





# SLOVAK UNIVERSITY OF TECHNOLOGY IN BRATISLAVA

Faculty of Civil Engineering

# Mgr. Cyril Siman

Dissertation Thesis Abstract

Influence of catchment parameters on water quality indicators in selected profile of surface stream







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## ABSTRAKT

Dizertačná práca skúma vzťah medzi parametrami povodia a kvalitou vody v ukazovateľoch celkový dusík a celkový fosfor vo vybranom profile povrchového toku v 20-tich povodiach na území Slovenska.

Metodicky je práca rozdelená na dve časti. Prvý, štatistický prístup, hodnotí vzťah medzi parametrami povodia a kvalitou vody v 15-tich povodiach prostredníctvom Pearsonovho a Spearmanovho koeficientu. Parametre povodia s významným vplyvom na kvalitu vody sú označené ako efektívne parametre. Boli použité v jednoduchom lineárnom regresnom modeli na odhad dlhodobých mediánových koncentrácií celkového dusíka a fosforu v povodiach bez meraných údajov o kvalite vody. Druhý prístup, využívajúci model MONERIS, prezentuje vplyv parametrov povodia na emisie celkového dusíka a celkového fosforu do povrchových vodných tokov v povodiach s rozdielnymi prírodnými ako aj antropogénne podmienenými podmienkami.

Výsledky poukazujú na pozitívnu závislosť medzi koncentráciami celkového dusíka ako aj celkového fosforu a nasledovnými parametrami povodia: podiel urbanizovaných oblastí, ornej pôdy a nepriepustných hornín na celkovej rozlohe povodia, atmosférická depozícia, počet obyvateľov, a bodové zdroje znečistenia. Negatívna závislosť bola potvrdená v súvislosti s týmito parametrami povodia: priemerná nadmorská výška, priemerný sklon, priemerný úhrn zrážok, priemerný prietok ako aj podiel priepustných hornín a lesných areálov na celkovej rozlohe povodia. Vplyv pôdnej textúry ako aj odvodňovacích kanálov na koncentrácie v oboch ukazovateľoch kvality vody bol väčšinou len zanedbateľný.

Na celkovej emisii dusíka sa najviac podieľa podpovrchový odtok, v povodiach s vyšším zastúpením priemyslu a urbanizovaných oblastí, predovšetkým na západe Slovenska, aj bodové zdroje znečistenia. V prípade celkového fosforu je najvýznamnejším zdrojom znečistenia erózia z poľnohospodársky využívaných oblastí, významným prispievateľom je aj difúzny vnos z urbanizovaných oblastí a bodové zdroje znečistenia. V horských oblastiach má dominantný vplyv na celkové emisie fosforu aj podpovrchový odtok. Opatrenia vedúce k zníženiu erózie pôd a vstupu živín z bodových zdrojov sú predpokladom ďalšieho zlepšenia kvality vôd na území Slovenska.

**Kľúčové slová:** parametre povodia, kvalita vody, dusík, fosfor, MONERIS, povrchový tok, Slovensko

# TABLE OF CONTENTS

Introduction			
1	The current state of art		5
2	2 Aim of the thesis		7
3	Mat	erials and methods	8
	3.1	Study area	8
	3.2	The statistical approach	9
	3.3	The MONERIS model's application	10
4	Resu	ılts	12
	4.1	Results from statistical approach	12
	4.2	Results from the MONERIS model application	16
5	Con	lusion	22
References			23
List of author's publications related to problematic of the study 29			

## Introduction

In this thesis, two different methods in order to examine the impact of river catchment parameters on surface streams water quality in selected river catchments in Slovakia have been used. Firstly, it has been used statistical analysis to evaluate influence of selected river catchment parameters on water quality that is in this work expressed by  $N_{total}$  and  $P_{total}$  water quality indicators. Secondly, it has been applied the MONERIS model to demonstrate impact of river catchment characteristics on nutrient emissions, to evaluate the proportion of emission pathways to overall  $N_{total}$  and  $P_{total}$  emissions and in-river nutrient loads.

The thesis is divided into three main parts. The first part is theoretical and it is dedicated to literature overview. The next sections create practical part of the thesis. The second part starts with introducing of the work's goals which is followed by the presentation of the study area, data and methods. The third, the most important, part is dedicated to the results of the thesis. They are first described briefly and after that in more detail also with comparison and discussion with results from other studies. The most important findings and remarks are one more time summarized in work conclusion at the very end of the thesis.

#### **1** The current state of art

The Water Framework Directive (European Community, 2000) defines water quality as the level of deviation from the type-specific 'reference conditions'. Water quality is mostly affected by a combination of anthropogenic as well as natural factors, the relative influences of which change with temporal and spatial scale (Meybeck *et al.*, 1989; Mouri *et al.*, 2011).

To better manage water quality at a catchment scale, many studies have evaluated the influence of catchment characteristics (e.g. land-use types, land-use patterns, morphology, hydrology, soil type, soil texture, soil drainage, and geology) on river water quality (Thornton and Dise, 1998; Jarvie *et al.*, 2002; Meynendonckx *et al.*, 2006; Davies and Neal, 2007; Onderka *et al.*, 2012; Zhou *et al.*, 2017; Elwan, 2018).

