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THE FLATTENING PHENOMENON IN A SEASONAL VARIABILITY ANALYSIS OF THE TOTAL NITROGEN LOADS IN RIVER WATERS

ZJAWISKO WYPŁASZCZENIA PODCZAS SEZONOWEJ ZMIENNOŚCI AZOTU OGÓLNEGO W POWIERZCHNIOWYCH WODACH PŁYNĄCYCH

Abstract

This article shows the results of analyses conducted of the seasonal variability of nitrogen concentrations and loads, depending on plants growing season, this doesn't seem to work, consider changing to something like 'dependent upon the stage of the plant growing season,' if that is what you mean as well as river flow and the precipitation levels in the basins of Middle Warta, Reda and Rega. The Macromodel DNS/SWAT, implemented for three basins, has been calibrated in calculations profiles of three river basins this is vague and unclear, the repetition of 'three (river) basins' is particularly confusing. The analysis confirmed the significant impact of cover crops on the retention of water and nutrients. The phenomenon of periodic decreases and stabilisation of nitrogen concentrations and loads in the surface waters flowing through the profiles of the enclosing water body was observed and analysed. The flattening phenomenon analysis of the phenomenon to me, the repetition of 'phenomenon' is confusing, you could clarify this by defining the second use of 'phenomenon' by, for example, inserting 'of these decreases and stabilisation' here can be used to assess the state of the ecosystem in the basin area.

Keywords: water pollution, environmental analysis, nutrients, bioaccumulation, nonpoint sources

Streszczenie

W artykule przedstawiono wyniki analiz sezonowej zmienności azotu ogólnego w zależności od sezonu wegetacyjnego, a także przepływu rzeki i wielkości opadów występujących na zlewni środkowej Warty, Redy i Regi. Do tego celu został wykorzystany Makromodel DNS/SWAT, który został skalibrowany dla profili ujściowych wybranych zlewni. Przeprowadzona analiza potwierdziła znaczący wpływ roślin okrywowych na retencję wody i składników odżywczych. Zaobserwowano okresowe zmniejszanie się stężenia azotu w powierzchniowych wodach płynących. Zaobserwowane zjawisko może zostać wykorzystane do oceny stanu ekosystemu w obszarze dorzecza, a także umożliwia ocenę rzeczywistego wpływu zarządzania zlewnią na cykl azotu.

Słowa kluczowe: energetyczne wykorzystanie biogazu

1. Introduction

Studies concerning the sources of nutrient emissions in Europe have confirmed that the largest share of these pollutants in most countries, including Poland, comes from diffuse sources [21]. Agricultural land occupies approximately 60% of the total area of Poland and has a significant impact on the levels of nitrogen discharged into surface waters [13]. Agricultural activity is one of the primary forms of human activity affecting the environment. Increased agricultural anthropopressure, i.e. human agricultural activities affecting the natural environment in the river basins, causes quantitative and qualitative changes in the aquatic environment [18]. The impact of agricultural pollution on the aquatic environment is directly related to the intensity of fertiliser economy (intensity of fertilization) and soil use. Fertiliser economy and agricultural practices which are beneficial with regard to crop production are not always beneficial to the environment and lead to dynamic changes in the amount of nitrogen in surface waters over time. The size of the nitrogen run-off into surface waters depends, inter alia, on land use, weather conditions, plant cover and soil properties [19, 49]. The responsibility for the study of surface water quality as well as the processing and dissemination of information on the aquatic environment in Poland belongs to the State Environmental Monitoring Department [11]. At present, mathematical models based on detailed data relating to land use, soil types, climatic and meteorological data are widely used. A *study* concerning the analysis of variability in concentrations of biogenic compounds has been carried out by the Institute of Meteorology and Water Management – National Research Institute in Poland, in ‘Modelling of Water Pollution Section from 2012. The mentioned studies were initiated by IMGW-PIB due to problems that occurred during the model calibration of nutrients with the use of the mathematical model Macromodel DNS (discharge nutrient sea) [32]. The use of Macromodel DNS enabled us to obtain the full range of data with daily time steps of the analysed parameters at selected control points. This enabled the carrying out of a wide range of analyses, including an analysis of the seasonal variability of nutrients over a multi-year period. The seasonal variability of nutrients, i.e. seasonal fluctuations in the amount of nutrients in surface waters, depends, inter alia, on the hydrological regime, the biological activity of the river, and land use in the basin.

Nutrient load fluctuations occurring in surface waters over time led us to carry out research concerning the relationship between the nitrogen uptake of plants and its subsequent quantity in surface waters. The aforementioned seasonal variability of pollution is the subject of many research studies [35, 41, 42, 44, 46]. Processes such as the uptake of nutrients by plants, surface and point pollution run-off from the area as well as the impact of nutrients on the biological elements of the ecosystem, are analysed in detail. In publication [39], it is also stated that during the growing season, there are changes in the amount of nutrients discharged into surface waters as a result of their uptake by plants from the environment. The participation of plants in the nitrogen cycle in the environment is important and cannot be ignored in the analysis of the seasonal variability of nutrients in surface waters; the same is true of the stage of the season of plant growth, this can also have a significant impact on the amount of nutrients in surface waters throughout the year and this relationship was analysed.

Knowledge concerning seasonal variability can provide a good basis for determining, inter alia, the validity of multiple scenarios and action plans developed by the state administration and research units [6, 51], it is therefore important to continue research.

2. Materials and Methods

2.1. Objectives of study

The main objective of this work was to analyse the seasonal variability of the total nitrogen loads in the calculation profile. Analyses of the amount of the total nitrogen load are crucial for the proper assessment of nutrient balance in the basin; therefore, it is important to identify the seasonal fluctuations of loads in the river calculation profiles. In order to determine the sum of the total daily nitrogen load at the calculation profile of the basin in over a period of several years, a cumulative mass curve was used. Analyses were carried out for three pilot basins: the Rega, the Middle Warta and the Reda. Macromodel DNS [32] was used to simulate the total daily loads of nitrogen at the rivers calculation profiles.

