



Determination of pollutant concentrations in the Krasny Brod River profile based on the Buckingham theorem

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ABSTRACT

The paper deals with an application of the model which determines concentrations of pollutants in a water stream and which is developed based on dimensional analysis. The most important part is the selection of appropriate variables for model development. The use of dimensional analysis, the Buckingham theorem, for water quality modeling is a new approach. This method could be used for prediction of any pollutant in a water stream. The obtained results demonstrate that dimensional analysis and use of the π theorem is an appropriate approach to water quality modeling. The model presented in the article has universal validity for pollutants in streams that are characterized by at least approximate geometric characteristics. But for each pollutant (and particular stream of course), the parameters of linear function, i.e. regression coefficients, have to be determined separately. The differences between the concentrations calculated from the developed model and actually measured concentrations are also discussed in this paper, as well as the rate of uncertainty.

Keywords: Model; Pollutant; Water stream; Dimensional analysis

1. Introduction

The Water Framework Directive (2000/60) [1] demands new approaches for managing and improving surface and groundwater quality across the European Union, with emphasis shifting from chemical toward ecological water quality standards. However, it is recognized that the nutrient status of river

systems reflects the combined contribution of sources: fertilizer inputs, atmospheric deposition, and sewage discharges [2]. Superimposed on these anthropogenic inputs, an integrated management approach is required [3]. In particular, such an approach is needed to assess the likely impacts of land management and climatic change on EU river nutrient concentrations and loads [2]. European management strategies have tended to address single issues (e.g. diffuse or point

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sources of pollution) or particular regions (e.g. upland or lowland areas). The pollution arising from these and other sources, such as use of agricultural pesticides, has led to the increasing need for rigorous assessment of river water quality.

The variation of pollutant concentrations in surface waters shares broad interest by scientists and researchers in the field of water pollution control. Most important environmental problems in river water quality are eutrophication, acidification, and emission dispersion where non-point source pollution has become increasingly important within the last few decades [4]. Monitoring of river water quality is primarily done to detect the status and trends and to identify whether observed trends are due to natural or anthropogenic causes. Protection of water bodies for all purposes, such as drinking, recreational activities, and fish and wildlife, requires regular assessing and monitoring of their quality status [5].

Dimensional analysis is a well-known methodology in physics, chemistry, and other traditional engineering areas. It has been used in many experimental studies—description of the capillary rise of liquids in porous media [6], prediction of friction losses in irrigation facilities [7], calculation of emissions produced in wood combustion [8], formation and prediction of nitrogen oxides in indoor environment [9,10], calculation of nitrogen concentration in streams [11,12]. In the last century, dimensional theory has been profoundly investigated: its highest achievement is the Buckingham theorem (or pi-theorem, π theorem), which states that any equation modeling a physical problem can be rearranged in terms of dimensionless ratios, thus reducing the number of variables to be handled, and especially enriching the inner physical knowledge of the studied phenomenon [8–11,13].

Dimensional analysis in general is a technique that allows the transformation of dimensional variables describing the phenomenon into a set of dimensionless numbers, the number of which is always less than the number of physical quantities used [14,15]. In its simplest form, it is used to check the meaningfulness of a set of equations (dimensional homogeneity) [16,17]. The choice of variables is influenced by the ability of an organization to provide the facilities, and trained operators, to enable the selected measurements to be made accurately. Full selection of variables must be made in relation to assessment objectives and specific knowledge of each individual situation [18].

The paper presents an instructive approach to determine pollutant concentrations in a river profile using dimensional analysis. Modeling pollutant occurrence in a river is complex. This issue is influenced by a lot of natural as well as artificial phenomena,

particularly human activities in the catchment area. Its importance is for water management in general, to calculate pollutant concentration in a stream and to save a lot of expensive monitoring equipment and its maintenance as well as laboratory work, and finally prediction of pollutant concentration in the river will be able to achieve good water status according to the Water Framework Directive. We chose the main variables that could influence concentrations of pollutants in a stream to present the possibility of using dimensional analysis as a tool for calculation of pollutant concentration in a river profile.

2. Material and methods

2.1. Study area

The application of the model for determination of various pollutant concentrations is presented in the Krasny Brod River profile (Fig. 1), Laborec River, Bodrog River basin, Slovak Republic. The Bodrog River catchment area covers a large part of eastern Slovakia, and has a total area of 7,275 km².