In the research of the relationship between water quality and catchment parameters is possible to identify several generations of authors. The first one was already in the early 60s of the 20th century engaged in physical (Kuehne, 1962, 1966; Harrel and Dorris, 1968) and chemical (Hynes, 1960) water quality indicators (e. g. concentrations of dissolved oxygen, temperature and turbidity) and their relationship to some statistical and geomorphological parameters of river

catchment (e. g. area of river catchment or river order). The second generation of authors that published results of their works during the next decade focused on the understanding of the relationships between river catchment parameters and water quality in surface streams as well as on quantification of non-point (diffuse) sources of pollution on water quality in surface streams (Bormann *et al.*, 1969; Likens *et al.*, 1970; Thomas and Crutchfield, 1974; Omernik, 1976; Burton *et al.*, 1977a, 1977b; Correll *et al.*, 1977). The third generation of authors have started to use advantages of remote sensing, geographical information systems and multivariative statistic in order to evaluate river catchment parameters and water quality connections (Osborne and Wiley, 1988; Johnston *et al.*, 1990; Richards and Host, 1994; Richards *et al.*, 1997).

Comprehensive summarization of more factors influencing water quality is possible to find in Giri and Qiu (2016) and Lintern et al. (2018). Several works have focused on research of the relationship between land cover and sediment or nutrient concentrations in surface streams (Hill, 1981; Osborne and Wiley, 1988; Pekárová and Pekár, 1996; Allan et al., 1997; Sylaios et al., 2005). Research on spatial variability of land cover in relation with water quality was published for instance in Allan et al. (1997) or in Basnyat et al. (1999), while mainly research in Sliva and Williams (2001) was focused on comparison of influence of riparian zone and whole catchment characteristics on water quality in surface streams. Some studies investigated in research of the combined impact of climate, geology and human activities on nutrients concentrations and biological activity of organisms in surface streams (Biggs et al., 1990). Relatively great attention has been also paid to the research of the effects of seasonal variability on the concentrations of water quality indicators (Arheimer et al., 1996; Johnson et al., 1997; Sliva and Williams, 2001; Bramley and Roth, 2002; Ahearn et al., 2004). For example in Arhaimer (1996) monthly data on nitrogen concentrations and daily discharge data in the ten year period in twenty small forested catchments in Sweden and Finland was used. Original and actual are also studies dealing with the influence of landscape fragmentation (Rutledge, 2003) and different spatial proximity of land cover categories (Omernik et al., 1981; Tufford et al., 1998; Gikas et al., 2006; Tran et al., 2010) on water quality in surface streams. The increasing negative trend in water quality in relation to increasing activity of human in the landscape as well as in river catchment have been well documented by many authors (Sliva and Williams, 2001; Ngoye and Machiwa, 2004; Gikas et al., 2006; Amiri and Nakane, 2009; Boskidis et al., 2010).

There is a relative lack of studies that have been focused only on the impact of geomorphological or only geographical characteristics on water quality in surface streams. On the other hand, there are some works which have been devoted to examining the relationship between geographical and morphometrical parameters on water quality in lakes (Larson, 1989; Nõges, 2009). In Johnson et al. (1997) authors analysed impact of river catchment area, average slope of river catchment as well as soil texture on water quality in surface streams (see also Richards et al., 1996). Interesting characteristic implemented also in Johnson et al. (1997) was also a standard deviation from an altitude characterizing topographical heterogeneity of the territory. Similar morphometrical characteristic, standard deviation from slope, in relation with water quality was analysed also by authors of the study Sliva and Williams (2001). In this work, the authors also deal with the influence of soil grain size (soil texture) and catchment area on water quality. In the study Fatehi et al. (2015) soils were divided by texture into four categories and so-called hydrologic soil groups have been created (Brakensiek and Rawls, 1983). Besides of that, in this study also classes of geological permeability were created. Impact of above-mentioned physical parameters on concentrations in several water quality indicators was examined together with land use parameter.

# 2 Aim of the thesis

Scientific goal of the thesis is the quantification of the impact of river catchment parameters on water quality in the selected profile of surface stream. To achieve the main goal of study partial targets had to be set:

- a) analysis of river catchment parameters in subbasins of Slovakia with focusing on:
  - natural parameters such as geomorphological characteristics, soil and geology structure or climate,
  - anthropogenically conditioned parameters such as point and nonpoint pollution sources and land cover,
  - b) selection of reference river catchments (with the area in order of tens to hundreds square kilometres) that will represent prevailed proportion of certain morphometrical and anthropogenically conditioned parameters,
  - c) analysis of river catchment parameters in selected reference river catchments with focusing on:
    - natural parameters such as geomorphological characteristics, soil and geology structure or climate,

- anthropogenically conditioned parameters such as point and nonpoint pollution sources and land cover,
- d) proposal of the methodology for prediction of water quality in the selected profile of surface stream in dependence on morphometrical and anthropogenically conditioned parameters,
- e) verification of the methodology on pilot river catchments of mixed type (with different proportion of evaluated parameters),
- evaluation of impact of river catchment characteristics on nutrient emissions, in-river nutrient loads and proportion of emission pathways on overall nutrient emissions by MONERIS model application.

# **3** Materials and methods

Analysis of the impact of the river catchment parameters on water quality is divided into two approaches. In the first approach, the statistical analysis has been used. In the second approach, the MONERIS model has been applied in order to demonstrate impact of river catchment parameters on simulated nutrients emissions, pathways share and in-river loads in selected river catchments within the Slovak territory. The time period on which we have been focused on starts with 2006 and ends with 2017. However, due to data availability, the MONERIS model simulations have been performed only for the last year of the above-mentioned time period -2017.