In order to determine the total nitrogen load flowing out of a basin area at the calculation profile basin over a given period of time, a mass curve was used. The mass curve of the size of the total nitrogen load is a curve in which the ordinate of each point indicates how the total volume of load flowed from the beginning of the period until a specified abscissa of this point in the calculation profile of the river. The values for the establishment of the curve are the total daily loads of total nitrogen treated as daily averages the mean. The curve is obtained by totalling up the required intervals of daily loads of total nitrogen to give the ordinates of the curve. By applying the size of the load a picture of the rising curve during the considered period is obtained. The line graph is a constantly rising curve with a number of inflection points [5, 33, 47]. Constructed in this manner, the curve helps to indicate, in the later stages of the work, seasonal variations in the total nitrogen load in the basin calculation profile during the analysed years. The main preconditions to construct a correct curve are aggregated daily items of data relating to the total nitrogen load.

2.2. Macromodel

In order to obtain daily data at selected control points in the study, the Macromodel DNS (discharge nutrient sea) mathematical model with SWAT (soil and water assessment tool) module was used. Macromodel DNS/SWAT was designed by the Institute of Meteorology and Water Management-National Research Institute for the analysis of processes taking place in a basin, such as water and matter cycles [30, 31]. It enables the simulation of the long-term impact of land use on water quality and the impact of pollutants discharged to surface waters. The SWAT module uses the hydrological transport model which is based on meteorological and hydrological data, the extent of surface run-off and the amount of fertiliser *contained within* in order to analyse phenomena and processes related to the transport of nutrients in the watershed [30]. The general scheme of Macromodel DNS is shown in Figure 1.

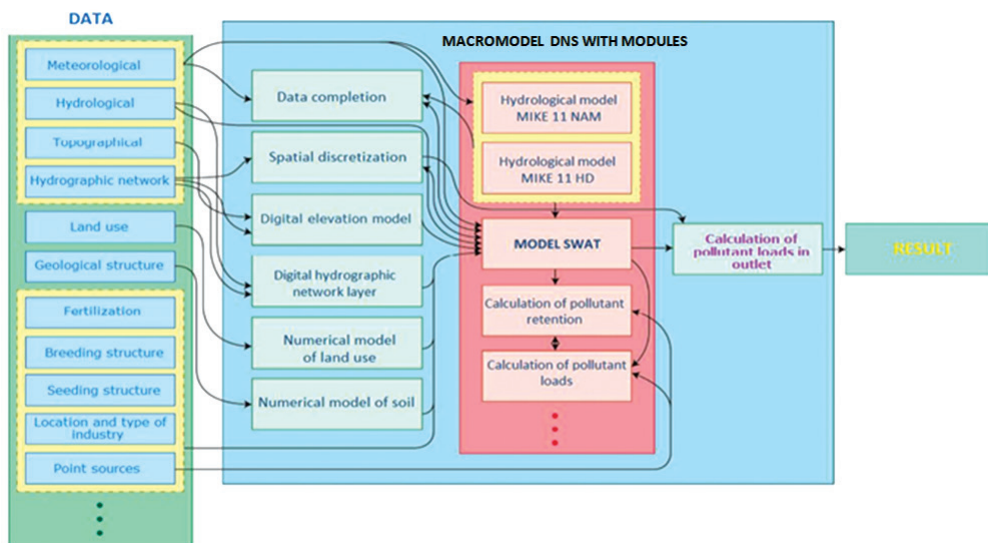


Fig. 1. The general scheme of Macromodel DNS [32]

The SWAT module is an element of Macromodel DNS and is used to analyse the processes of water cycles and organic matter in the basin [30, 31]. This allows us to carry out simulations of the long-term impact of land use management on water quality and to examine the amount of pollutants discharged from particular surface water bodies (SWB) to other surface water bodies. This module uses a hydrological transport model, which is based on, inter alia, meteorological data, the quantity of surface run-off and the amount of soil fertilisation; it also enables us to carry out analyses of phenomena and processes connected with the transportation of nitrogen loads in the sub-basin [31]. With the use of the Macromodel DNS/SWAT, all the elements form a homogenous, numerical sub-basin model that enables us to analyse different scenarios of sub-basin exploitation in different meteorological and hydrological conditions. The Macromodel DNS/SWAT can be used to analyse the efficiency of the proposed measures aimed at reducing the quantity of total nitrogen loads discharged into surface waters [17, 18, 32].

The *validity* of the use of Macromodel DNS/SWAT to study the variability of the total nitrogen load was confirmed by numerous scientific works carried out with the use of the mentioned model, including work concerning the modelling of the discharge of nutrients into the Baltic Sea [32], *analyses* concerning the impact of agricultural anthropopression on surface water quality [18] and analyses of the river absorption capacity [48].

For the analysis of the size of the total nitrogen load on the river estuary and its seasonal variability in the calculation profile, three pilot basins were selected.

2.3. Descriptions of the Basins

The Middle Warta basin (Fig. 2a) constitutes a part of the Warta basin and is closed by two profiles – Nowa Wieś Podgórna and Oborniki. The acreage of the basin is 6,039 km² and constitutes 11% of all the acreage of the entire Warta basin (around 54,500 km²). There are

a few tributaries on the examined section of the river of which the most important are the Lutynia river, the Mosiński Canal and the Mogilnica river. The analysed section of the basin is characterised by a significant proportion of the area being exposed to nitrogen pollutants of agricultural origin. The largest agglomeration of the basin is the city of Poznań. The parent rocks of the basin area are post-glacial sediments, mainly sandy and loamy soils, the majority being brown and podzolic soils. The long-term observation studies of the Warta river indicate that the water quality is *varies* in particular sections. The major source of pollution is the constant and seasonal discharges of domestic, economic and industrial sewage from cities located near the river, and surface run-offs from agricultural areas [8, 38].

The basin of the Rega river (Fig. 2b) covers an area of 2766.8 km², and the length of the watercourse from the spring in Połczyn-Zdrój district to the Baltic Sea constitutes 187.57 km (35.4 miles), which makes it the fourth longest of the rivers flowing into the Baltic Sea (after the Wisła, the Odra and the Pasłęka rivers). There are six wastewater treatment plants in the basin: Świdwin, Gryfice, Łobez, Dobra, Resko, Węgorzyno. Within the region, podzolic soils comprised of sands and gravels as well as brown soils comprised of loamy sands and glacial tills dominate. The Rega basin is agriculturally dominant – agricultural areas constitute 54.5% of the acreage. The average size of an individual farm is > 15 ha, agricultural holdings constitute 17.3% and 5.8%, respectively [40].

