

Investigation of Selected Qualitative and Quantitative Water Parameters Using Correlation Analysis

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Received: 29 November 2016 / Accepted: 19 April 2017 / Published online: 18 May 2017
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Abstract The paper aims at presenting the results of correlation analysis between concentration of pollutants and minimum monthly discharge and minimum daily discharge respectively measured during 38 years. Considered pollutant concentrations were nitrate nitrogen, ammonium nitrogen and biochemical oxygen demand. Their values were measured once a month at three hydrometric stations, i.e., Svit (River Poprad), Košické Olšany (River Torysa) and Ižkovce (River Laborec), in the period from year 1975 till 2013. It was found that the concentration of ammonium nitrogen in the rivers of eastern Slovakia has a decreasing trend but in Torysa river in Košické Olšany, it exceeded the limit value during the whole monitored period. In Torysa river, the concentration of nitrate nitrogen also exceeded the limit value. Concentrations of BOD_5 at all hydrometric stations showed a decreasing trend and a significantly decreasing trend was well visible for hydrometric profiles in Ižkovce (River Laborec) and Svit (River Poprad).

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Keywords Mathematical approach · Minimum monthly discharge · Minimum daily discharge · Pollutant spreading · Water pollution

1 Introduction

Civil and environmental engineers make frequent use of mathematical models to handle free-surface hydraulics problems, such as simulation of river and channel flow, flood prediction, assessment of sediment and pollutant transport. Kerger et al. (2010) presented the need for consistent models to simulate water flows and transport processes. The variation of pollutant concentrations in surface waters shares a broad interest by scientist and researchers in the field of water pollution control. Monitoring of river quality is primarily done to detect the status and trends, but also to identify the causes (natural or anthropogenic) of the trends. The Water Framework Directive (2000/60/EC) demands new approaches in managing and improving surface and groundwater quality across the European Union. The major pressures on the European waters are pollution, scarcity (including droughts), floods, and modification to water bodies. In particular, pollutants of the aquatic ecosystem have their origin in agriculture industry, municipalities and other sources (Tsakiris 2015). A water quality standard refers to a physical, chemical, or biological characteristics of water in relation to a specified use or designated use defined by government numerically or narratively. The term pollution refers to water that has been degraded or defiled in some way by human activities (Kenneth et al. 2013). The source of the pollution requires a whole watershed system thinking approach (point-source and non-point source pollution). Based on monitoring data of 78 monitoring stations from 2003 to 2012, five key water quality indices (i.e., biochemical oxygen demand: BOD_5 ; permanganate index: COD_{Mn} ; dissolved oxygen: DO ; ammonium nitrogen: NH_3-N ; and total phosphorus: TP) were selected to analyze their temporal and spatial characteristics in the highly disturbed Huaihe River Basin via Mann-Kendall trend analysis and boxplot analysis (Dou et al. 2016). The majority of monitoring stations recorded a large fluctuation for the monitoring indices in 2003 and 2004, which indicated that the water quality concentrations were unstable.

Several mathematical and numerical models have been developed to simulate water quality in watersheds and pollutant spreading in streams, e.g.: ZNEC (Říha et al. 2000), MODI (Velísková 1995), SIRENIE (Pekárová and Velísková 1998), and others. The models simulating pollutant transport in open channels require the determination of the dispersion coefficient among other input data. For determination of dispersion coefficient calculated in Velísková et al. (2014), which can be used for future numerical simulation of investigated water stream or a similar one (valid for “transitional” zone primarily) statistical evaluation was used (and other two methods). Two-dimensional modelling of the transport processes is fairly accurate, if applied to shallow waters without strong thermal stratification (Velísková et al. 2014). The science of flow management for the sustainable management of natural ecosystems is complex, as is the technical language used to describe the underlying concepts. The terminology used in environmental flow assessment literature is also variable, and includes terms such as “instream flow needs”, “environmental flows”, and “ecological flows” (DFO 2013). According to Policy summary of CIS guidance document No. 31, it is important to recognize that water quality and quantity are intimately related within the concept of “good status”. This would require an EU-wide acknowledgement of the ecological flows, i.e., the “amount of water required for the aquatic ecosystem to continue to thrive and provide the services we rely upon

(Policy summary of CIS guidance document No. 31. 2015). Environmental flows describe the timing and amount of water that lakes, rivers, streams and estuaries need to sustain natural functions, processes and resilience in harmony with thriving agriculture, cities, and industries (Pitt and Kendy 2017).

Rizo-Decelis and Andreo (2016) characterized the river water quality and recognized some overall pollution sources, using two different information references: a dataset of 5 years from the Jalisco State Water Commission and a 14-year dataset from the National Water Commission. Two zones have been identified as the main sources of pollution. The authors attempted to offer a methodological approach for a more accurate assessment of the river water quality and may assist in interpreting the sampling results derived from the regular monitoring, conducted by the state water authorities, while emphasizing the natural attenuation capacity of the Santiago River.

Indices of water quality, heavy metal pollution and contamination were computed by Abdel-Satar et al. (2017). The values of the most studied variables showed a seasonal pattern of change and remained low during the rainy season with high river flow. Sites located upstream seemed to have the lowest values of various monitored variables, while anthropogenic impact locations held the higher pollution risk.