## 3.1 Study area

For evaluation of the impact of the river catchment parameters on water quality twenty river catchments from different parts of the Slovak territory have been selected based on three conditions as follows:

- the selected river catchments had to meet the definition of a river catchment (see Miklós and Izakovičová, 1997),
- the presence of a water quality monitoring station of the Slovak Hydrometeorological Institute (SHMI) in a given area, the best at the outlet of the river catchment,
- size in the order of hundreds of squares kilometers.

River catchments have been divided into two groups. The first group consists of the river catchments that have been in the statistical approach used as the predictor catchments while in the MONERIS model approach some of them have been used for the evaluation of the model performance (we called them *data catchments*). The second group includes river catchments without water quality

data – it will be estimated based on our analysis (so-called *no data catchment*) (*Figure 3.1*).



Figure 3.1: Localization of water quality measurement points, hydrological stations and investigated river catchments in the Slovak territory.

#### 3.2 Statistical approach

The river catchment parameters that have been used in the statistical analysis of the thesis are divided as follows:

natural parameters:

- mean elevation (m a. s. l.),
- mean slope (%),
- rocks permeability (area of consolidated and of unconsolidated rocks) (%),
- soil texture (area of sandy, loamy, silty and clayey soils) (%),
- long-term (2006 2017) annual and summer half (IV IX) precipitation (mm·y<sup>-1</sup>),
- long-term  $(1981 2010)^{1}$  annual evapotranspiration (mm·y<sup>-1</sup>),
- long-term (2006 2017) annual discharge ( $m^3 \cdot s^{-1}$ ),

<sup>&</sup>lt;sup>1</sup> Since data in the period 2006 - 2017 has not been available we have used mean evapotranspiration in the period 1981 - 2010 provided by SHMI.

- antropogenically conditioned parameters:
  - proportion of urban areas to the total are of the river catchment (%),
  - proportion of agricultural land (arable land, pastures) to the total are of the river catchment (%),
  - proportion of only arable land to the total are of the river catchment (%),
  - proportion of woodland and shrubland to the total are of the river catchment (%),
  - proportion of drained agricultural land to the total are of the river catchment (%),
  - long-term (2006 2017) annual number of inhabitants (inhabitants y<sup>-1</sup>),
  - long-term (2000 2017) annual nitrogen (NH<sub>4</sub>-N + NO<sub>3</sub>-N) atmospheric deposition (mg·m<sup>-2</sup>·y<sup>-1</sup>) (only for nitrogen),
  - total nitrogen as well as total phosphorus emissions (loads) from wastewater treatment plants (WWTPs)  $(t \cdot y^{-1})$ .

For statistical evaluation of the relationship among river catchment parameters and N<sub>total</sub> as well as P<sub>total</sub> concentrations in investigated catchments correlation analysis has been used. Primarily, Pearson's method (Pearson, 1895) using a significance level of  $\alpha = 0.05$  has been used. In order to obtain higher objectiveness of statistical analysis another correlation coefficient has been implemented, namely Spearman's correlation coefficient (Spearman, 1904; Gauthier, 2001). The Spearman's correlation coefficient is defined as the Pearson's correlation coefficient between the rank variables.

Based on correlation analysis, variables that resulted in a p-value less than 0.05 at least in one of the correlation tests (either in Pearson's or in Spearman's correlation) have been selected as an "effective river catchment parameters" that have significant influence on  $N_{total}$  and  $P_{total}$  concentrations. According to this condition (p-value less than 0.05 at least in one of the correlation test), the "effective river catchment parameters" have been used in a simple linear regression model for prediction of long-term concentrations in  $N_{total}$  as well as  $P_{total}$  water quality indicators in five river catchments that we called *no data catchments*.

#### **3.3 MONERIS model application**

The MONERIS model simulates nutrient emissions via individual pathways, proportion of these pathways on overall emissions and also in-river nutrient loads. Out of eleven pathways, nine will be presented in the results of this thesis as follows:

- emissions from point sources (nutrient emissions from WWTPs and industrial sources),
- emissions via atmospheric deposition,
- emissions via surface runoff,
- emissions via agricultural erosion,
- emissions via natural erosion,
- emissions via tile drainage systems,
- emissions via subsurface flow,
- > emissions from urban areas connected to sewer system,
- > emissions from urban areas not connected to sewer system.

In this thesis,  $N_{total}$  and  $P_{total}$  emissions via individual pathways are displayed in kg per hectare per year (kg ha<sup>-1</sup> y<sup>-1</sup>). The proportion of emission pathways is displayed in percentages.

The MONERIS model's performance or efficiency can be assessed by graphical comparison of measured in-river nutrient loads to modelled loads (either in kg ha<sup>-1</sup> y<sup>-1</sup> or in t y<sup>-1</sup>) (Zessner *et al.*, 2011; Wenz, 2016; Pastuszak *et al.*, 2018). This is done using a scatter plot that shows the agreement between modelled (simulated) and measured (observed) loads. Points (values in catchments) are clustered around a 1:1 line (perfect agreement) with two lines indicating 30% overand underestimation. In our investigation, the performance of the MONERIS model is evaluated based on in-river loads in twelve of fifteen data river catchments (Figure 4.4). It is because in modelled year (2017) data on water quality is missing in three river catchments (the Trnávka, the Handlovka and the Štiavnica river catchments). It has been therefore not possible to calculate measured annual total nitrogen and total phosphorus in-river loads in these river catchments. However, for the total phosphorus, the MONERIS model's performance evaluation has been done based on in-river loads only from eleven catchments due to the high uncertainty of some input data in the Krivánsky river catchment.