The Laborec River is 126.4 km long with a catchment area of 4,522.5 km². The Krasny Brod River profile is situated at rkm 108.3. The Laborec flows N–S through the Prešov and Košice regions. The main tributaries of the river include the Cirocha and Uh rivers. The Laborec River flows into the Latorica River which together with the Ondava River creates the Bodrog River [19]. Natural conditions in the upper and lower parts of the Bodrog River basin are entirely different, but the common feature of both parts is a significant deterioration of the basin. The quality of surface water in the Laborec River is significantly affected by sources of pollution, which are the core points of pollution in the stream. In the Laborec River basin, there are 66 discharges of wastewater, particularly from industry, mining, schools, healthcare facilities, social care homes, and sewerage. The pollution in the river is aggravated apart from the point sources of pollution also by diffuse sources of pollution from agriculture and forestry, from population without sewage systems, and landfilling.

The most important chemical stressors for the Laborec basin have been identified as follows: biochemical oxygen demand (BOD₅) and chemical oxygen demand (COD_{Cr}), which indicate the amount of oxygen required for oxidation of organic compounds. The next are ammoniacal nitrogen (N–NH₄⁺), nitrate nitrogen (N–NO₃⁻), nitrite nitrogen (N–NO₂⁻) as a product of decomposition of organic nitrogen compounds or biochemical reaction. The amount of ammonia, nitrate, and nitrite nitrogen is expressed as an

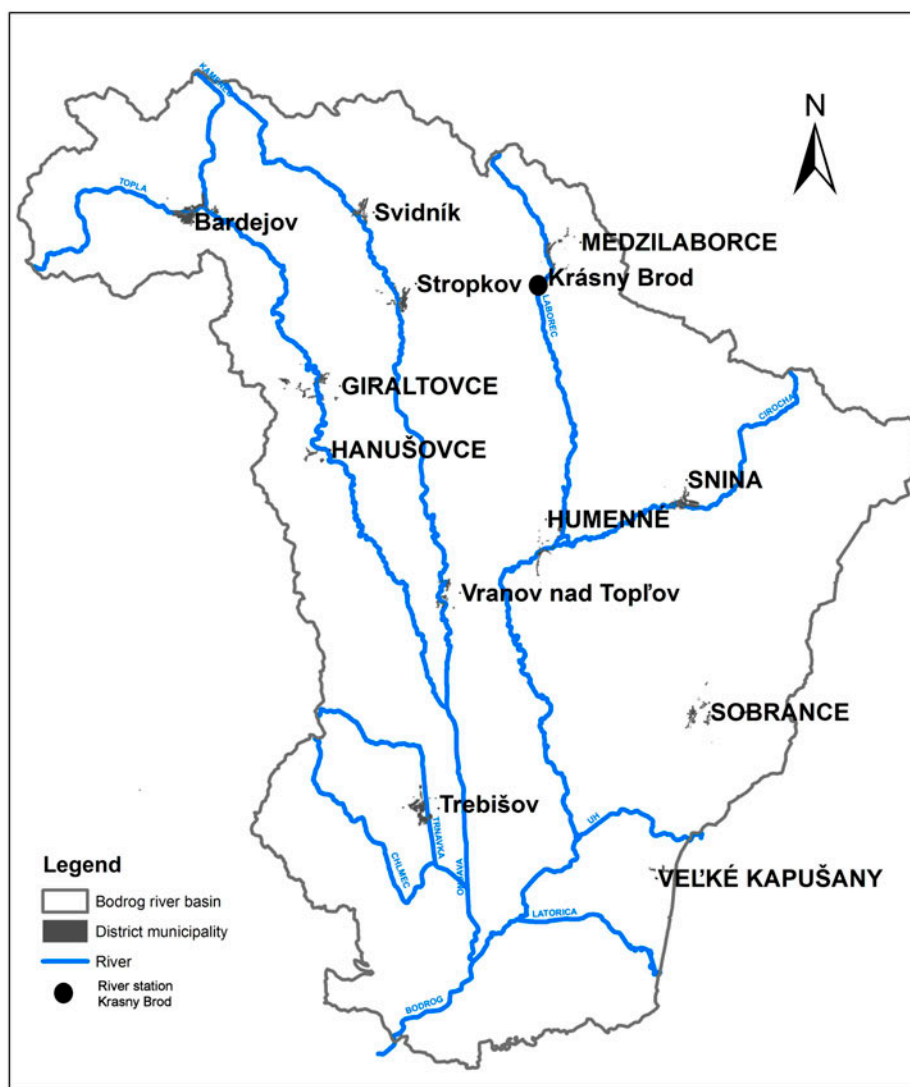


Fig. 1. Bodrog River catchment area [19].

indicator—total nitrogen (N_{tot}). Another significant pollutant, mainly from diffuse sources of pollution, is phosphorus (P_{tot}).