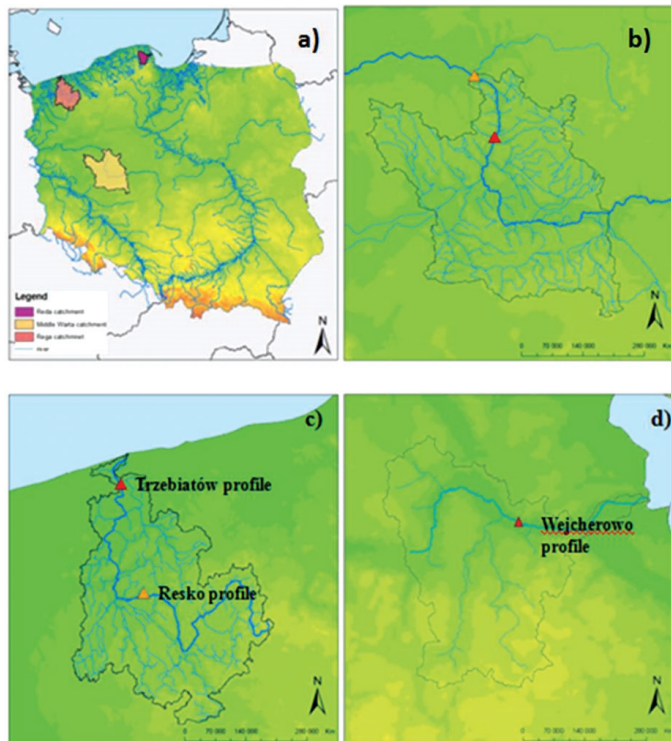


Fig. 2. a) Location of basins in Poland; b) the Middle Warta basin; c) the Rega basin; d) the Reda basin (indication of profiles for calibration and verification [red] and validation [orange]) [28]

The acreage of the Reda basin (Fig. 2c) is around 485.55 km². The length of the watercourse from its sources in Strzebielin to the Baltic Sea is 50.6 km (31.4 miles). The soils of The Reda and its tributaries are characterised by a significantly sandy terrain.. In the valleys, there are peat soils, very light clay soils and alluvial mud soils. The basin area is mainly used as agricultural land and grasslands. Moreover, special characteristics of the Reda tributaries are the relatively high river gradients that are typical for mountain rivers. The lakes of the basin are situated in the vicinity of the sources of the river tributaries. The total acreage of the lakes equals 3.187 km². In the Orle locality, there are artificial dammed reservoirs (the Nowe Orle and the Stare Orle), that were created from the exploitation of calcium deposits [22].

2.4. Model input data

For the use of the Macromodel DNS/SWAT, the following input data was prepared: digital elevation model (DEM); hydrology map; soil map; land use map; data concerning wastewater treatment plant; the daily meteorological and hydrological data; the amount of fertilisers. The gathered data formed the database that was required by the model [1, 42, 43].

2.4.1. Sub-basins

The Middle Warta river basin was divided into 70 sub-basins according to SWB, the Rega basin into 52 sub-basins and the Reda basin into 30 sub-basins according to the boundaries of the Surface Water Bodies, which are the basic units of water management in Poland, according to [11].

2.4.2. DEM

The DEM remains the national, central geodesic and cartographic level resource and is created on the basis of aerial photographs within a flat rectangular coordinate system labelled 'PUWG1992'. The terrain data corresponds to map sheets within the flat rectangular coordinate system '1992' on a scale of 1:10 000. The grid interval is assumed to be 10 to 50 m with an average error of 0.8 to 2 m. The data was based on aerial imaging and topographic maps. A triangulated irregular network map was used – this is a digital format of a continuous spatial data representation in which information about elevations are assigned to vertices of triangles and interpolated between them.

2.4.3. MPHP

The map of hydrographical divisions of Poland [28] is the basis for the information system of water management. The map which was used contains the details of river networks and bodies of water within the boundaries of the analysed catchments on a scale of 1:50 000.

2.4.4. Wastewater

Data concerning wastewater treatment plants located in the area of the analysed basins was obtained from the National Water Management Authority in Poland. The data contained detailed information including the geographical coordinates of any given wastewater treatment plant the amount of public wastewater treated within a year in thousands $\text{m}^3 \text{yr}^{-1}$, total suspended solids (mg L^{-1}), total nitrogen (mg L^{-1}) and total phosphorus (mg L^{-1}).

2.4.5. Meteorology

Meteorological input data with a daily time step included solar radiation, wind speed, precipitation, relative moisture, and maximum and minimum temperatures. Table 1 shows the meteorological stations used in the models of the basins selected for analysis.

Table 1. Meteorological stations for the analysed basins

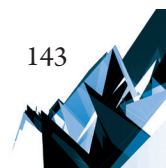
River basin	Number of weather stations used to build the model	Station names
Middle Warta	9	Koło, Piła, Gorzów Wlkp., Gniezno, Gorzyń, Pobiedziska, Nowa Wieś Podgórna, Poznań, Kalisz
Rega	7	Goleniów, Kołobrzeg, Łabędzie, Resko, Wierzchowo Pom., Starnin, Trzebiatów
Reda	9	Rozewie, Żelazno, Lębork, Wejherowo, Tepcz, Żelistrzewo, Rębiska, Gdynia, Gdańsk

2.4.6. Soil maps

Soil maps at a scale of 1:100 were obtained from the Institute of Soil Science and Plant Cultivation National Research Institute for the following types of soil: very light, light, average, heavy [23] (Tab. 2). Classification was made according to a granulometric soil group with data and system adopted by the IUNG-PIB.

Table 2. Percentages of the different soil classes found within the basin area [%][23]

Basin soil class	Middle Warta	Rega	Reda
very light	32.9	10.13	43.8
light	30.6	50.71	7.04
average	33.9	39.17	37.14
heavy	2.4	-	11.15



2.4.7. Land use

Land use maps of the Middle Warta and the Rega basin were created based on the CORINE LAND COVER information system [3, 9] which divides land use into six classes attributing relevant abbreviations to it which are acceptable and readable by the model (Tab. 3).

Table 3. Percentages of the different land use types found within the basin area [%] [9]

Basin land use types	Middle Warta	Rega	Reda
artificial surfaces	6.17	1.8	6.34
agricultural areas	72.82	54.5	38.91
forests	20.04	32.7	39.84
wetland areas	0.1	0.1	0.02
water bodies	0.85	1.2	0.71
meadows	-	9.7	14.18

2.4.8. Fertilisers

Input data used to calculate phosphorus loads from manure and mineral fertilisers were obtained from the Local Database [2] including information regarding livestock and the surface area of arable lands in hectares at the provincial level. The dominant crops with appropriate agricultural management operations are specified for each hydrological response unit (HRU) in the analysed basins. HRUs are comprised of unique land cover, soil and management combinations. Crops identified for basin areas are shown in Table 4. Each crop from Table 4 requires a different dose of fertiliser; however, doses were averaged for modelling purposes. The average dose of nitrogen fertilisers in the Middle Warta catchment was 156.6 kg N/ha, in the Rega catchment it was 85.6 kg N/ha, and in Reda catchment it was 105.9 kg N/ha.

