  $N_{tot}$  for arable land, forest, and pasture and meadow land use categories agree with published values under similar climatic conditions [14,

20, 21, 24-26]. The results from all river basins confirmed the dominance of intensively used arable land on nitrogen and phosphorus exports per area. As elsewhere, the lowest values of export were estimated in forested areas.

Higher diffuse N emissions estimated in agriculture-dominated lowland river basins can be explained by large artificially drained areas that increase nitrate leaching. Tile drainage, which is common agricultural practice to improve moisture and aeration conditions, shortens the residence time of water in the soil and is therefore an important pathway for nutrients into adjacent water bodies. Nitrogen losses are always larger under drained soil conditions compared to undrained ones [27, 28]. Behrendt and Bachor [29] estimated that 47% of the nitrogen and 12% of the phosphorus emissions from the federal state Mecklenburg-Vorpommern (northeastern Germany) to the Baltic Sea originate from tile drainage. At the field scale, annual nitrate-nitrogen losses up to 105 kg·ha<sup>-1</sup> have been measured [30, 31]. The annual leaching rates of 25-101 kg·ha<sup>-1</sup> via drainage systems also have been reported in Lithuania [21, 32, 33]. On the other hand, the significantly higher value of N export coefficient for arable land reflects the effect of fertilization.

The results from this study also suggest that river basins lying over the sandy aquifers can experience less effect of nitrogen leaching because larger quantities of nitrate-nitrogen can be removed by denitrification in those basins. For example, in southern Sweden it was estimated that 48% of the nitrogen losses from arable land is removed during transport to surface waters [34]. Hetling et al. [35] observed that the loss of nitrogen in fertilizers, once they had been spread on the field, by denitrification and volatilization could be about 10-30% of the agricultural input.

The estimated values of diffuse  $P_{tot}$  emissions, 0.13-0.30 kg·ha<sup>-1</sup>·yr<sup>-1</sup>, correspond well to the data from field-scale measurements conducted under different land use conditions in Lithuania [32]. However, the obtained annual exports from the study basins were found to be lower than published data: 0.2-0.8 kg·ha<sup>-1</sup> in different basins of the northern temperate zone [36], 0.5-2 kg·ha<sup>-1</sup> in England [50], and up to 2.5 kg·ha<sup>-1</sup> in Ireland [37]. The differences can be attributed to the lower specific runoff and other characteristics for loading and storage of phosphorus in Lithuanian basins. In general, the soils in Lithuania are poor in phosphorus. Therefore, this results in low risk of phosphorus leaching even in the basins with intense drainage. Nevertheless, loss of phosphorus in particulate form by erosion may be an important component of the riverine phosphorus in the basins where steeper slopes and higher precipitation prevail.

This study confirmed the results from previous investigations that retention in surface waters is higher for nitrogen than for phosphorus. The retention of total nitrogen (67-78% relative to the input) obtained in this study showed it to be higher compared with evaluations made by other authors in basins of similar climatic conditions. Arheimer and Brandt [38] estimated that in Southern Sweden 45% of the annual nitrogen gross load was reduced during transport. Howarth et al. [13] reported nitrogen retention values between 0 and 45% for different European catchments.

Lepistö et al. [17] has determined that of the total N input to Finnish river-systems, 0% to 68% is retained in surface waters, with a mean retention of 22%. The highest retention of N (36-61%) was observed in basins with the highest lake percentages. The lowest retention (0-10%) of N was in basins with practically no lakes. However, Vassiljev and Stålnacke [23] indicate that up to 80% of nitrogen input can be retained in river basins in the Nordic-Baltic region. The study made by Trepel and Palmeri [39] in Germany also shows that nitrogen removal efficiency in river basins varies between 22 and 77%. This implies that nitrogen retention varies greatly and is site-specific. It depends on the size of the water body and flow conditions and is greatly affected by several biogeochemical and physical processes, including plant uptake, denitrification, and sedimentation.

The retention of total phosphorus (24-63%) obtained in this study falls in the range reported in the literature [23, 40, 41].

Information regarding retention allocation between lakes and river network in the Baltic countries is scarce. According to Taminskas et al. [42], the retention of total phosphorus in the lakes of the Dovinė River basin, southern Lithuania, varies between 27 and 56%. Research done in Estonia indicates that 33% of nitrogen and 35% of phosphorus is retained in lakes. The in-stream retention is lower – 11 and 14%, respectively [23].

As stated by Howarth et al. [13], nitrogen retention in lakes in the North Atlantic Ocean region ranges from 20 to 80%. Jansson et al. [43] proposed that productive lakes might remove up to 50% of total N input. Studies carried out in Sweden show 50% retention of total nitrogen in two eutrophic lakes [44]. Regarding in-stream retention, the values change from 2 to 30% for nitrogen and from negative (due to desorption and resuspension processes in streams) up to 60% positive for phosphorus have been reported in the literature [41, 46, 47]. These values are within the variation range of retention obtained in this study (Table 5).

Estimations made in this study also indicate that much more nitrogen and phosphorus is retained in lakes and reservoirs than in river networks. There is no doubt that lakes in the study basins act as nutrient sinks. Regarding in-stream retention, the obtained results suggest that flow conditions are the most important factor that controls nutrient removal. The importance of flow conditions to retain nutrients has been emphasized in other studies, too. Grizzetti et al. [47] pointed out that nutrient removal increases in particular during summer, when low flow and higher temperatures allow higher sedimentation and acceleration of biological processes. They also observed that nitrogen removal by denitrification and settling decreases in deeper channels, where exchange of stream waters with benthic sediments is reduced. Withers and Jarvie [41], after examination of in-stream retention and cycling of phosphorus, have determined that P inputs delivered to streams under high flows will be flushed through without entering the stream biogeochemical pathways. In-stream P retention rates from 10% to over 30% were recorded under a wide range of flow conditions by House [48], while Jarvie et al. [49] recorded up to 60% net retention under low flow in the River Kennet in England.



## Conclusions

Due to its uncomplicated structure, the MESAW model proved to be a simple but reliable tool for simultaneous estimation of nutrient sources and retention in river basins. Moreover, the approach based on implementing export coefficients in MESAW turned out to be useful for estimating the total annual loads of nutrients from diffuse sources to a water body, and hence can be used to estimate the relative contribution of each N and P source to riverine export. The methodology used in the MESAW can serve to quantify riverine load of nutrients from non-monitored areas in particular.

The export coefficients of N and P from all studied river basins showed much higher values from arable land compare to the export from forested land and pastures and meadows. Although the methods used in the MESAW do not indicate the specific mechanisms causing surface runoff and nutrient transport, the derived coefficients can be used to estimate the diffuse source pollution loadings from the major land use classes.

The study also revealed substantial capabilities to retain nitrogen and phosphorus in river basins in Lithuania: from 67 to 78% of total nitrogen and from 24 to 63% of total phosphorus relative to input is retained in surface waters. Estimation of retention was found to be larger in lakes: 27-59% for nitrogen and 11-31 for phosphorus. In-stream retention appeared to be much lower, and varied from 11 to 15% for total N and from 3 to 12% for total P.

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