2.2. Dimensional analysis

The most important part of dimensional analysis for the model development of predicting pollutant concentration in a water stream, as mentioned above, is the selection of appropriate variables [11,12]. The choice of variables will also be influenced by the ability of an organization to provide the facilities, and suitably trained operators, to enable the selected measurements to be made accurately [17]. Full selection of variables must be made in relation to assessment objectives and specific knowledge of each individual situation.

For determination of pollutant concentration in a water stream by using dimensional analysis, it is essential to state the parameters which characterize the water stream, and if possible to measure them [11,12]: flow Q ($\text{m}^3 \text{s}^{-1}$), or mass flow Q_m (kg s^{-1}), area of watershed F (m^2), velocity of water in the stream v (m s^{-1}), temperature of water T_w (K), temperature of air T_a (K), and pollutant concentration C_i (kg m^3). All the given variables are presented in basic dimensions, which is the condition for dimensional analysis application.

The model describing pollutant concentration in a water stream is based on the formation of dimensionless arguments π_i from the stated variables influencing the pollutant concentration. The dimensional matrix-relation (1) has the rank of matrix $m = 4$

(dimensions—m, s, kg, K) and its lines are dimensionally independent of each other:

$$\begin{matrix} \text{m} \\ \text{kg} \\ \text{s} \\ \text{K} \end{matrix} \left\| \begin{array}{cccccc} Q_m & F & v & T_w & C & T_a \\ 0 & 2 & 1 & 0 & -3 & 0 \\ -1 & 0 & -1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 1 \end{array} \right\| \quad (1)$$

From $n = 6$ independent variables (Q_m, F, v, T_a, C, T_w) at matrix rank m , it is possible to set up $n - m$ non-dimensional arguments. In this model, two independent vectors—non-dimension arguments π_1 (2) and π_2 (3)—are presented as a result of solution of the dimensional matrix (1):

$$\pi_1 = Q_m^1 \cdot v^{-1} \cdot F^{-1} \cdot C_i^{-1} \quad (2)$$

$$\pi_2 = T_a^{-1} \cdot T_w^{-1} \quad (3)$$

The input data for Buckingham π theorem calculation are presented in Table 1. Data of flow, velocity, temperatures were obtained from the Slovak Hydrometeorological Institute, Košice Branch (SHMI).

Table 2 presents measured pollutant concentrations. Required data of pollutant concentrations were obtained from the Slovakian Water Management Company, Košice Branch (SWME). Concentrations of the following pollutants were modeled:

- biochemical oxygen demand (BOD₅),
- chemical oxygen demand (COD_{cr}),
- nitrogen (N_{tot}),
- nitrite nitrogen (N-NO₂⁻),
- nitrate nitrogen (N-NO₃⁻),

- ammonium nitrogen (N-NH₄⁺), and
- phosphorus (P_{tot}).

The monthly data monitored over a period of six years from 2003 to 2008 (12 values in a year) and statistically processed [20] (one value monthly averaged over six years) input data were used for calculations. The data from this period were used for model calibration.

The relation between independent non-dimensional argument π_2 and dependent non-dimensional argument π_1 can be defined by the exponential equation depicted in Fig. 2:

$$\pi_1 = A \cdot \pi_2^B \quad (4)$$

From this function dependency it is possible to obtain values of regression coefficients A, B and then calculate the values of pollutant concentrations in the water stream. Fig. 2 depicts the dependency for BOD₅.