Relationships of pollutant discharges and water quality were investigated by Tsuzuki (2015) for annual average data and daily data for total phosphorus and total nitrogen, because long-term water quality monitoring data could be obtained for these parameters. The comprehensive relationship between pollutant discharge and water quality, which includes “better” and “worse” river water quality conditions, is that perturbation or dynamic equilibrium alteration occur with rapid or excess pollutant discharge increase based on linear relationship. It may be possible to say that *BOD* is usually applied in the rivers with anthropogenic pollution effects, e.g., 3–20 mg/L or more, and when *BOD* is less than 4 mg/L, river water quality can be more effectively monitored with nitrogen and phosphorus parameters as well as biological parameters. *BOD*, nitrogen and phosphorus have their own characteristics in pollutant discharge and water quality. The results of this research showed that based on the linear relationship, perturbation or dynamic equilibrium changes occur at the time of rapid increases or excesses of pollutant discharges both in a short-term and a long-term. “Better” water quality conditions might generally more likely lead to a hysteresis at the flood event than “worse” conditions because of the large contributions of diffuse sources than point sources in “better” water quality conditions.

Nitrate can get into water directly as a result of runoff with fertilizers containing nitrate. Some nitrate enters water from the atmosphere, which carries nitrogen-containing compounds derived from automobiles and other sources. Nitrate can also be formed in water bodies through the oxidation of other, more reduced forms of nitrogen, including nitrite, ammonia, and organic nitrogen compounds such as amino acids. Ammonia and organic nitrogen can enter the water through sewage effluent and runoff from land where manure has been applied or stored (USGS 2016). Excessive concentrations of nitrate in lakes and streams, greater than about 5 mg/L (measured as nitrogen), depending on the water body (269/2010 Coll.), can cause excessive growth of algae and other plants, leading to accelerated eutrophication or ‘aging’ of lakes, and occasional loss of dissolved oxygen. Animals and humans cannot use inorganic forms of nitrogen, so nitrate is not a nutrient for them.

Sources of nitrogen (*N*) include the fixation of *N* gas by certain bacteria and plants, additions of organic matter to water bodies, and small amounts from the weathering of rocks. Nitrogen occurs in several forms, including NH_4^+ , gaseous NO , NO_2^- , and NO_3^- . Organic *N*

breaks down into NH_4^+ , which eventually becomes oxidized to NO_3^- , a form available for plants. In the absence of oxygen, the process of denitrification can convert NO_3^- back to NH_4^+ and N gas that typically escapes into the atmosphere (Kenneth et al. 2013). Biochemical oxygen demand is a measure of the quantity of oxygen used by microorganisms (e.g., aerobic bacteria) in the oxidation of organic matter. Natural sources of organic matter include plant decay and leaf fall. However, plant growth and decay may be unnaturally accelerated when nutrients and sunlight are overly abundant due to human influence. Urban runoff carries pet wastes from streets and sidewalks; nutrients from lawn fertilizers; leaves, grass clippings, and paper from residential areas, which increase oxygen demand. Oxygen consumed in the decomposition process robs other aquatic organisms of the oxygen they need to live (Environmental Technology 2015).

Islam et al. (2015) estimated high degree of pollution from the waste of many industrial, municipal and agricultural sources in the river system around Dhaka City, Bangladesh. The pollutants enter into the river system by direct discharges or surface runoff. The results of the study showed that the overall levels of pollution in these rivers (*DO* - dissolved oxygen, *BOD* - biochemical oxygen demand and *EC* - electrical conductivity values) were above the standard. The pollution levels showed a seasonal pattern of change. The values of almost all the parameters remained high during the dry season with a lower river flow as compared to the rainy season. Alternatively, during the rainy season the concentration was diluted from the higher water flow. Therefore, river pollution is largely dependent on the upstream river flow, which indicates that the control of different upstream rivers in India and China indirectly controls the river pollution in Bangladesh.

Processing and evaluating the course of pollutant concentration (nitrate nitrogen, ammonium nitrogen and biochemical oxygen demand) in selected monitored rivers is presented in the paper. Concentrations of pollutants (by Slovak Water Management Enterprise) were measured in three hydrometric station Svit (River Poprad), Košické Olšany (River Torysa) and Ižkovce (River Laborec) in the period from the year 1975 till 2013. Minimum monthly discharge during 38 years (1975–2013) in the monitored hydrometric stations was also assessed. The progress of the minimum monthly discharge has been processed into graphs for each hydrometric station. Similar graphs were done for minimum daily discharge and for each pollutant presented in River Torysa, River Poprad and River Laborec. Trends of concentrations of pollutants at the same hydrometric stations for the same time period were evaluated. Provided minimum monthly discharges, and minimum daily discharges (by Slovak Hydrometeorological Institute) in selected hydrometric station were used for verifying the hypothesis that dependency between the concentration of pollutants in the stream, and discharge (minimum monthly discharge or minimum daily discharge) exist.

2 Study Area

River Poprad (Fig. 1) is in river basin district of Vistula and is the only Slovak river that drains its waters into the Baltic Sea. It sources in the High Tatras over Popradské mountain lake. It flows to the southeast direction up to Svit city (Fig. 1). The river mouths into River Dunajec from the right side, in Poland, river km 117.00. It drains an area of 1890 km². There are 83 surface water bodies all in the category of the flowing waters/ivers. Five groundwater bodies exist in the basin while 1 is in quaternary sediment, 1 is geothermal waters and 3 are in pre-quaternary rocks. River Poprad has 27 transverse structures without fishpass in operation.

Significant industrial and other pollution sources in the catchment are production of plastics, production of white goods, heat systems, machine and civil engineering, renewable energy resources and biogas plants. From the point of view of environmental loads, there are 17 high-risk localities which have been identified in the river basin. Diffuse pollution is from agriculture and municipalities without sewerage. In the basin, there is 19.7% of arable land, 22.4% of other agricultural land, 43.8% of forests, 7.3% shrubs and grasses and 6.3% is other land.