Table 4. Crops in the analysed basins

Relevance for catchment			Crops
Middle Warta	Reda	Rega	
•	•	•	wheat
•	•	•	rye
•		•	barley
•	•	•	potatoes
•		•	sugar beets
•	•	•	rape
	•	•	oat

2.5. Sensitivity analysis and calibration, verification and validation processes

In further work, sensitivity analysis of the parameters in the model was carried out. The main purpose of applying sensitivity analysis was to define a set of parameters with the highest sensitivity, meaning those which have the greatest impact on the parameters affecting the flow and nitrogen load in the analysed calculation profile of the river. The method of sensitivity analysis in the ArcSWAT interface combines the Latin Hypercube (LH) and One-factor-At-a-Time (OFAT) sampling. A parameter is randomly selected and its value is changed from the previous simulation by a user-defined percentage for a number of LH loops. SWAT is run on the new parameter set and a different parameter is then randomly selected and varied.

Correct analysis of the modelling simulations is necessary in order to obtain reliable results. For this reason, it should be checked whether the modelling results fit the observed data during performance of the calibration, verification and validation processes, which are respectively defined as:

- ▶ adjustment of model parameters in order to obtain the greatest convergence of modelling results and observations conducted in calculation profile;
- ▶ checking at a measuring point whether the model is a good representation of the conceptual model – this is performed on independent data during the process of calibration conducted in calculation profile;
- ▶ final checking at a different measuring point to the calibration and verification point of whether the model is a good representation of reality by comparing the modelling results with observations conducted in a profile different from the calculation profile.

Observation data was obtained from State Environmental Monitoring (SEM) which, according to the law, is supposed to provide reliable information about the state of the environment. SEM leads analysis of water samples in selected monitoring sections of rivers in accordance with the scope and frequency specified in regulations [36, 37].

To evaluate the degree to which observations and simulations match, the following three statistical measures were applied: the coefficient of determination (R^2); the Nash-Satcliffe coefficient (NSE); the percent bias (PBIAS) [20, 29, 41]. The evaluation of the statistical measurements was conducted in accordance with the criteria shown in Table 5.

Table 5. Performance rating [27, 29, 32, 41]

Performance rating	NS	PBIAS		R^2
	flow/nutrients	nutrients	flow	flow/nutrients
very good	$0.75 < NSE \leq 1$	$< \pm 25$	$< \pm 10$	$0.64 < R^2$
good	$0.5 < NSE \leq 0.75$	$\pm \leq 25$ Pbias $< \pm 40$	$\pm \leq 10$ Pbias $< \pm 15$	$0.49 < R^2 \leq 0.64$
satisfactory	$0 < NSE \leq 0.5$	$\pm 40 \leq$ Pbias $< \pm 70$	$\pm 15 \leq$ Pbias $< \pm 25$	$0.36 < R^2 \leq 0.49$
nonsatisfactory	$NSE \leq 0$	Pbias $\geq \pm 70$	Pbias $\geq \pm 25$	$R^2 \leq 0.36$

For each of the selected pilot basins, a different body of data for the calibration, verification and validation. This was related to the availability of monitoring data over different periods



which was used to build models of the basin. In Table 6, information for each basin is shown regarding the analysis period, the monitoring point for which monitoring data was available from the SEM.

Table 6. Information regarding the analysis period, the monitoring point and the amount of available monitoring data for pilot basin [18, 48]

Phase Flow		The Middle Warta river		The Rega river		The Reda river	
		Total Nitrogen	Flow	Total Nitrogen	Flow	Total Nitrogen	Flow
Calibration	period of analysis	01.01.2000-31.12.2006		01.01.2001-31.12.2006		01.01.2002-31.12.2004	
	river monitoring point/ miles*	Poznań – Roch Bridge/127.45 miles		Trzebiatów/8.01 miles		Wejherowo/15.8 miles	
	total data quantity (TDQ)	2557		2191		1096	
	the data amount	2557	120	2191	157	1096	72
	percentage of TDQ	100%	5%	100%	7%	100%	7%
Verification	period of analysis	01.01.2007-31.12.2009		01.01.2007-31.12.2009		01.01.2005-31.12.2005	
	river monitoring point/ miles*	Poznań – Roch Bridge/127.45 miles		Trzebiatów/8.01 miles		Wejherowo/15.8 miles	
	total data quantity (TDQ)	1096		1096		365	
	the data amount	1096	25	1096	50	365	22
	percentage of TDQ	100%	2%	100%	5%	100%	6%
Validation	period of analysis	01.01.2003-31.12.2006		01.01.2002-31.12.2008		-	
	river monitoring point/ miles*	Oborniki/127.5 miles		Resko/33 miles		-	
	total data quantity (TDQ)	1461		2557		-	
	the data amount	1461	84	2557	48	-	-
	percentage of TDQ	100%	6%	100%	2%	-	-

In the case of the Reda river, validation of the model was not conducted due to a lack of observation data on another profile separate from the calculation profile (one river control profile).

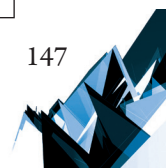
3. Results and discussion

3.1. Sensitivity analysis results and the results of the calibration, verification and validation processes

For pilot basin models of the Middle Warta and Rega, within the functionality of SWAT, being in this case a DNS Macromodel module, a sensitivity analysis of the parameters associated with the flow and the total levels of nitrogen was conducted according to the description in Section 3.4. The results of this sensitivity analysis are presented in Table 7. For the Middle Warta basin, there are 16 parameters which are most sensitive and associated with the flow at the control point. For the Middle Warta basin, there are 16 parameters; for the Reda basin, there are 9 parameters; for the Rega basin, there are 11 parameters. For total nitrogen loads, from the range of parameters that may be manipulated during the calibration of the model, 9 parameters for the Middle Warta, 7 for Reda and 9 for Rega obtained the highest sensitivity. The parameters selected during the sensitivity analysis were used for the calibration of the model.