The developed model [11,12] of pollutant concentration in the water stream based on dimensional analysis is Eq. (4):

$$C = A^{-1} \cdot T_a^{-B} \cdot v^{-1} \cdot F^{-1} \cdot Q_m \cdot T_w^B \quad (5)$$

2.3. Uncertainty analysis

The determined concentrations of pollutants in the Krasny Brod River profile, Laborec River, eastern Slovakia, were compared with actual monitored values of concentrations in the river profile.

The average uncertainty was calculated using the following equation:

$$\sigma = \frac{1}{n} \cdot \sum_{i=1}^n \frac{|C_{\text{measured}} - C_{\text{calculated}}|}{C_{\text{measured}}} \quad (6)$$

where $C_{\text{calculated}}$ and C_{measured} are the calculated and measured values of pollutant concentration in the river, n is the number of data.

The model performance with values of accuracy was also stated with a coefficient of determination and Nash–Sutcliffe efficiency (NSE). These coefficients explain the goodness-of-fit of the water quality prediction model.

The coefficient of determination (R^2) describes the degree of co-linearity between the simulated and measured data. R^2 describes the proportion of the variance in measured data explained by the model. R^2 ranges

Table 1
Values of relevant variables

	Q_m (kg/s)	F (m ²)	v (m/s)	T_a (K)	T_w (K)
January	1,995.17	158.10 ⁶	0.9678	270.22	275.08
February	2,153.50	158.10 ⁶	1.0319	270.78	274.57
March	5,463.83	158.10 ⁶	2.0078	274.98	276.08
April	4,247.33	158.10 ⁶	1.6523	281.42	279.93
May	2,180.00	158.10 ⁶	1.0203	286.84	285.25
June	1,248.67	158.10 ⁶	0.6851	290.31	288.82
July	1,749.33	158.10 ⁶	0.8445	292.07	290.68
August	1,070.67	158.10 ⁶	0.5971	290.87	290.92
September	814.33	158.10 ⁶	0.5198	285.17	286.07
October	745.50	158.10 ⁶	0.4816	281.05	282.30
November	1,804.67	158.10 ⁶	0.9259	276.63	278.10
December	1,477.17	158.10 ⁶	0.8098	272.74	275.28

Table 2
Values of measured concentrations (C_i) of each pollutant

	BOD ₅ (kg/m ³)	COD _{cr} (kg/m ³)	N _{tot.} (kg/m ³)	N-NO ₂ ⁻ (kg/m ³)	N-NO ₃ ⁻ (kg/m ³)	N-NH ₄ ⁺ (kg/m ³)	P _{tot.} (kg/m ³)
January	0.0032	0.0233	0.0014	0.000005	0.001189	0.000053	0.00006
February	0.0028	0.0248	0.0021	0.000011	0.001429	0.000032	0.00007
March	0.0021	0.0262	0.0025	0.000005	0.001316	0.000043	0.00004
April	0.0019	0.0256	0.0005	0.000003	0.001244	0.000018	0.00006
May	0.0018	0.0281	0.0020	0.000013	0.000827	0.000043	0.00008
June	0.0028	0.0286	0.0015	0.000008	0.001017	0.000079	0.00006
July	0.0027	0.0262	0.0009	0.000009	0.001093	0.000024	0.00007
August	0.0029	0.0275	0.0012	0.000008	0.001096	0.000107	0.00004
September	0.0029	0.0272	0.0013	0.000010	0.001115	0.000056	0.00005
October	0.0030	0.0292	0.0011	0.000010	0.001480	0.000047	0.00003
November	0.0031	0.0274	0.0009	0.000017	0.000984	0.000070	0.00009
December	0.0022	0.0249	0.0017	0.000002	0.001074	0.000071	0.00002

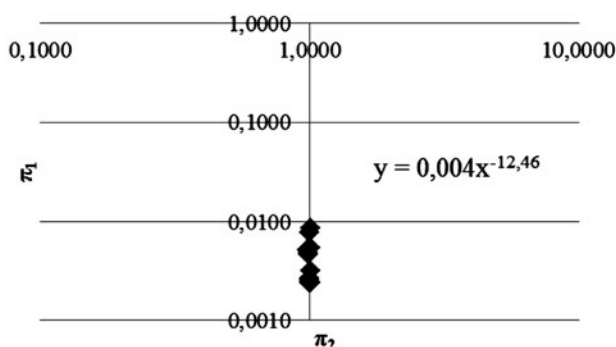


Fig. 2. Non-dimensional arguments and regression in logarithmic coordinates.

from 0 to 1, with higher values indicating less error variance [21].