Characteristics that have been used to statistically assess the MONERIS model's performance are as follows: the coefficient of determination  $(R^2)$ , the Nash-Sutcliffe efficiency (NSE), the RMSE-observations standard deviation ratio (RSR), the percent bias (PBIAS).

#### **4** Results

#### 4.1 Results from statistical approach

The highest Pearson's correlation coefficient between N<sub>total</sub> and some of the river catchment parameters is in the case of proportion of urban areas (%) to the total area of the river catchment ( $R_p = 0.87$ ). Also in total phosphorus WQI, proportion of urban areas seems to be the most influential parameter controlling its concentrations ( $R_p = 0.89$ ). This quite strong positive correlation suggests that with an increasing proportion of urban areas in river catchments also total nitrogen as well as total phosphorus concentrations will be increasing reliably. Another suitable predictor for N<sub>tota</sub> concentrations from land cover categories seems to be the proportion of a able land on total area of the river catchment ( $R_p = 0.77$ ). Also proportion of woodland has obvious impact on water quality but its influence is negative. This has been confirmed in both WQIs (look in Figure 4.1 and 4.2) but tighter relationship has been detected in N<sub>total</sub> WQI. In N<sub>total</sub> WQI, the second highest correlation coefficient is in nitrogen atmospheric deposition (Rp = 0.84). From this relationship is possible to make an assumption that with increasing nitrogen atmospheric deposition also N<sub>total</sub> concentrations in surface streams will be higher. Since data on P<sub>total</sub> atmospheric deposition has been possible to obtain only from literature and we used only one value for all river catchments, it has been not possible to analyze the impact of total phosphorus deposition rate on concentrations in P<sub>total</sub> WQI. Nevertheless, another important parameter that probably controls N<sub>total</sub> as well as P<sub>total</sub> concentrations in surface streams to a high extent has been detected. It is a load (or discharge) of  $N_{total}$  and  $P_{total}$  (both in t y<sup>-1</sup>) from wastewater treatment plants, respectively. In the first case (N<sub>total</sub>), Pearson's correlation coefficient is the fourth highest (Rp = 0.80, only considering positive relationship), immediately after urban areas, nitrogen atmospheric deposition and evapotranspiration. In Ptotal WQI, resulted correlation coefficient is only 0.65 which is still possible proclaimed as a statistically significant at least at significance level  $\alpha = 0.05$ . Furthermore, in P<sub>total</sub> WQI it is the third highest positive correlation coefficient immediately after urban areas and evapotranspiration. The third (in  $N_{total}$  WQI  $R_p = 0.83$ ) and the second highest (in  $P_{total}$  WQI  $R_p = 0.81$ ) positive correlation coefficient belongs to evapotranspiration. A higher positive correlation coefficient than 0.60 in N<sub>total</sub> WQI occurred also in the case of the number of inhabitants and the proportion of unconsolidated rocks on total area of river catchment. In the case of Pttotal WQI (Figure 4.2), also proportion of sandy soil seems to be significantly positively associated with P<sub>total</sub> concentrations but only

using Pearson's correlation coefficient ( $R_p = 0.62$ ;  $R^2 = 0.38$ ; p-value = 0.014). On the other side, analysis of this relationship using Spearman's correlation coefficient not confirmed significant association between the proportion of sandy soil and total phosphorus concentrations in surface streams, at least in our investigated catchments.

On the side of a negative association between  $N_{total}$  and  $P_{total}$  WQIs and river catchment characteristics, the highest correlation in  $N_{total}$  WQI is in the case of mean elevation ( $R_p = -0.82$ ) and annual discharge in  $P_{total}$  WQI ( $R_p = -0.76$ ). In  $N_{total}$  WQI, also summer precipitation ( $R_p = -0.80$ ), mean slope ( $R_p = -0.79$ ), annual precipitation ( $R_p = -0.76$ ), already mentioned woodland ( $R_p = -0.73$ ), annual discharge ( $R_p = -0.66$ ) and consolidated rocks ( $R_p = -0.63$ ) have been associated significantly to  $N_{total}$  concentrations (*Figure 4.1*). In  $P_{total}$  WQI, situation is more complicated but is still possible to claim that significant negative correlation coefficient is at least in the case of mean elevation ( $R_p = -0.74$ ), mean slope ( $R_p = -$ 0.72), summer ( $R_p = -0.69$ ) and annual precipitation ( $R_p = -0.62$ ), woodland ( $R_p = -$ 0.51) and consolidated rocks ( $R_p = -0.48$ ) (the last two only in Spearman's correlation test) (*Figure 4.2*).

In generall, in both WQIs not significant association has been found in the case of soil texture categories and also proportion of drained agricultural land to the total area of the river catchment. In  $P_{total}$  WQI, proportion of sandy soil seems to have a tighter relationship with Ptotal concentrations but this has been confirmed only using Pearson's correlation test. Also correlation analysis between  $P_{total}$  concentrations and proportion of agricultural land is not convincing and it resulted in correlation coefficient only 0.34 ( $R_p$ ) and 0.55 ( $R_s$ ), respectively.

Resulted from correlation analysis, altogether 15 river catchment characteristics that we considered as potentially having a significant influence on concentrations in both water quality indicators ( $N_{total}$ ,  $P_{total}$ ) have been selected. However, in the case of the river catchment characteristic – *total nitrogen and total phosphorus load from WWTPs*, linear regression model has not been used since not for all *no data catchments* this data has been available (in the case of the Radošinka and the Sobranecký river catchments). Thus, linear regression model has been applied for 14 river catchment parameters.