River Poprad is in good chemical status. According to ecological status, River Poprad can be divided into 3 stretches - the upper achieving high status, the middle achieving poor status and the lower boundary stretch with Poland achieving moderate status. Of the total number of water bodies in the river basin, only 19% (16) are failing to achieve good status. The water bodies of quaternary sediments and pre-quaternary rocks achieve good chemical and quantitative status.

River Torysa is a 129 km long river in eastern Slovakia. Its source is in the Levoča Mountains and it flows through the towns of: Lipany, Sabinov, Veľký Šariš, Prešov, and mounts into River Hornád near Nižná Hutka, southeastern of Košice. Sub-basin of River Hornád belongs to the River basin of Danube. The drainage area of the River Hornád is 4414 km². In the basin, there is 27.6% of arable land, 15.7% of other agricultural land, 47.4% of forests, 2.7% shrubs and grasses, and 6.6% is other land. There are 165 surface water bodies with 162 in the category of the flowing waters/ rivers and 2 in the category of standing waters/ reservoirs. Ten groundwater bodies exist in the basin, while 1 is in quaternary sediment, 2 are geothermal waters and 7 are in pre-quaternary rocks. River Hornád has 11 transverse structures without fishpass in operation. Significant industrial and other pollution sources in the catchment are steel production, mining, metallurgy industry, brewery, pharmacy, salt production and power engineering. From the point of view of environmental loads, there are 11 high-risk localities which have been identified in the river basin. Diffuse pollution is from agriculture

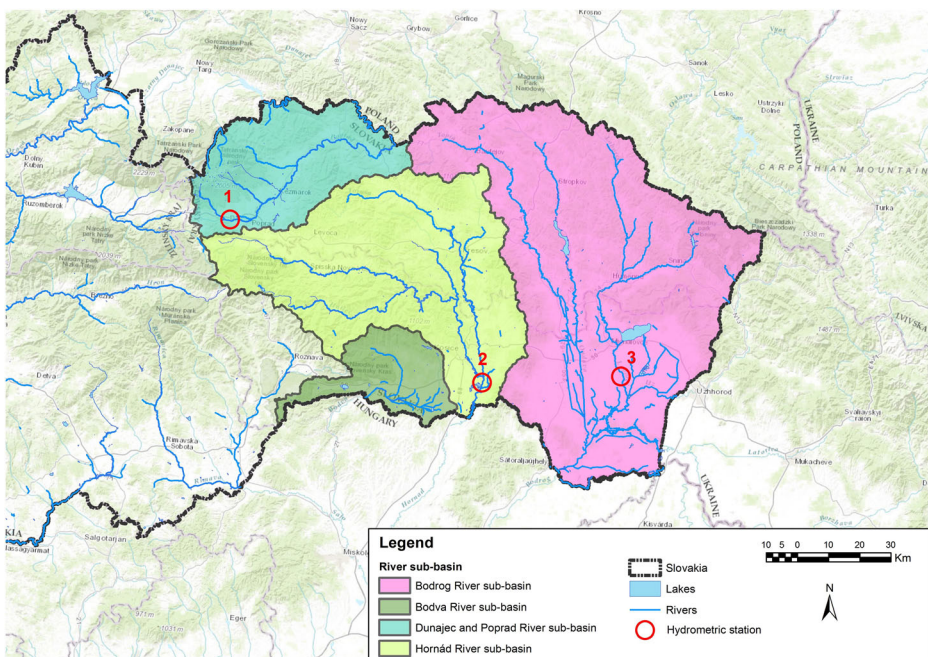


Fig. 1 Location of sub-basin of Rivers Poprad and Dunajec, River Hornád and river Bodog

and municipalities without sewerage. The upper stretch of River Hornád to Spišská Nová Ves is in good ecological status which gets worse to poor status or potential by pollution and hydromorphological pressures. From Ružín Water Reservoir, River Hornád achieves moderate ecological status. According to chemical status assessment, River Hornád is in good status. 56 water bodies (34%) are failing to achieve good ecological status in Hornád river basin. The water body of intergranular ground waters of quaternary alluviums of River Hornád basin achieves poor chemical status (pollution from point and diffuse sources) and poor quantitative status identified on the basis of long-term decrease of groundwater levels. The water bodies of pre-quaternary rocks are in good status - quantitative and chemical.

The hydrometric profile Košické Olšany (Fig. 1) is situated at 185.83 m a.s.l. and the catchment area is 1298.3 km². River Laborec is a river in eastern Slovakia that flows through the districts of Medzilaborce, Humenné, and Michalovce in the Košice Region, and the Prešov Region. The river drains in Laborec Highlands. Tributaries of the River Laborec include River Uh which joins River Laborec near the city of Drahňov in Michalovce District, and the River Cirocha. River Laborec itself is a tributary, flowing into the River Latorica. Catchment area of Ižkovec hydrometric profile at River Laborec is 4364 km² and it is situated at 94.36 m a.s.l. (Gregor 2013).

Sub-basin of River Bodrog belongs to the river basin of Danube. The drainage area of River Bodrog is 7272 km². In the basin, there is 34.6% of arable land, 17.8% of other agricultural land, 37.2% of forests, 4.4% shrubs and grasses, and 6.1% is other land. There are 257 surface water bodies while 254 are in the category of the flowing waters/ivers and 3 are in the category of standing waters/reservoirs. Eleven groundwater bodies exist in the basin with 4 in the quaternary sediment, 2 in geothermal waters and 5 in pre-quaternary rocks. River Bodrog basin has 4 transverse structures without fishpass in operation (River Ondava). Significant industrial and other pollution sources are from production of bleached paper pulp, coal power plant and also gas supplier and electricity suppliers which are located in the catchment. From the point of view of environmental loads, there are 48 high-risk localities which have been identified in the river basin. Diffuse pollution is from agriculture and municipalities without sewerage. River Bodrog is in poor ecological status, specifically the parameter macrobenthos. Even though River Bodrog achieves good chemical status, its tributaries are in poor chemical status: River Ondava (cadmium concentration) and River Latorica (PAHs - polycyclic aromatic hydrocarbons). More than half of the water bodies in the river basin (65%) achieve good or high ecological status; the remaining 35% of the water bodies in the river basin achieve moderate ecological status. The water bodies of quaternary sediments and pre-quaternary rocks achieve good chemical and quantitative status.