NSE is a normalized statistic that determines the relative magnitude of the residual variance compared to the measured data variance [21,22]. NSE indicates how well the plot of measured versus calculated data fits the 1:1 line. It is computed as:

$$NSE = 1 - \frac{\sum_{i=1}^n (C_{\text{measured}} - C_{\text{calculated}})^2}{\sum_{i=1}^n (C_{\text{measured}} - C_{\text{mean}})^2} \quad (7)$$

where $C_{\text{calculated}}$ and C_{measured} are the calculated and measured values of pollutant concentration in the river, C_{mean} is the mean of measured data, n is the number of data.

NSE ranges between $-\infty$ and 1. Values between 0 and 1 are generally viewed as acceptable levels of performance.

Uncertainty and also sensitivity analysis are important tools for exploring complex models. Saltelli [23] clearly shows the key role of these tools within the wider context of the building, validation, and use of process models. The sensitivity analysis was performed evaluating the effect produced by the variation of the input data. Plots were used for the representation of the calculations [24,25].

The results of modeling are discussed in the following section.

3. Results and discussion

The model for the determination of pollutant concentrations was calibrated for seven pollutants over six years 2003–2008 and verified in the next two years 2009–2010. This paper presents comparisons of concentrations of BOD₅, COD_{Cr}, N_{tot.}, N-NO₂⁻, N-NO₃⁻, N-NH₄⁺, and P_{tot.} in the Krasny Brod River profile calculated from the model developed based on dimensional analysis (5) and monitored values obtained from SWME.

It was necessary to calculate new regression coefficients A and B for each pollutant whose concentration is determined according to model (5). Table 3 presents coefficients A and B for each calculated pollutant concentration.

Values of calculated ($C_{i \text{ calculated}}$) and monitored ($C_{i \text{ measured}}$) concentrations of pollutants in the river profile are presented in Fig. 3. This figure presents comparisons of 96 values of pollutant concentrations: 72 values for the calibrated period from 2003 to 2008 and 24 values for 2009 and 2010—the period in which the model was verified (except for some missing monitored values).

Table 3
Regression coefficients for each pollutant

Pollutant	A (-)	B (-)
BOD ₅	0.004	-12.46
COD _{Cr}	0.0004	-8.067
N _{tot.}	0.0079	10.395
N-NO ₂ ⁻	1.5671	-25.47
N-NO ₃ ⁻	0.0122	10.091
N-NH ₄ ⁺	0.3317	-30.29
P _{tot.}	0.1057	-16.53