In both water quality indicators, the predicted concentrations are the highest in the Radošinka river catchment. Calculated total nitrogen median concentration in this river catchment is 5.8 mg  $l^{-1}$  with minimum concentration 2.49 mg  $l^{-1}$  and maximum value 7.86 mg  $l^{-1}$ , respectively. In P<sub>total</sub> WQI median

concentration is 0.4 mg  $1^{-1}$  (also the highest from no data catchment) with minimum concentration 0.14 mg  $1^{-1}$  and maximum value 0.47 mg  $1^{-1}$ , respectively. The second highest  $N_{total}$  median concentration occurred in the Ol'šava river catchment (3.8 mg  $1^{-1}$ ) and very similar value we got also for the Sobranecký river catchment (3.7 mg  $1^{-1}$ ). Also in the case of  $P_{total}$  WQI, the second highest value is in Ol'šava but also in the Sobranecký river catchment (0.2 mg  $1^{-1}$ ). The lowest  $N_{total}$  concentration has been calculated in the Biela Orava river catchment (2.1 mg  $1^{-1}$ ) while in the Laborec river catchment second lowest value occurred (2.6 mg  $1^{-1}$ ). It is the same also in  $P_{total}$  WQI, but the lowest value is not only in the Biela Orava river catchment but also in the Laborec river catchment and it is in both cases 0.1 mg  $1^{-1}$  (*Figure 4.3*).



Figure 4.1: Pearson's correlation matrix between independent (catchment parameters) and dependent ( $N_{total}$  concentrations) variables based on data from data catchments.



Figure 4.2: Pearson's correlation matrix between independent (catchment parameters) and dependent ( $P_{total}$  concentrations) variables based on data from data catchments.



Figure 4.3: Estimated total nitrogen and total phosphorus concentrations based on linear regression model for five no data catchments.

#### 4.2 Results from the MONERIS model application

As the first step, the modelled nutrients in-river loads have to be compared to measured loads at water quality monitoring places. In this thesis, we have compared modelled versus measured  $N_{total}$  as well as  $P_{total}$  in-river loads in t y<sup>-1</sup>.

In the case of  $N_{total}$ , the coefficient of determination is 0.79, the NSE 0.79, the RSR 0.46 and the PBIAS about -3 %. It can be therefore concluded that the MONERIS model has been successfully set up and shows a good model performance for  $N_{total}$  WQI. For  $P_{total}$ , the model performance is hardly satisfactory. Deviations are quite large at many comparison sites, especially in the Topl'a, the Hnilec, the Zolná, the Bebrava and the Štiavnica river catchments. In the first two mentioned river catchments, an overestimation of the modelled loads is noticed. Contrarily, in the Štiavnica, the Zolná and the Bebrava river catchments an underestimation of the modelled in-river loads has occurred. Finally, the coefficient of determination is 0.42, the NSE 0.36, the RSR 0.8 and the PBIAS about 6 % (*Figure 4.4*).

Considering all river catchments together, the highest contribution on annual Ntotal emissions has subsurface flow (62.1 %), followed by drainage systems (11.5 %) and point sources (9.0 %). Surface runoff contributes by about 8 % and urban areas not connected to sewer system by slightly more than 4 %. Only small contribution on annual N<sub>total</sub> emissions (less than 4 %) have emission pathways as follows: agricultural erosion, urban areas connected to sewer systems, atmospheric deposition and natural erosion. When we compare individual river catchments, subsurface flow is dominant emission pathway in 17 of 20 river catchments. It is obvious mainly in river catchments located in mountainous regions of the Slovak territory. The highest contribution of subsurface flow emission pathway on annual total nitrogen emissions has been calculated in the Topl'a river catchment. In this river catchment woodlands and grasslands are dominant land cover categories that prevail over arable land and urban areas. Furthermore, loamy soil is dominant soil type and consolidated rocks with bad permeability cover almost 80 % of the catchment area. Contribution of subsurface flow pathway higher than 70 % has occurred also in river catchments as follows: the Rajčianka, the Štiavnica, the Bystrica, the Zolná, the Biela Orava, the Hnilec, the Laborec, and the Sobranecký river catchments. In three of the twenty river catchments, the highest contribution on annual total nitrogen emissions has not been via subsurface flow pathway. For example, in the Mláka river catchment, the most total nitrogen emissions entry surface streams via point sources (~41 %). This is also the case in the Trnávka river catchment where even  $\sim 62$  % of annual total nitrogen emission is caused by point sources. The main reason is the presence of quite a big wastewater treatment plant and also bigger city upstream to water quality measurement point. Point sources contribute on annual N<sub>total</sub> emissions significantly also in the Handlovka river catchment (29.6 %). In contrast, in the Radošinka river catchment, N<sub>total</sub> emissions entry surface streams mostly via drainage systems (59 %). In this river catchment, drained agricultural land accounts for about 17 km<sup>2</sup> which is slightly more than 5 % of the catchment area. It is the highest proportion of drained agricultural land from all investigated catchments. With respect to diffuse sources, in addition to subsurface flow emission pathway, in investigated catchments located in mountainous regions also surface runoff contributes to annual nitrogen emissions to a higher extent. This is possible to see in river catchments as follows: the Biela Orava (18.1 %), the Bystrica (16.7 %), the Laborec (16.0 %), the Slaná (12.8 %), the Sobranecký (11.5 %), and the Rajčianka (11.0 %) river catchments. It has been already mentioned that in the Radošinka river catchment the highest