3 Datasets and Methodology

All data used for verification (pollutants concentrations, minimum monthly discharges and minimum daily discharge) were from years 1975 to 2013. Studied pollutants were concentrations of *N-NO₃* - nitrate nitrogen, *N-NH₄* - ammonium nitrogen and *BOD₅* - biochemical oxygen demand measured in the particular day as the minimum daily discharge. Data about pollutant concentrations were provided by Slovak Water Management Enterprise and data about the discharges were provided by Slovak Hydrometeorologic Institute. All pollutants were measured according to standards: nitrate nitrogen according to STN EN ISO 10304-1 (2007) by liquid chromatography; ammonium nitrogen by spectrometry according to STN ISO 7150-1(1984); and biochemical oxygen demand by electrochemical probe method according to STN EN ISO 5814 (2012).

The use of statistical method in civil engineering to handle problems with pollutant transport leads to the formulation of two hypotheses. First hypothesis was that the concentrations of pollutants $N\text{-NO}_3$, $N\text{-NH}_4$ and BOD_5 are dependent on river minimum monthly discharge (the days of measurement of pollutant was not the same as the day of discharge measurement). Dependency of minimum monthly discharge and concentrations of pollutants was investigated by correlation analysis and the correlation coefficient was calculated. The second hypothesis aimed at the investigation of correlation dependency calculation using minimum daily discharge and concentrations of pollutants. Measurements of pollutant concentrations as well as minimum daily discharges were done exactly at the same day of the month during all 38 years.

The limit values of concentrations are established by Decree no. 269/2010 Coll. - Regulation of the Government of the Slovak Republic, laying down the requirements to achieve good status of water bodies, namely Appendix 1 (SR Government Regulation 269/2010 Coll.). Limit concentrations of pollutants pursuant to this Regulation are 5 mg/L for $N\text{-NO}_3$, 1 mg/L for $N\text{-NH}_4$ and 7 mg/L for BOD_5 .

Correlation dependency of minimum monthly discharge/minimum daily discharge and concentrations of pollutants was done. Correlation analysis can be described as follows (Kreyszig 2011): Let us observe or measure two quantities simultaneously, so that we get samples of pairs of values $(x_1, y_1), (x_2, y_2), \dots, (x_n, y_n)$. In practice, we may distinguish between two kinds of experiments, correlation analysis and regression analysis. In correlation analysis both quantities are random variables and we are interested in relations (“correlation”) between both set of samples x and y . Exact information about an existence of linear correlation in case of the two-dimensional statistical set gives the correlation coefficient R_{xy} (Eq. 1).

$$R_{xy} = \frac{n \sum_{i=1}^n x_i y_i - \left(\sum_{i=1}^n x_i \right) \left(\sum_{i=1}^n y_i \right)}{\sqrt{\left[n \sum_{i=1}^n x_i^2 - \left(\sum_{i=1}^n x_i \right)^2 \right] \left[n \sum_{i=1}^n y_i^2 - \left(\sum_{i=1}^n y_i \right)^2 \right]}} \quad (1)$$

Its values are in the interval $\langle -1, 1 \rangle$. Increasing of the absolute value of the R_{xy} is proportional to linear correlation. If $R_{xy} = 1$, the correlation is fully linear; if $R_{xy} = -1$, then the correlation is inversely linear and if $R_{xy} = 0$, the pairs of values are fully independent. Let us call the degree of the relative closeness as: medium, if $0.3 \leq |R_{xy}| < 0.5$; significant, if $0.5 \leq |R_{xy}| < 0.7$; high, if $0.7 \leq |R_{xy}| < 0.9$; and very high, if $0.9 \leq |R_{xy}|$. The correlation coefficient was for the purposes of our assessment obtained using the “Pearson” function in Microsoft Excel.

4 Results and Discussion

4.1 Minimum Monthly Discharges and Minimum Daily Discharges

Figure 2 shows the course of the minimum monthly discharge in all three hydrometric stations during the reporting period. The values of minimum monthly discharge are on axis “y” and evaluated time period (1975–2013) is on axis “x”. The red straight lines (Figs. 2 and 3) present the linear trend of the discharge.

The trend of the minimum monthly discharges during 38 years was almost stable. The graphs of Fig. 2 show no hydrologic extremes such as floods or droughts in the selected river basins. The trend of minimum monthly discharge is slightly increasing in River Poprad (Svit hydrometric station) and slightly decreasing in River Torysa (Košícké Olšany hydrometric station). In River Ižkovce, the trend is almost constant. The conditions connected to the water quantity were relative stable - oscillating around the trend line, so these data were used as one of the input data for correlation analysis (no quantitative extremes in the catchments).

The second task aimed on correlation dependency calculation using minimum daily discharge and concentrations of pollutants measured in the same particular day during whole 38 years period (Fig. 3).

Figure 3 shows the course of the minimum discharge in all three hydrometric stations during the reporting period. The minimum daily discharge in eastern Slovakia shows a decreasing trend for all three hydrometric stations (most visible for River Torysa). Minimum daily discharges depicted in Fig. 3 are values from the particular day when the concentration of pollutants were measured. The values of these minimum daily discharges are presented with different colours in the graphs and red line stands for the trend of the discharge during the evaluated period.