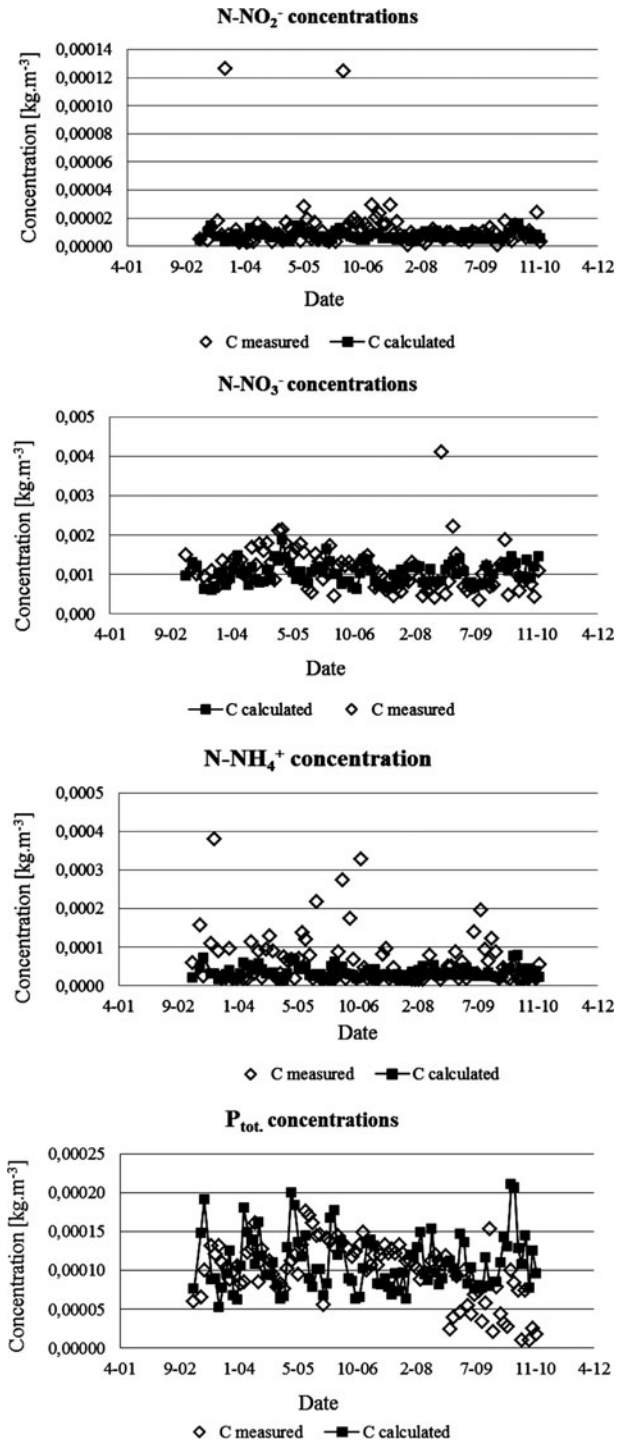
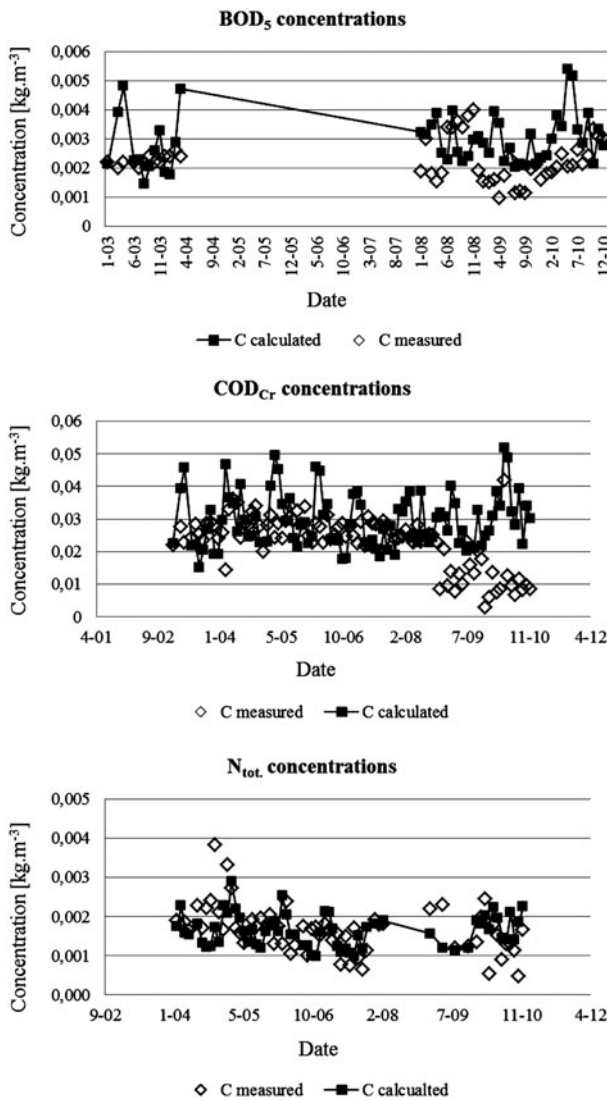


Fig. 3. Values of calculated and monitored concentrations of pollutants.

Differences between measured and predicted pollutant concentrations can occur because selections of relevant parameters are not necessarily involved in

Fig. 3. (Continued).

all aspects on which the pollutant concentration depends. Another reason is that measured values are not exactly stated. Differences occur due to a variety of reasons such as rainfall, influence of pollution source, or outflow of wastewater. Major differences

could occur because of errors in taking the samples, or errors in the determination of concentrations in the lab. Also relevant parameters are required to be used for dimensional analysis.

The difference between the calculated and monitored pollutant concentrations was evaluated using Eq. (6). The goodness of fit of the water quality prediction model was explained with values of accuracy such as the coefficient of determination and NSE (7). The values of uncertainty—error for each pollutant, coefficient of determination, and NSE statistic—are presented in Table 4.