contribution on annual nitrogen emissions is accounted for drainage systems. This is the second most important emission pathway also in Bebrava river catchment where it contributes by 27.7 %. Possible reason is that the Bebrava and the Radošinka river catchments are located in the same region and they have a similar proportion of drained agricultural land to the total area of the river catchment These catchments are followed by the Krivánsky (17.5 %), the Teplica (16.0 %), the Trnávka (15.7 %), the Ol'šava (15.2 %), the Žitava (15.1 %), the Nitrica (13.1 %), the Sobranecký (12.8 %), the Štiavnica (11.6 %), and the Zolná (8.4 %) river catchments in which drainage systems emission pathway is also second most important contributor of nitrogen emissions in 2017. Negligible contribution have natural erosion and atmospheric deposition pathways. Agricultural emission pathway contributes significantly only in the Radošinka river catchment (15.8 %) and it is also the fourth highest contributor of nitrogen emissions in the Žitava river catchment (7.1 %). The Radošinka river catchment is covered dominantly by agricultural land, mostly by arable land (72 % of the catchment area belongs to agriculture). In the Žitava river catchment the proportion of agricultural land to the total area of river catchment is about 53 %. From urban areas emission pathway, the highest contribution is in the case of not connected urban areas, this is mostly the case in the Mláka river catchment where even 22.6 % of annual nitrogen emission is caused by not connected urban areas.

For the P<sub>total</sub> WQI, the highest contribution on annual emissions has agricultural erosion that accounts for about 36.1 %. The second most important emission pathway is subsurface flow (23.5 %). Less significant are emission pathways as follows: point pollution sources that contribute by 14.1 % on annual total phosphorus emissions and urban areas not connected to the sewer system with 12.6 % contribution. Only negligible contribution have urban areas connected to the sewer system (6.6 %), surface runoff, natural erosion, atmospheric deposition and drainage system (Figure 4.5). The contribution of emission pathways on annual Ptotal emissions is slightly more evenly distributed as in the case of the Ntotal. While for the N<sub>total</sub>, in 17 of 20 river catchments has the highest contribution on annual nutrient emissions the subsurface flow, for the P<sub>total</sub> only in 10 of 20 river catchments is the most important emission pathway agricultural erosion. However, in 6 river catchments, the highest contribution has the subsurface flow and in 4 river catchments even point sources contribute most significantly. Agricultural erosion is absolutely dominant emission pathway in the Radošinka river catchment where it contributes by about 91.0 % on annual Ptotal emissions. The second most

important emission pathway in this river catchment is urban areas not connected to the sewer systems that, however, contributes only by about 4 %. Similar conditions is possible to find also in some other river catchments located in the southwest part of the Slovak territory. This is the case mainly in the Žitava river catchment (emissions via agricultural erosion accounts for 69.1 %) and the Teplica river catchment (55.4 %). From central and east Slovakia also in the Stiavnica and the Ol'šava river catchments, agricultural erosion has a significant contribution on annual P<sub>total</sub> emissions. In the Ol'šava river catchment, it is even 61 %, in the Štiavnica catchment it is 51.8 %. In all of the mentioned river catchments, except for the Ol'šava river catchment, the proportion of agricultural land on the total area of river catchment is higher than 40 %, however, also in the Ol'šava river catchment it is only slightly less than 40 %. The subsurface flow is the most significant emission pathway responsible for most of the annual total phosphorus emissions for example in the Biela Orava river catchment (77.4 %) which is similar to the Bystrica (53 %) and the Sobranecký (51.2 %) river catchments. Point sources have the highest contribution in the Mláka river catchment (50.7 %). which is followed by the Handlovka (48.3 %), the Trnávka (46.2 %) and the Krivánsky (31.9%) river catchments. In some river catchments, also urban areas contribute significantly on annual total phosphorus emissions. In general, the higher contribution have urban areas not connected to the sewer system in comparison with urban areas connected to sewer system. This is, for example, the case in the Mláka river catchment where urban areas not connected to the sewer system is the second most important emission pathway contributing by about 43 %. Similar situation as in the Mláka river catchment is also in the Nitrica catchment where the contribution of not connected urban areas is 24.8 %, more than 20 % contribution is also in the Rajčianka river catchment (20.2 %). In the Hnilec and the Zolná river catchments, also urban areas connected to the sewer system have more than 20 % contribution on annual total phosphorus emissions.



Figure 4.4: Comparison of measured and modelled total nitrogen (upper plot) and total phosphorus (bottom plot) in-river loads in 2017.



Figure 4.5: Proportion of pathways on annual total nitrogen (upper plot) and total posphorus (bottom plot) emissions in all investigated catchments in 2017.

## **5** Conlusion

Statistical analysis has shown that the key factor influencing N<sub>total</sub> as well as Ptotal concentrations in surface streams is the proportion of urban areas to the total area of the river catchment. Apart from urban areas, also the proportion of unconsolidated rocks, proportion of arable and agricultural land, atmospheric deposition, N<sub>total</sub> load from WWTPs, number of inhabitants and evapotranspiration have been positively associated with N<sub>total</sub> concentrations. In contrast, the proportion of consolidated rocks and woodland and also mean discharge, precipitation, mean slope and mean elevation have been significantly negatively associated with N<sub>total</sub> concentrations. The slightly different situation has occurred in the case of P<sub>total</sub> water quality indicator. Using the Pearson's correlation coefficient only proportion of urban areas, evapotranspiration, Ptotal load from WWTPs and proportion of sandy soils have been significantly positively associated with P<sub>total</sub> concentrations. Spearman's coefficient has shown also significant positive influence of unconsolidated rocks, arable land, agricultural land and number of inhabitants. Mean precipitation, mean slope, mean elevation and mean discharge have negative impact on P<sub>total</sub> concentrations according to the Pearson's coefficient. According to the Spearman's coefficient also woodland and consolidated rocks may control P<sub>total</sub> concentrations significantly.