Data presented in Fig. 3 were used as input data for verification of the second hypothesis that the concentrations of $N-NO_3$, $N-NH_4$ and BOD_5 are decreasing with increasing river discharge. It was presented in Fig. 2 that the trends of minimum monthly discharges were not varying during 38 years, so the linear correlation should be used for verification of the second hypothesis. Both hypotheses are based on verification of relation between quantity and quality parameters, i.e., quantity parameters (minimum monthly discharge - 1st hypothesis; minimum daily discharge - 2nd hypothesis) are not varying but quality parameters are varying.

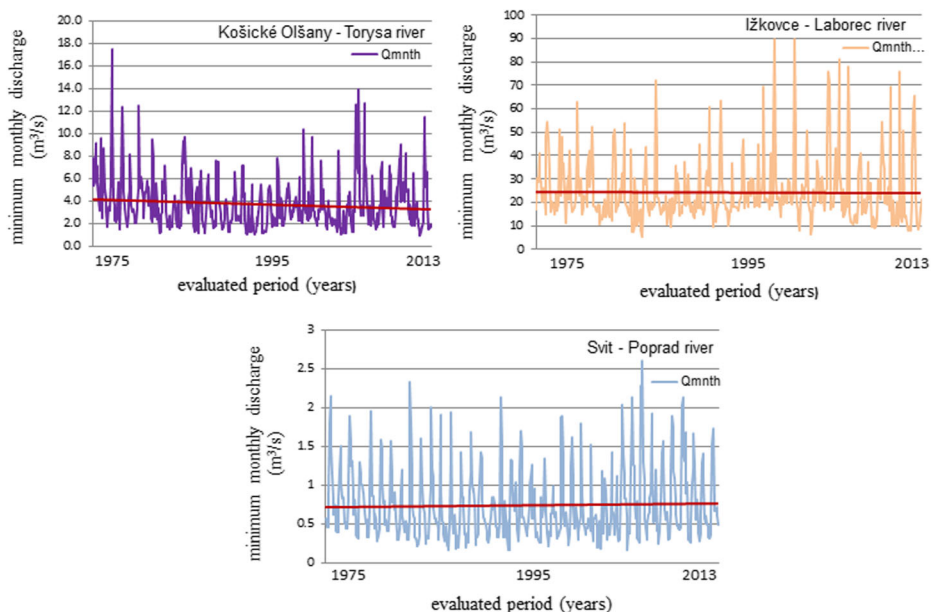


Fig. 2 Minimum monthly discharge in monitored hydrometric stations

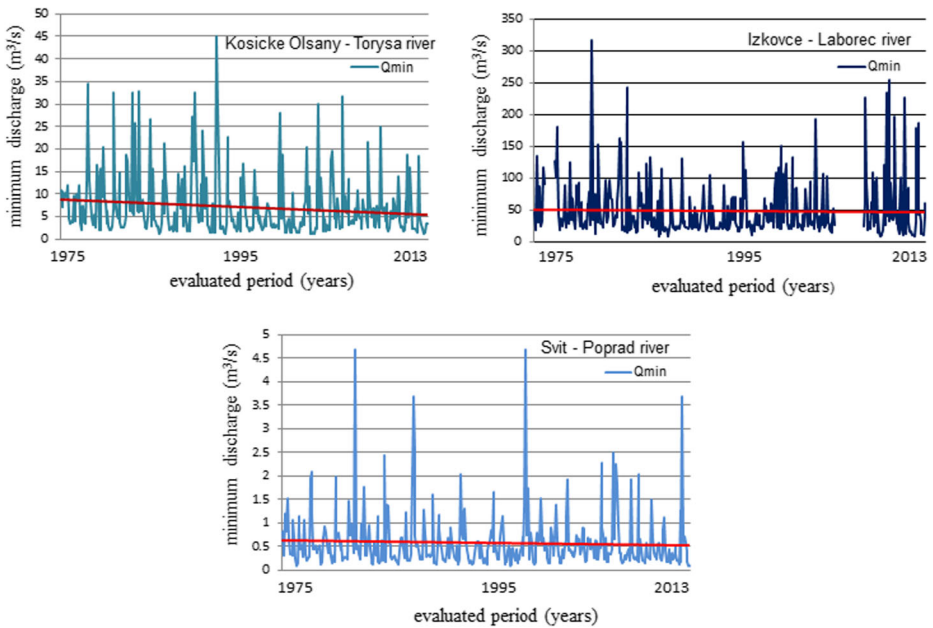


Fig. 3 Minimum daily discharge in monitored hydrometric stations

The following part is devoted to processing and evaluating the course of pollutant concentrations (nitrate nitrogen, ammonium nitrogen and biochemical oxygen demand) in selected monitored rivers. The concentrations were measured during 38 years (1975–2013) in the monitored hydrometric stations. The measured concentrations have been processed into graphs, and also have been used to express the trend (red line) of concentrations for each evaluated pollutant in each hydrometric station at River Poprad (station Svit), River Torysa (station Košické Olšany) and River Laborec (station Ižkovce).

4.2 Nitrate Nitrogen

The trend of nitrate nitrogen concentrations in three hydrometric station are presented in Fig. 4. The concentrations were measured every day during the period from January 1975 till December 2013. The gaps in the graphs means that measurement was not done in the particular dates because of unforeseen occurrences.