Table 7. The most sensitive parameters obtained from the sensitivity analysis in the SWAT model for the analysed basins [18, 48]

Relevance for basin			Parameter	Parameter description
Middle Warta	Reda	Rega		
1	2	3	4	5
Flow parameters				
•	•	•	ALPHA_BF	base flow alpha factor [days]
•			BLAI	maximum potential leaf area index
•	•		CANMX	maximum canopy storage [mm H ₂ O]
•	•	•	CH_K(1)	effective hydraulic conductivity in tributary channel alluvium [mm/hr]
•	•	•	CH_K(2)	effective hydraulic conductivity in main channel alluvium [mm/h]
•	•	•	CN2	initial SCS runoff curve number for moisture condition II
•			EPCO	plant uptake compensation factor
•	•	•	ESCO	soil evaporation compensation factor
		•	GW_DELAY	ground water delay time [days]
•	•	•	GWQMN	threshold depth of water in the shallow aquifer required for return flow to occur [mm H ₂ O]



Tab. 7 (cont.)

1	2	3	4	5
•		•	GW_REVAP	groundwater 'revap' coefficient
	•	•	RCHRG_DP	deep aquifer percolation factor
•			SOL_ALB	moist soil albedo
		•	SOL_K	saturated hydraulic conductivity [mm/hr]
•		•	SURLAG	surface runoff lag coefficient
•	•		TIMP	snow pack temperature lag factor
	Total nitrogen parameters			
•			AL1	fraction of algal biomass that is nitrogen
•		•	BC1	rate constant of biological oxidation of NH ₄ to NO ₂ in the Reach at 20°C in well aerated conditions
•	•	•	BIOMIX	biological mixing efficiency
	•	•	CDN	rate factor for humus mineralisation of active organic nutrients (N and P)
•	•		CH_N2	Manning's n value for the main channel
	•	•	CMN	rate factor for humus mineralisation of active organic nutrients (N and P)
•	•	•	ERORGN	nitrogen enrichment ratio for loading with sediment
•	•	•	NPERCO	nitrate percolation coefficient
•	•	•	N_UPDIS	nitrogen up take distribution parameter
		•	RCN	concentration of nitrogen in rainfall
•			RS4	organic N settling rate coefficient
•		•	SDNCO	denitrification threshold water content

The results of the statistical measurement of the calibration, verification and validation processes are shown in Table 8. Due to the utilisation of three statistical coefficients, it is essential to define a hierarchy in the assessment of coefficients in order to introduce an unequivocal interpretation. Therefore, the coefficient of determination (R^2) was treated as a priority.

The analysis carried out with the use of three statistical measures showed that in the examples of the Middle Warta river and the Rega river, the assessment of matching the flow observations to simulations obtained from Macromodel DNS/SWAT, with regards to R^2 , was very good in almost all cases in other words, there was a strong match between the observed and simulated flows. Only the calibration phase of the Reda river obtained a good value. For the remaining rivers, the flow provided good and satisfactory results for the NSE and PBIAS statistical measures. As far as total nitrogen loads are concerned, the strongest match between observations and simulations were obtained for the Middle Warta river and the Rega river, where for those rivers, the results oscillated between very good and satisfactory values. For The Reda river, the values for R^2 and PBIAS were respectively satisfactory and very good.

Only in the case of the NSE were results unsatisfactory for the calibration and verification phase – this was mainly due to the sensitivity of statistical measures on a small amount of available data. The results obtained thus confirm the high degree of agreement between the results of modelling and the data obtained through observation – this confirms that the model is a good representation of reality.

Table 8. Results for the model calibration, verification and validation phase for statistical measures with robust statistics for pilot rivers [18, 48]

Basin	Coefficient phases	Flow			Total nitrogen		
		R ²	NSE	PBIAS [%]	R ²	NSE	PBIAS [%]
Rega	Calibration	0.81	0.47	15.04	0.5	0	23.32
	Verification	0.87	0.75	-11.19	0.55	0.47	-13.06
	Validation	0.69	0	2.53	0.57	0.38	28.39
Middle Warta	Calibration	0.93	0.91	6.07	0.65	0.59	-0.44
	Verification	0.93	0.81	-0.84	0.81	0.57	0.14
	Validation	0.94	0.85	14.51	0.47	0.06	-0.58
Reda	Calibration	0.59	0.37	22	0.4	-1.13	12
	Verification	0.7	0.3	21	0.3	-2.37	23
	Validation	-	-	-	-	-	-

3.2. Analysis results

In order to analyse the size of the total nitrogen load flowing through the calculation profile of a given basin and the seasonal variability in the pilot basins which were calibrated, verified and validated with the Macromodel DNS/SWAT. This enables us to obtain coherent and comparable results for all three basins.

Cumulative curves of total nitrogen loads were produced (Figs. 3a-3c) in order to analyse the total amount of nitrogen compound that entered the calculation profile during the considered years, separately, as well as the average values for the analysed years which are marked with a black dashed line (Figs. 3a-3c).

The cumulative mass curve of the size of the total nitrogen load indicates changes in the total volume of the load which flowed from the beginning of the period in the calculation profile. As far as the Rega and the Middle Warta river are concerned, a reduction in the size of the total nitrogen load can be observed from March to April followed by a decrease and stabilisation of the total nitrogen load and again from November to December, followed by increased loads. In the case of the Reda river basin, these relationships are not so clear; however, a minimal reduction of the total nitrogen load in the months April to May and an increase after the months of October to November can be observed. In order to conduct an accurate analysis of changes in the total size of the average total daily nitrogen load within



the period 2002-2005 (Figs. 3a-3c, black dashed line), further detailed analyses were carried out. To this end, the average daily total nitrogen load from the 2002-2005 period was collated and analysed with the flow and precipitation in the growing season (in Poland, this lasts from around early March to around the end of October). Analyses of the period relating to the plant growing season is important because it has a significant influence on changes in the size of total nitrogen loads in surface waters. The analysis of seasonal changes in the total nitrogen loads for the analysed period showed that at the beginning of the plant growing season, the total nitrogen loads is the highest and decreases during the plant growing season until reaching the lowest value (Figs. 4-6). The highest value on the graph relating to the average daily total nitrogen load from the multi-year period is indicated by 'MAX' and the lowest value is indicated by 'MIN' for each of the analysed basins (Figs. 4-6). After the end of the growing season, the size of the total nitrogen loads in the calculation profile increases again. The size of the total nitrogen loads in the calculation profiles of the pilot rivers shows a decrease and stabilisation during the plant growing season. This phenomenon was observed for all analysed basins, and is called the *flattening phenomenon* this is defined as a periodic decrease and stabilisation of the size of the total nitrogen loads in the calculation profile during the plant growing season. The maximum and minimum loads of total nitrogen determines the precise boundaries of the *flattening*. These dependencies are illustrated in Figs. 4-6 with an indication of the average flow, precipitation, and a period of plant growing season in reference to total nitrogen load and total nitrogen concentration.