According to the MONERIS model calculation, emissions of both nutrients into surface streams from diffuse pollution sources prevail significantly over point pollution sources. The highest contribution on overall  $N_{total}$  emissions has subsurface flow. Except for subsurface flow, also drainage systems, point sources and surface runoff are important pathways for total nitrogen. Emissions from urban areas and point sources have higher proportion on overall  $N_{total}$  emissions in river catchments with higher proportion of urban areas on the total area of the river catchment. Only low significance have atmospheric deposition and agricultural erosion pathways. In the case of the P<sub>total</sub> WQI, the most important pathway is agricultural erosion which is followed by subsurface flow, point sources and urban areas not connected to sever system. Less significance have drainage systems, surface runoff, natural erosion and atmospheric deposition.

The impact of river catchment parameters has been observable also in the results of the MONERIS model's simulation. The contrast of landscape between river catchments located in mountainous regions of Slovakia and the river catchments in Slovakian lowlands resulted in the contrasting apportionment of emission pathways between these regions. In river catchments located in lowlands

of Slovakia, point sources and drainage systems are important emission pathways for  $N_{total}$ . For the  $P_{total}$ , these are agricultural erosion, point sources, and urban areas. In river catchments located in mountains of Slovakia, the important pathway for  $N_{total}$  is subsurface flow and to some extent also surface runoff. For the  $P_{total}$ , the situation is more complex, but the subsurface flow is also more dominant in the mountainous regions of Slovakia than in the lowlands.

Higher inconsistency in correlation analysis has been shown in the case of  $P_{total}$ . Also the MONERIS model's performance has been lower in the case of the  $P_{total}$  in comparison with the  $N_{total}$ . Nevertheless, by including the sediment delivery ratio in the calculation of sediment input from natural covered land we improved the MONERIS model's performance for the  $P_{total}$ . It resulted in significant decrease of deviations between the modelled and the measured total phosphorus in-river loads.

At the end of this thesis, it is in general possible to issue a recommendation that measures that lead to a decrease of erosion and input of nutrients originating from point pollution sources are a prerequisite of further improvement of surface streams water quality in the Slovak territory.

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# List of author's publications related to problematic of the thesis

# ABC Chapters in scientific monographs published by foreign publishers

<u>VELÍSKOVÁ, Yvetta</u> - SOKÁČ, M. - <u>SIMAN, Cyril</u>. Assessment of Water Pollutant Sources and Hydrodynamics of Pollution Spreading in Rivers. Marek Sokáč, Cyril Siman. In Water Resources in Slovakia: Part I Assessment and Development : The Handbook of Environmental Chemistry. - Berlin ; Heidelberg : Springer International Publishing, 2019, p. 185-212. ISBN 978-3-319-92853-1. ISSN 1867-979X.

# ABD Chapters in scientific monographs published by domestic publishers

<u>SIMAN, Cyril</u> - <u>VELÍSKOVÁ, Yvetta</u>. Zdroje znečistenia povrchových tokov Slovenska a hydrodynamický prístup k transportu znečistenia v tokoch. In Hydrologický výskum v podmienkach prebiehajúcej klimatickej zmeny. -Bratislava : Veda, 2018, s. 344-379. ISBN 978-80-224-1691-7.

# ADEB Scientific papers in other foreign journals not impacted

<u>SIMAN, Cyril</u> - <u>VELÍSKOVÁ, Yvetta</u>. Consumption of fertilizers in districts of Slovakia in the period. In Acta Agraria Debreceniensis - Journal of Agricultural Sciences, 2018, issue 74, pp. 389-398. ISSN 1587-1282.

# ADFB Scientific papers in other foreign journals not impacted

<u>SIMAN, Cyril</u> - <u>VELÍSKOVÁ, Yvetta</u>. Pollution transport in surface streams – elementary terms and principles of modeling (in Slovak). Yvetta Velísková. In Acta Hydrologica Slovaca, 2017, roč. 18, č. 1, p. 39-48. ISSN 1335-6291.

<u>SIMAN, Cyril</u> - <u>VELÍSKOVÁ, Yvetta</u>. Analýza zdrojov znečistenia povrchových tokov na území Slovenska – časť I. Bodové zdroje [Analysis of surface streams pollution sources in Slovakia – part I. Point sources] (in Slovak). Yvetta Velísková. In Acta Hydrologica Slovaca, 2018, roč. 19, č. 1, s. 133-141. ISSN 1335-6291.

<u>SIMAN, Cyril</u> - <u>VELÍSKOVÁ, Yvetta</u>. Analysis of surface streams pollution sources in Slovakia. Part II. Nonpoint sources (in Slovak). In Acta Hydrologica Slovaca, 2018, roč. 19, č. 2, s. 262-271. ISSN 1335-6291.