Excessive concentrations of nitrate in lakes and streams greater than about 5 mg/L (measured as nitrogen), depending on the water body, can cause excessive growth of algae and other plants, leading to accelerated eutrophication or ‘aging’ of lakes, and occasional loss of dissolved oxygen. Concentration of nitrate nitrogen measured during the period from 1975 till 2013 (Fig. 4) showed an increasing trend in River Torysa in Košické Olšany hydrometric station and in River Poprad in Svit station. Limit concentrations (5 mg/L) of $N-NO_3$ are not exceeded during the last 15 years in Svit station and Ižkovce station, except for one exemption in each hydrometric station (Svit: March 2013 and Ižkovce: July 1998). Most of the values measured for Košické Olšany hydrometric station are in the range slightly above and slightly under the limit during the whole monitored period (with some exceptions).

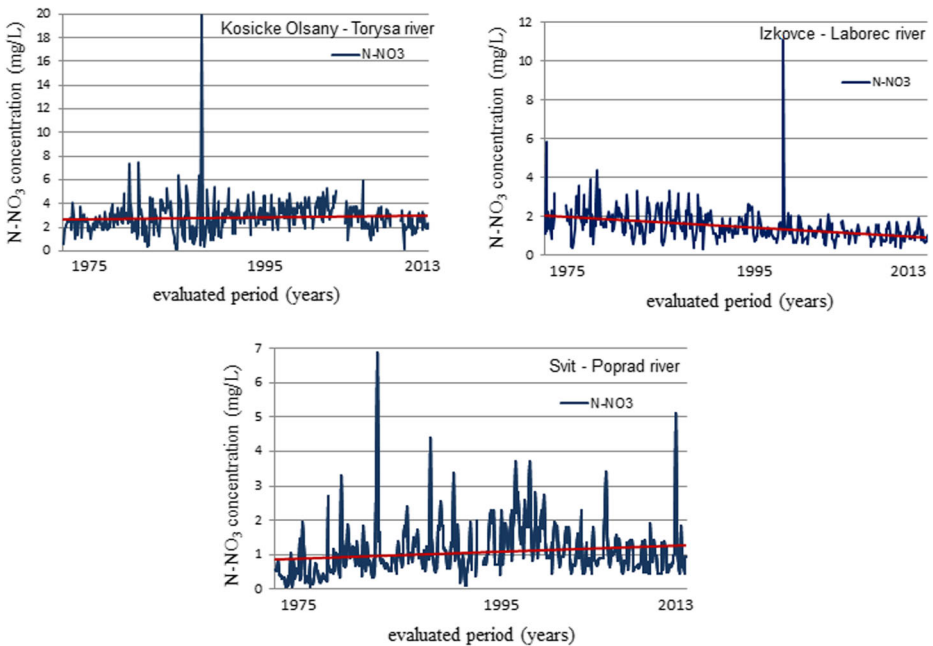


Fig. 4 Concentrations of $N\text{-NO}_3$ in monitored hydrometric stations

4.3 Ammonium Nitrogen

A decreasing trend of concentration of ammonium nitrogen (marked with red line) in selected rivers of eastern Slovakia is presented in Fig. 5. The limit value of ammonium nitrogen concentration is given by Decree no. 269/2010 Coll. as 1 mg/L. The River Torysa in Košické Olšany, the profile exceeds the limit value during the whole monitoring period. The lowest concentrations of $N\text{-NH}_4$ were measured in the years 1993–2013 in River Poprad (except March 1999), and from year 1990, the limit value (1 mg/L) is not exceeded in this river. The limit value of ammonium nitrogen concentration in River Laborec was exceeded only twice, i.e., the extreme value of 5.02 mg/L in March 2008 and the slightly exceeded value of 1.07 mg/L in March 2013.

If ammonium nitrogen levels in surface waters are too high, they can be toxic to some aquatic organisms. If the levels are only moderately high, plant and algal growth will usually increase due to the abundance of nitrogen available as a nutrient. This will have a ripple effect on other attributes of water quality, such as increasing biochemical oxygen demand and lowering dissolved oxygen levels.

4.4 Biochemical Oxygen Demand

The biochemical oxygen demand is the most widely used parameter to quantify organic pollution of water. Figure 6 illustrates the course of the concentrations of BOD_5 in all monitored hydrometric stations.

The trend of the concentration of this pollutant in the river is depicted with the red line in the graphs. From Fig. 6, it is apparent that the trend of BOD_5 concentration in all hydrometric stations is decreasing. A significantly decreasing trend is well visible for Ižkovce and Svit