It is evident from Table 4 that the model is applicable mainly to the pollutants N_{tot} , $N\text{-NO}_3^-$, where the relative error of calculation was within 0.40 (low) [26]. Coefficient of determination for N_{tot} , $N\text{-NO}_3^-$ are the highest of all the values, and NSE is positive for $N\text{-NO}_3^-$. For indicators $N\text{-NO}_2^-$, $N\text{-NH}_4^+$, the model cannot be applied since the relative error was between 0.60 and 0.80 (high), low R2 of 0.003–0.004, so we recommend its use in conjunction with other methods of modeling. These pollutants in surface water are difficult to determine because they readily oxidize to a higher degree of oxidation. This model cannot be used to determine pollutants COD_{Cr} and P_{tot} either because the relative error according to the calculations went as high as undesirable, R2 close to 0 and NSE negative. The presence of these two substances in surface waters in large quantities can be the result of natural processes or human activities. In the case of biological oxygen demand (BOD_5), relative error was 0.60, which seems to be of medium uncertainty, but R2 is close to zero and NSE is the lowest value. So, the other methods of modeling are appropriate.

Although R2 has been widely used for model evaluation, this statistic is oversensitive to high extreme values (outliers) and insensitive to additive and proportional differences between model predictions and measured data [27]. It would therefore be interesting to apply this model without extreme values.

Table 4
Uncertainty analysis of the monitored period 2003–2010 for measured pollutants

Pollutant	σ (-)	R2 (-)	NSE (-)
BOD_5	0.566	0.002	-2.687
COD_{Cr}	0.760	0.007	-1.480
N_{tot}	0.358	0.071	-0.116
$N\text{-NO}_2^-$	0.734	0.004	-0.124
$N\text{-NO}_3^-$	0.372	0.080	0.005
$N\text{-NH}_4^+$	0.764	0.003	-0.228
P_{tot}	0.817	0.000	-0.991

Within the research, sensitivity analysis was performed for a selected indicator of pollution in surface $N\text{-NO}_3^-$. We followed up as the value of each parameter (T_w , T_a , Q , v , F) increased or decreased, depending on the decrease/increase by 1%. Results from the sensitivity analysis are presented in Fig. 4.

Fig. 4 depicts the effect on the pollutant concentration due to different input data. The temperature of air and the temperature of water have major influences on the pollutant concentration. The model developed shows little sensitivity to the flow, velocity of water in the stream, and catchment area.

There are some values of the monitored pollutant concentrations that occasionally have extreme deviations from the yearly measurement of the relevant indicator (e.g. COD_{Cr}). Extreme values are related to the deterioration of any other monitored parameter (e.g. simultaneously measured high levels of suspended solids in the analyzed samples of surface water). This indicates the earliest adverse effect of surface run-off due to intense rainfall, which would be an indication of increased flow in the stream. Overall, based on the results of laboratory measurements, water quality in the River Laborec has a natural tendency to deterioration at the lower monitoring points in the direction of water flow. The Krasny Brod River profile is situated in the upper part of the River Laborec basin. Occasional fluctuations in water quality during the year are to some extent contingent on polluting discharges from industrial and municipal point sources of pollution, situated in a specified section of the Laborec River basin, and further diffuse sources of pollution flushed into the river from the surrounding terrain during abundant rainfall, and seasonal temperature fluctuations (risk of overheating of water at high temperatures, the long-term and low flow rate of water, resulting in a decrease in the dissolved oxygen in the surface water and therefore to deterioration of the self-cleaning process).

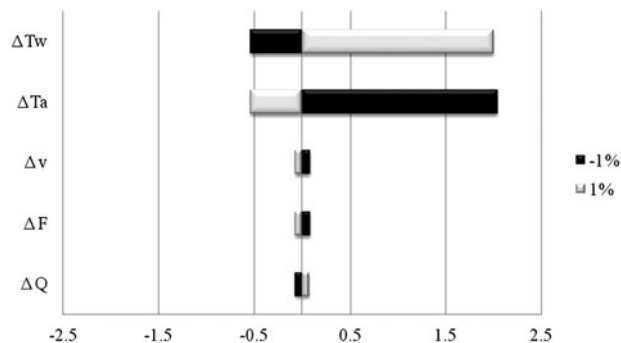


Fig. 4. Sensitivity analysis for pollutant $N\text{-NO}_3^-$.