# AEDA Scientific papers in domestic peer-reviewed proceedings, shorter chapters / articles in domestic monographs or university textbooks

<u>SIMAN, Cyril</u> - <u>VELÍSKOVÁ, Yvetta</u>. Searching for relationship between water quality and catchment parameters in Slovakia territory. In 26. Posterový deň s medzinárodnou účasťou a Deň otvorených dverí na ÚH SAV - Transport vody, chemikálií a energie v systéme pôda-rastlina-atmosféra : zborník recenzovaných príspevkov [elektronický zdroj]. - Bratislava : Ústav hydrológie SAV, 2019, s. 186-199. ISBN 978-80-89139-44-6.

## AFD Published papers at domestic scientific conferences

<u>SIMAN, Cyril</u> - <u>VELÍSKOVÁ, Yvetta</u>. Consumption of fertilizers in agriculture in Slovakia – factor Influencing water quality of surface streams (in Slovak). In 24th International Poster Day and Institute of Hydrology Open Day : proceedings of peer-reviewed contributions. Editor: Anežka Čelková ; recenzenti: Veronika Bačová Mitková, Milan Gomboš, Ladislav Holko, Branislav Kandra, Radka Kodešová, Pavol Nejedlík, Tomáš Orfánus, Kálman Rajkai, Jana Skalová, Peter Šurda, Andrej Tall. - Bratislava : Ústav hydrológie Slovenskej akadémie vied, 2017, s. 245-257. ISBN 978 - 80 - 89139 - 40 - 8.

<u>SIMAN, Cyril</u> - <u>VELÍSKOVÁ, Yvetta</u>. Odhad kvality vody v povrchových tokoch s využitím analýzy krajinnej pokrývky. Yvetta Velísková. In 25th International Poster Day and Institute of Hydrology Open Day : Proceedings of peer-reviewed contributions. - Bratislava : Institute of Hydrology SAS, 2018, s. 129-137. ISBN 978 - 80 - 89139 - 42 - 2.

<u>SIMAN, Cyril</u> - <u>VELÍSKOVÁ, Yvetta</u>. Sources of surface streams pollution in Slovakia. Yvetta Velísková. In Influence of anthropogenic activities on water regime of lowland territory : Proceedings of peer-reviewed contributions. Bratislava ; Michalovce : Ústav hydrológie SAV : Výskumná hydrologická základňa Michalovce, 2018, s. 255-265. ISBN 978 – 80 – 89139 – 41 – 5.

## AFG Abstracts of papers from foreign conferences

<u>SIMAN, Cyril</u> - <u>VELÍSKOVÁ, Yvetta</u>. Use of land cover analysis for estimating the water quality in surface streams. In HydroCarpath International Conference: Catchment processes in regional hydrology: experiments, patterns and predictions : abstracts of the Conference. - Sopron : University of Sopron Press, 2018, s. 43-43. ISBN 978-963-334-199-5.

<u>SIMAN, Cyril</u>. Relationship between land cover and water quality indicators in selected basins of Slovakia (in Slovak). In Zborník príspevkov : 30. konferencia mladých hydrológov [elektronický zdroj]. - Bratislava : Slovenský hydrometeorologický ústav, 2018, s. 1-13. ISBN 978-80-88907-98-5.

<u>SIMAN, Cyril</u> - <u>VELÍSKOVÁ, Yvetta</u>. Agriculture as one of the possible negative factors affecting water quality in surface streams. In HydroCarpath International Conference: Catchment processes in regional hydrology: experiments, patterns and predictions : Abstracts of the Conference. - Sopron : University of Sopron Press, 2017, s. 37-38. ISBN 978-963-359-092-8.

<u>SIMAN, Cyril</u> - <u>VELÍSKOVÁ, Yvetta</u>. Trend in consumption of industrial and organic fertilizers in Slovakia (potential source of surface water pollution). In Abstract book 17th Alps-Adria Scientific Workshop - Conference. - Gödöllő : Szent István Egyetemi Kiadó Nonprofit Kft., 2018, s. 126-127. ISBN 978-963-269-734-5.

<u>SIMAN, Cyril</u> - <u>VELÍSKOVÁ, Yvetta</u>. Land cover analysis as a tool for water resources quality assessment – example study from selected river basins of Slovakia. In Abstract book 18th Alps-Adria Scientific Workshop - Conference. -Gödöllő : Szent István Egyetemi Kiadó Nonprofit Kft., 2019, p. 140-141. ISBN 978-963-269-818-2.

# AFH Abstracts of papers from domestic conferences

<u>SIMAN, Cyril</u> - <u>VELÍSKOVÁ, Yvetta</u>. Consumption of fertilizers in agriculture in slovakia – factor Influencing water quality of surface streams (in Slovak). In 24th International Poster Day and Institute of Hydrology Open Day : proceedings of peer-reviewed contributions. - Bratislava : Ústav hydrológie Slovenskej akadémie vied, 2017, s. 346-347. ISBN 978 - 80 - 89139 - 40 - 8.

# **BEF** Papers in domestic proceedings (conference and non-conference, peer-reviewed and non-peer-reviewed)

<u>SIMAN, Cyril</u>. Agriculture, important source of surface streams pollution] (in Slovak). In Zborník príspevkov : 29. konferencia mladých hydrológov. Bratislava : Slovenský hydrometeorologický ústav, 2017, s. 1-14. ISBN 978-80-88907-94-7.

# In print:

<u>SIMAN, Cyril</u> - <u>VELÍSKOVÁ, Yvetta</u>. Impact of different proportion of agricultural land in river catchments on nitrogen surface streams pollution. In Acta Hydrologica Slovaca, 2020, roč. 21, č. 1, ISSN 1335-6291.