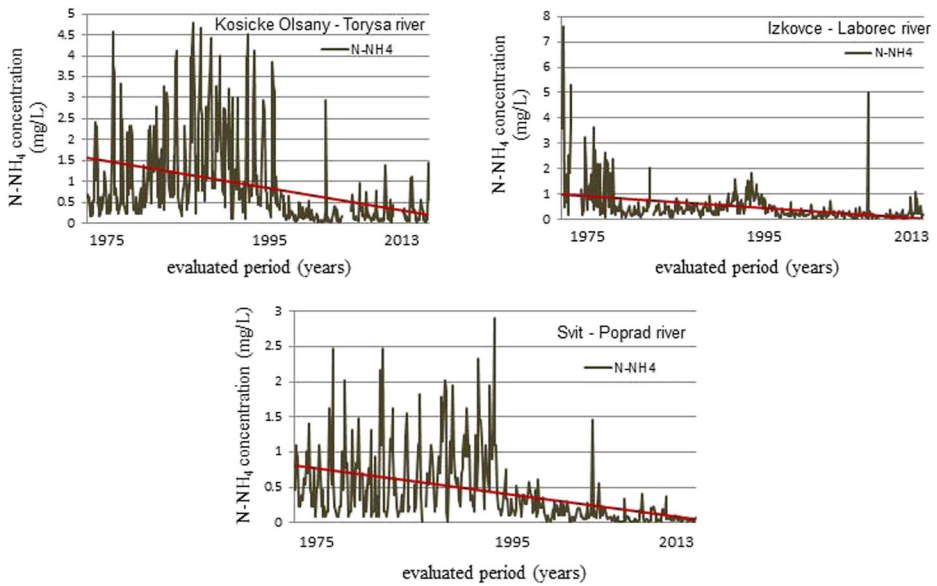


Fig. 5 Concentrations of $N-NH_4$ in monitored hydrometric stations

hydrometric stations. In Svit station the limit value of 7 mg/L was exceeded quite often in the past, but as it can be seen from the graph, at present, this limit value is quite often respected (except December 2001 and March 2003). The limit value in Ižkovce station was exceeded only once in the last 15 years in June 2011 and in November 2013. The limit value was exceeded in Košické Oľsany hydrometric station in the period from 1975 to 1995 the most.

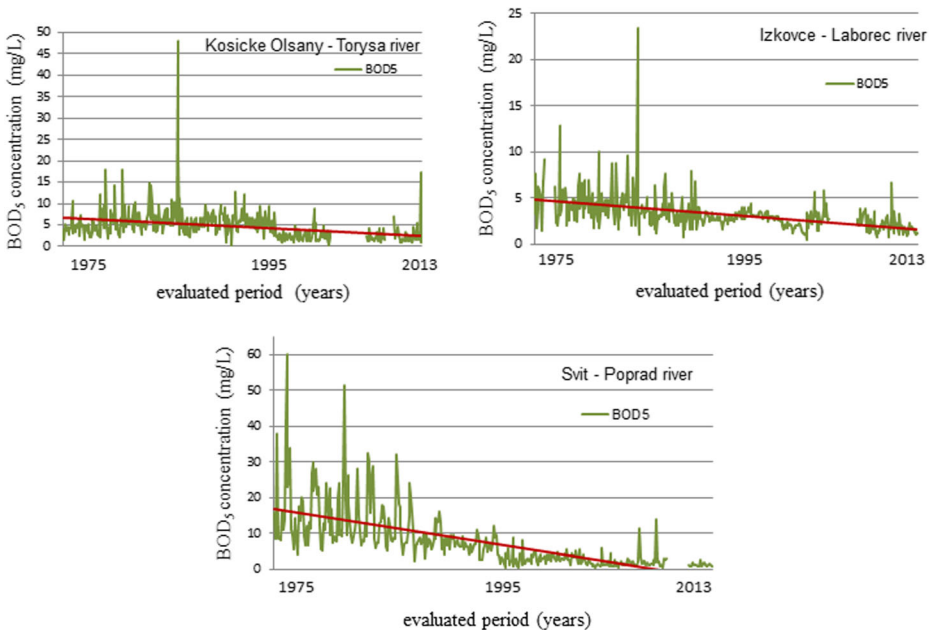


Fig. 6 Concentrations of BOD_5 in monitored hydrometric stations

4.5 Correlation Coefficient

The dependency between the minimum monthly discharge and quality of the water in the river with the aim to verify, confirm or refute the hypothesis about the existence of relation between two parameters was investigated using correlation coefficient. Trends of ecological flow in the selected hydrometric stations of eastern Slovakia as well as pollutants (nitrite nitrogen and phosphorus) during 18 years were investigated by Ondrejka Harbuľáková et al. (2016). Correlation analysis was used to investigate the relationship between evaluated parameters. Two hypotheses were verified by correlation coefficient.

Correlation coefficient was obtained by “Pearson” function in Microsoft Excel. Concentrations of pollutants measured once a month were compared with a minimal monthly discharge (\bar{Q}_{mth}) in the three hydrometric stations. The results are shown in Table 1.

From the results presented in Table 1, it is evident that the correlation between the concentration of pollutants in the stream and the minimum monthly discharge is very small or almost no dependency exists. The correlation coefficient achieved in all cases had a very low value (close to 0). Only in the case of $N\text{-NH}_4/\bar{Q}_{\text{mth}}$ in Košické Olšany and Svit hydrometric stations a dependence was demonstrated. We cannot speak about any dependency, thus the hypothesis was not proven. This is probably due to the time variation of measured minimum monthly discharges and concentrations of pollutants in the stream. It was also assumed that the calculated very low or no correlation was due to differences in the dates of pollutant and discharge measurement.

In the next part of the paper the dependency of the concentrations of pollutants and minimum daily discharges (Q_{min}) were evaluated (both values were measured in the same day). We assume that hypothesis about existing dependency on the relationship between the concentration of pollutants and minimum daily discharge both measured at the same particular day will be confirmed. It would probably mean that the lower minimum daily discharge is associated with an increased concentration of pollutants in the water flow.

Table 2 presents results from correlation analysis of relation between pollutant concentrations and minimum discharge in evaluated hydrometric stations measured at the particular date.

Also the 2nd hypothesis about existence of relationship between the concentrations of pollutants in the stream and the minimum daily discharge measured exactly in the same day was not confirmed. No correlations were found (one exception in Košické Olšany river profile - medium correlation between $N\text{-NO}_3$ and Q_{min}). Investigation of dependency between quantity parameter (discharge) and quality parameters (concentrations of pollutants) showed no correlation. Increasing trend of discharge has not influence on decreasing trend of concentrations of selected pollutants (nitrate nitrogen, ammonium nitrogen, biochemical oxygen) as it was assumed in hypotheses. This points to the fact that influence of land use, agriculture and

Table 1 Correlation coefficient of pollutant concentration and minimum monthly discharge in evaluated river stations

Pollutant/minimum monthly discharge	Correlation coefficient		
	$N\text{-NO}_3 / \bar{Q}_{\text{mth}}$	$N\text{-NH}_4 / \bar{Q}_{\text{mth}}$	$BSK_5 / \bar{Q}_{\text{mth}}$
Svit station	0.21	0.34	0.14
Košické Olšany station	0.04	0.26	0.06
Ižkovce station	0.14	0.01	0.05

Table 2 Correlation coefficient of minimum daily discharge and pollutant concentration

Pollutant/minimum daily discharge	Correlation coefficient		
	$N-NO_3 / Q_{\min}$	$N-NH_4 / Q_{\min}$	BSK_5 / Q_{\min}
Svit station	0.02	- 0.03	0.003
Košické Olšany station	0.22	- 0.04	0.19
Ižkovce station	0.17	- 0.02	0.012

industry are more prevalent than the effect of the pollutants measured in the same particular date in the hydrometric profile as minimum daily discharge.