Water quality involves a long list of individual components and physical, chemical, and biological constituents. Changes in water quality resulting from land-use activities on a watershed can make water unusable for drinking, but it can still be acceptable for irrigation or other uses. In some instances, we are required by laws or regulations to prevent water quality characteristics from being degraded from natural or background conditions defined as non-degradation, and as a consequence these characteristics are a key provision in the water quality standards. Phosphorus and nitrates in excess amounts can accelerate eutrophication, causing dramatic increases in aquatic plant growth and changes in the types of plants and animals that live in the stream. This in turn affects dissolved oxygen, temperature, and other indicators. Decomposition of organic matter lowers the dissolved oxygen level, which in turn slows the rate at which ammonia is oxidized to nitrite (NO_2) and then to nitrate (NO_3). Under such circumstances, it might be necessary to monitor for nitrites or ammonia as well, which are considerably more toxic to aquatic life than nitrates. Wastewater from sewage treatment plants often contains organic materials that are decomposed by microorganisms, which use oxygen in the process [28].

4. Conclusions

Water quality models are very useful in describing the state of a river system and predicting changes in this state when certain boundary or initial conditions are altered. Such changes may be due to morphological modifications to the water body, such as straightening, and discharge regulations using control structures (weirs, dams), changes in the pollution type (point or diffuse), amount and location of pollutant loading into the system, and changes in meteorological inputs due to changing trends in climate.

This paper presents a possible approach to determining pollutant concentrations in rivers using the Buckingham theorem, if we know the proper variables which form the input to the calculations. The Buckingham π theorem is the core of the dimensional analysis. It provides a method for computing non-dimensional arguments from the given variables. Input data and selection of relevant variables are the most important issues in determining pollutant concentration in a water stream. Full selection of variables must be made in relation to assessment objectives and specific knowledge of each individual situation [12]. Determining the pollutant concentrations in a water stream is a complex task. This issue is influenced by natural as well as artificial phenomena, particularly human activities in

the catchment area. To consider all the variables influencing this process is practically impossible [11,12]. We chose the main ones which we consider as parameters which most significantly influence pollutants' occurrence and their concentrations in a stream.

In this paper, we would like to point out the broad applicability of this model. It could be used in any river profile and for any pollutant. The important point is to calculate new regression coefficients A and B for each profile or each pollutant. The importance of this research is in the field of water quality modeling. Determining pollutant concentrations in a stream from model calculations will help to save expensive monitoring equipment and finally it will contribute to achieving good water status according to the Water Framework Directive. The model has an empirical basis, and if some changes are made to the river basin (e.g. regulation of river flow), the model needs new data to be calibrated.

Differences between measured and calculated values of pollutant concentrations occur for a variety of reasons, e.g. rainfall, influence of source of pollution, or outflow of wastewater, and also because of errors in taking samples or in determining concentrations. Differences can also occur because the selection of relevant parameters did not involve all the effects which pollutant concentration depends on. The last reason may be that the measured values are not exactly stated.

The main objectives of the present research were to investigate options for estimating the variables of the model and to develop a usable model for pollutant concentration determination or prediction in a stream. The variation of pollutant concentrations in surface waters stimulates broad interest among scientists and researchers in the field of water pollution control. To consider all the variables influencing this process is practically impossible. A model for the determination of pollutant concentrations has been developed and verified for the Krasny Brod River station on the River Laborec in eastern Slovakia. It can be concluded that the water quality model based on the Buckingham theorem is applicable.

Uncertainty analysis was performed. Table 4 presents the results of the goodness of fit of water quality model for each pollutant. Error value, coefficient of determination, and NSE proved the highest applicability of the developed model for N_{tot} and N-NO_3^- .

Sensitivity analysis carried out indicated the importance of the variables for the pollutant concentrations determined using the model. Fig. 3 shows the results from sensitivity analysis revealing how sensitive the model is to the choice of parameters. The model shows the highest sensitivity to the temperature of air and water.

This approach could be used to calculate the parameters for other similar water streams.

The developed model and its application could be of interest to the academic community, especially in water quality modeling and environmental statistics. Further work would be needed to explore how these coefficients vary between streams.

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