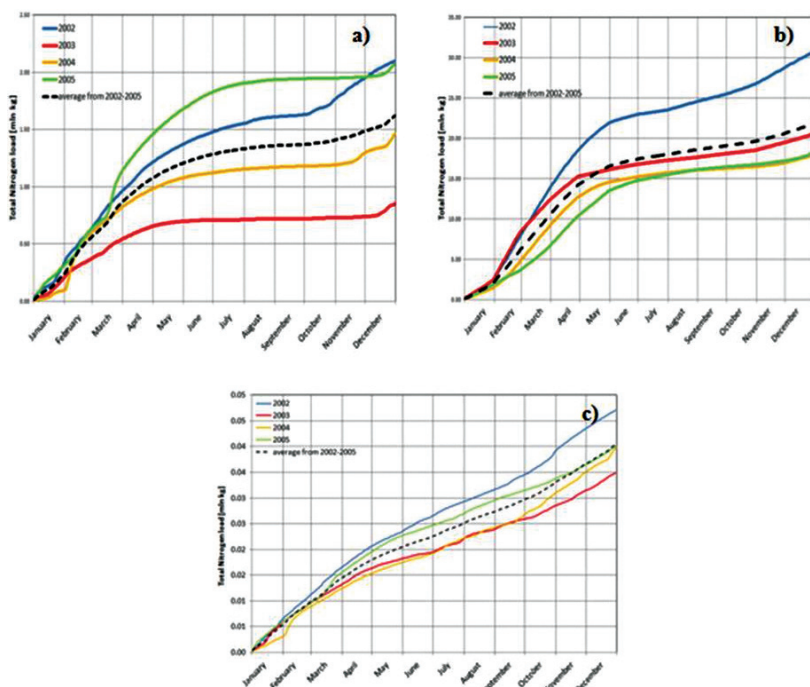


Fig. 3. Cumulative curves of the total nitrogen in the calculation profile of the Rega river (a), the Middle Warta river (b) and the Reda river (c) for separate years and the average cumulative curve (black dashed line) [own study]

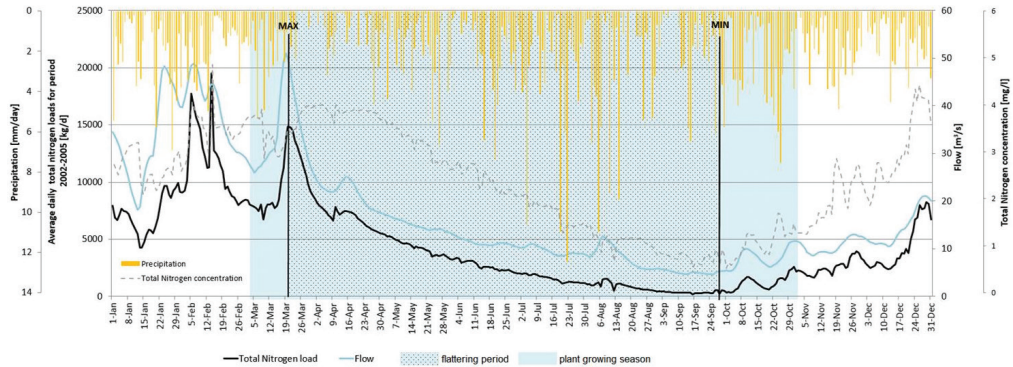


Fig. 4. Total nitrogen load, precipitation and flow rate with marked flattening period (MIN – MAX) and plant growing season in the Rega river basin for mean values for the period from 01/01/2002 to 31/12/2005 [own study]

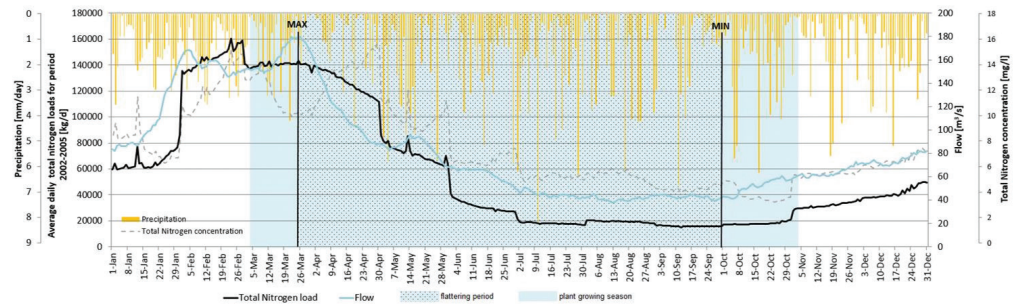


Fig. 5. Total nitrogen load, precipitation and flow rate with marked flattening period (MIN – MAX) and plant growing season in the Middle Warta river basin for mean values for the period from 01/01/2002 to 31/12/2005 [own study]

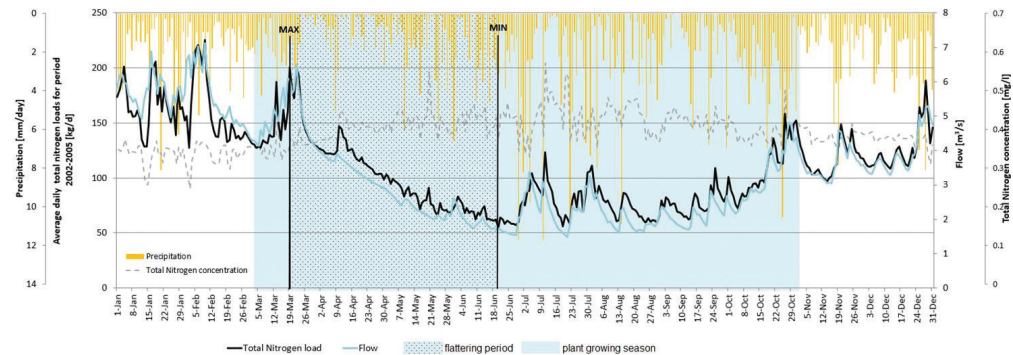


Fig. 6. Total nitrogen load, precipitation and flow rate with marked flattening period (MIN – MAX) and plant growing season in the Reda river basin for mean values for the period from 01/01/2002 to 31/12/2005 [own study]

Additionally, total nitrogen concentrations were analysed yearly. For the Rega and Middle Warta basins, the tendency observed for total nitrogen loads is similar for total nitrogen concentrations. The concentration of total nitrogen decreased during the vegetative season.