5 Conclusions

In terms of protection of water bodies and ecosystems depending on water in the Slovak Republic the following issues have to be considered: pollution of surface waters by organic pollution and nutrients, pollution of surface waters by priority substances and substances relevant to the Slovak Republic, hydromorphological alterations in water bodies, pollution of groundwater by nitrates and other chemical substances and poor qualitative status of groundwater. The pollution of surface waters by organic pollution and nutrients is quite significant concerning the low level of waste water collection and treatment from the agglomerations in the Slovak republic. The most significant impact of high nutrient load is the water eutrophication. This status causes undesirable disturbance of organisms in water and water quality deterioration. The main sources of this pollution are urban agglomerations, industries and agriculture.

These three factors were not changed significantly for the last four decades in the sub-basins discussed in this paper. The conditions are almost stationary (even the limits for pollutants were a little bit changed during the monitored period). The relationship between quality and quantity parameters was subject of correlation analysis with the aim to find the dependency between them. Trends of increasing/decreasing pollutant concentrations in river (qualitative point of view) and trend of minimum monthly discharge and minimum daily discharge (quantitative point of view) were also studied.

The article presents the evaluation of trends of minimum monthly discharges and concentrations of $N-NO_3$, $N-NO_4$ and BOD_5 , in three river stations at three different rivers in the eastern Slovakia, namely River Poprad (Svit hydrometric station), River Laborec (Ižkovce hydrometric station) and River Torysa (Košické Olšany hydrometric station). The results show that the minimum monthly discharge in eastern Slovakia has slightly increasing trend in Rivers Poprad, decreasing trend in River Torysa, while in River Laborec, the trend is constant. Then, the trend of $N-NO_3$, $N-NO_4$ and BOD_5 concentrations in selected river stations was evaluated. River Torysa (Košické Olšany profile) where the highest concentrations of all pollutants were measured is the most polluted water course. The least polluted water course is River Poprad, which is related to the fact that hydrometric station in Svit is located at the upper part of the water course and there is not so intense agricultural activity around River Poprad. Most exceeded limit concentrations were monitored for pollutant ammonium nitrogen ($N-NH_4$). For all pollutants and gauging stations, however, the decreasing trends of monitored pollutants were seen. Decreasing trend of pollutants in River Laborec was also confirmed by Zeleňáková et al. (2015) using Mann-Kendall non-parametrical test for trend detection. These findings

were based on decreasing agricultural activities of the catchments and intensification of the sewage system and the wastewater treatment plants in the studied areas. It is mainly due to stricter standards for industry and agriculture, as well as for growing network of public sewage systems that are connected to a wastewater treatment plant, also in small villages, which limits direct discharges of pollutants to the recipient. The values of most of the parameters remained high during the dry season with a lower river flow as compared to the rainy season. Alternatively, during the rainy season, the concentration was diluted from the higher water flow. Therefore, river pollution is largely dependent on the upstream river flow (Islam et al. 2015).

The findings by Islam et al. (2015) led to a mathematical investigation of the conditions of Slovak Republic which consisted of two tasks. The first research aimed on correlation analysis of minimum monthly discharges at the selected hydrometric stations, i.e., Svit (Poprad river), Košické Olšany (River Torysa) and Ižkovce (River Laborec) and the corresponding concentrations of pollutants at the same stations. The hypothesis that the concentrations of nitrate nitrogen, ammonium nitrogen and biochemical oxygen demand are dependent on river minimum discharge was investigated. The second hypothesis was derived from the second task - correlation analysis of minimum daily discharge and the concentration of pollutants in the mentioned river profiles was also investigated. It aimed to the more precise research that we considered minimum daily discharges and concentrations of pollutants measured at the particular day.

Results of our research work proved that no correlation exists between minimum monthly discharge and concentrations of pollutants and also no correlation exist between minimum daily discharge (even measured in the particular day as the concentrations) and concentrations in rivers. Water quality problems are dominated by various forms of uncertainties, caused primarily due to uncertain hydrological and meteorological conditions. Uncertainties in water quality model parameters and quality models themselves tend to complicate the problem further. Planning is sometimes done under simplified deterministic assumptions, using selected values for inputs and water quality model parameters. Although this appears to lead to a conservative management decision, even an insufficient decision may result depending on the parameters employed.

In the paper, the simple approach to investigation of relation between quantity and quality parameters was used. It revealed that in the next investigation considering the air/water temperature, climatic conditions, land use of selected area could show valuable results in the field of water quality in relation to water quantity evaluation.

Acknowledgements This work was supported by the Scientific Grant Agency of Ministry of Education, Science, Research and Sport of the Slovak Republic under grant 1/0609/14. A previous version of the paper has been presented in the 2nd EWaS International Conference: “*Efficient & Sustainable Water Systems Management toward Worth Living Development*”, Chania, Crete, Greece, 1-4 June 2016.

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