Consistent analysis of loads and concentrations proves the phenomena of the reduction of total nitrogen presence in nutrient balance during the vegetative season.

The study of Figures 4, 5 and 6 proves that the water retention process and the total nitrogen loads during the vegetative periods of plants is explicit for the Rega and Middle Warta rivers. In the Reda river basin, the *flattening phenomenon* based on loads analyses is less noticeable and shorter. Additionally, the total nitrogen concentration analysis shows that concentrations are nearly stable across the whole year. In the vegetative season, however, concentrations increase slightly in spite of the flow decrease.

Despite the fact that the total sum of precipitation for the periods of particular *flattening* between 01/01/2002 and 31/12/2005 is higher during the winter time (apart from the growing season) – the average flow in the rivers during this period is lower. In addition, the average amount of total nitrogen loads is lower during the *flattening* periods rather than outside this period as shown in Tables 9, 10 and 11. This has been acknowledged by the significant contribution of plants in the basin, including arable crops, in the retention of water and nitrogen compounds.

It is widely known that the surface run-off of nutrients from agricultural land depends on the retention capacity and erosivity of these areas. The retention capacity of agricultural areas is affected by cultivation and appropriate agricultural practices. In numerous studies [22, 35, 41, 42, 44], seasonal variation of loads discharged into the receivers was also observed. Nevertheless, analysis is required with regard to the cause of these relationships and for the determination of the cause of this variability in the context of changes in both hydrological and agricultural conditions.

Table 9. Comparison of average total nitrogen loads, total precipitation and average flow for the *flattening* period from 01/01/2002 to 31/12/2005 in the Rega basin (**flattening* period)

Period (dd-mm)	Units	20/03 (MAX)-28/09 (MIN)*	29/09-19/03	years/period 2002-2005
Total precipitation	[mm]	363.7	345.2	sum/total 708.9
Flow	[m ³ /s]	13.4	46.1	average 17.4
Nitrogen loads	[kg/d]	3389	11781.3	average 4425.2

Table 10. Comparison of average total nitrogen loads, total precipitation and average flow for the *flattening* period from 01/01/2002 to 31/12/2005 in the Middle Warta basin (**flattening* period)

Period (dd-mm)	Units	25/03 (MAX)-29/09 (MIN)*	30/09-24/03	years/period 2002-2005
Total precipitation	[mm]	287.8	262.3	sum/total 556.6
Flow	[m ³ /s]	69.1	198.7	average: 83.3
Nitrogen loads	[kg/d]	50 651.3	142691.1	average: 59 934.4

Table 11. Comparison of average total nitrogen loads, total precipitation and average flow for the *flattening* period from 01/01/2002 to 31/12/2005 in the Reda basin (**flattening period*)

Period (dd-mm)	Units	19/03 (MAX)-20/06 (MIN)*	21/06-18/03	years/period 2002-2005
Total precipitation	[mm]	133.3	373.2	sum/total 739.1
Flow	[m ³ /s]	2.9	9.3	average: 3.4
Nitrogen loads	[kg/d]	102	275.3	average: 110.6

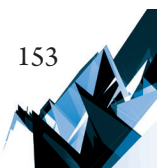
Numerous studies conducted worldwide suggest ground-cover vegetation as a factor influencing the run-off of nutrients into surface water [4, 7, 15, 26, 50]. In countries located in areas of temperate climatic conditions, with clearly marked seasons and thus a relatively short vegetation period, the problem of increases in the concentration of total nitrogen in the surface run-off of arable land at the end of the vegetation period is an important issue to be taken into account when assessing the status of surface waters flowing in agricultural catchments.

The consumption of nutrients (total nitrogen) by the plants with regard to the size of the surface run-off of these nutrients was analysed in [12]. Scenarios of changes in size of trailing with respect to crops were created. In article [45], it was observed that the run-off of nitrogen compounds in the periods known as 'fallow' periods was 30% higher than in the cropping period; however, this was not referenced to the volume of loads on the calculation profiles.

Publication [46] shows an analysis of the nutrient run-off to the eastern Santa Barbara Channel. The authors evaluated the river loading and the dispersal of dissolved macronutrients and commented on the biological implications of these nutrient contributions. The objective of research on the biological impact nutrient loads was to analyse algal responses and upwelling. It was difficult to isolate the impact of algal uptake on nutrient loads because of the run-off increase caused by the influence of changing meteorological conditions. Further research was needed.

In 2005, a paper on modelling nutrient export was published. In the publication [39], the authors describe the relationship between the type of land use and the amount of nutrients discharged to surface waters. Analysis of the variability of nutrients during the year was conducted, depending upon the occurrence of stormy meteorological conditions. The article noted the phenomenon of load stabilisation, which appears in the summer months, but no attempt was made to analyse the reasons for its creation. Additionally, the presented research results clearly indicated large differences in the surface confluence of nutrients from land upon which the use varied depending upon the season.

Monitoring data from field studies conducted at other polish rivers also shows the occurrence of the described periodic lowering of the concentration of nitrogen in surface waters. In 2011, the Institute of Soil Science and Plant Cultivation carried out studies on, inter alia, the impact of cover crops (legumes) on nitrate leaching from the soil. Studies have



shown that the role of this type of plant was significant in terms of water quality and that their presence, to some extent, conditioned the concentration of nitrates in surface waters [16].

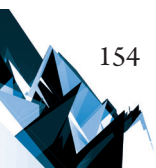
Decreases in the concentrations of nitrogen during the plant growing season and its subsequent rapid increases both in the soil and in nearby surface waters was also observed by the Institute of Technology and Life Sciences in Falenty during the analysis of selected watersheds [34].

The flattening phenomenon was also illustrated through the analysis of the content of nitrogen compounds in the waters of the Trzema river tributary of the Prosna river) [10] – collected monitoring data from several years confirms the occurrence of this phenomenon. At the same time in the indicated publication shows the differences between the behavior of total nitrogen and total phosphorus for which the flattening phenomenon does not occur. The significant influence of the plant growth period on the amount of nitrogen in the surface waters of the catchment areas dominated by agricultural land use was also observed on the San and Slina rivers [25]; however, it should be noted that these studies are based on small amounts of monitoring data and they do not specify either the scale of the decline in the amount of nitrogen concentration in surface waters or its duration – this information is crucial in terms of the possibilities of applying knowledge of the flattening phenomenon in, for example, the preparation of scenarios for action plans.

The described flattening phenomenon also confirms the need for change, which is used for environmental computations, for the flow of interest. At present, the so-called environmental flow should be used, which will take into account changes in the amount of pollutants depending on the seasons [24].

The *flattening phenomenon* is mainly a result of agricultural activities in the basin. At the beginning of the plant-growing season, high doses of fertiliser are applied on arable lands, this results in an increase of nutrients leaching to surface waters from areas without plant soil cover. During the plant growing season, a rapid increase of nitrogen uptake occurs – this is a consequence of the plants embedding it within their own cellular structures. Moreover, through the creation of soil cover, plants significantly reduce the nitrogen leaching which occurs through surface run-offs which result from intensive rains. In Table 7 (for the Rega basin) and in Table 8 (for the Middle Warta basin), the results show that during the *flattening* period (March to September) the total precipitation is higher than after the *flattening* period (October to March), and the size of the average flow is diminished by as much as 70%. This is confirmed by the total nitrogen concentration decrease. At the end of the vegetation period, the intense nitrogen uptake by plants decreases. At this time, nitrogen compounds located in the cells are redistributed inside the plant from leaves to stems and reproductive systems causing a continuous increase in biomass without up take from soils. In addition, harvesting crops from agricultural land (tantamount to biomass removal) deprives soil of plant cover – this causes an increase in surface run-off. At this time, a re-increase of nitrogen loads in surface waters is observed. These correlations have been confirmed in a separate dissertation [18], in which the effect of human agricultural pressure on the amount of nutrients and total suspended soils entering surface waters were analysed.

Analyses of the Reda basin show that the *flattening* occurs here as well but is not as visible as in the previously mentioned basins and lasts from mid May to mid July (Fig. 6). Although



additional analyses of concentrations proved that *flattening* does not occur. At this time, the size of total nitrogen loads in surface waters fluctuates, although total nitrogen concentration slightly increases. In order to find the reasons for this situation, the average content of mineral nitrogen in Polish soils [14] was compared with its content in the soils of the Reda basin (Tab. 12).

Table 12. Quantity of mineral nitrogen in the layers of Polish soils and in the Reda basin [14]

Soil profile	Average for Poland		Reda basin	
	Quantity of mineral nitrogen (NO ₃ -N + NH ₄ -N) [mg/kg]			
	Spring	Autumn	Spring	Autumn
0-30	9.0	11.6	16.7	19.4
30-60	6.7	6.9	8.2	11.6
60-90	5.8	5.1	8.9	10.2

It is noticeable that the soils in the Rega basin contain higher concentrations of mineral nitrogen than the rest of the country – this can have a significant impact on the size of the retention and thus the *flattening* effect. For both spring and winter, in all soil layers in the Reda basin, the amount of mineral nitrogen is much higher than the average values for Poland – by 70% on average. This situation might be caused by the long-term, excessive fertilisation of soils in the area, which might have caused the infiltration of nitrogen compounds into deeper soil layers. Nitrogen compounds accumulated in the deeper layers are relatively evenly leached to the river by subsurface run-off. Subsurface run-off, as opposed to surface run-off, is not as dynamic and is not associated with the time of the year and growing season – this can explain the lack of seasonal variability of nitrogen loads in the Reda river and the limited variability of nitrogen loads during the particular period. This observation shows that the absence of flattening can suggest an imbalance in the nutrient cycle in the basin.

4. Conclusions

The retention of vast amounts of precipitation waters by basin plants is vital as far as the diminishing quantities of total nitrogen loads in surface waters is concerned – this was confirmed by the results from the examined basins of the Rega and the Middle Warta rivers. When the growing season ends and the crops are removed from the fields, a period of increased total nitrogen concentration appeared at the analysed SWB calculation profiles in the Rega and the Middle Warta – this is mainly caused by surface run-off. The analyses indicate that crops have a crucial influence on the quantity of water retention and nitrogen compounds in the examined basin; simultaneously, they vastly influence the quantity of the surface run-off and the included nitrogen loads [18]. Water and nitrogen retention in the basin, even short term, is a desirable phenomenon since it is connected with the process of water regeneration. Withholding precipitation water in the soil and at the same time restricting the run-off of nitrogen originating from fertilisation, enables better use of fertilisers by plants. The *flattening phenomenon* does not perpetually occur and it greatly depends on the level of nitrogen



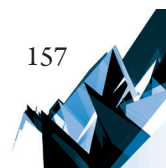
concentration present in the soil and the dynamics of the processes of its leaching to the waters. An example of a basin where nitrogen balance is disturbed by long-term fertilisation is the Reda basin. This case requires further analysis including the quantity of mineral nitrogen in the soils of the basin. The *flattening phenomenon* describes the dynamics of total nitrogen loads to surface waters and at the same time, it can be used to evaluate the conditions that make water eutrophication occur. Since the majority of total nitrogen in surface waters of Poland originates from farming [18] and is introduced by surface run-off, the analyses require information relating to the amounts of fertiliser used on the fields' crops. It has to be remembered that the temporary retention of total nitrogen in the soil does not lead to its total removal from the environment. It only helps plants to make better use of it on condition that the quantities of applied fertilisers are sufficient. The magnitude of *flattening* allows us to specify the relationship between the amount of nitrogen loads exported to waters in particular seasons, the occurrence of violent exceptional climatic events and periods of increase in the acquisition of these ingredients substances by plants. The lack of *flattening phenomenon* might prove that there is a strong correlation between the levels of nutrients consumed by plants and the leaching of pollutants to surface waters; therefore, it is very crucial to use adequate doses of fertilisers to meet the needs of plants, but this has to be preceded by an analysis of the chemical composition of the soil in order to establish the availability of nutrients. This enables us to estimate the doses of fertilisers that would allow a high *growth rate* of plants, and at the same time, reduces the excess of unused nitrogen leaching to surface waters and consequently limiting the eutrophication process. The *flattening phenomenon* can be used to assess the state of the ecosystem in the basin area and provides the opportunity to assess the actual impact of land use on the nitrogen cycle.

References

- [1] Abbaspour K.C., *SWAT-CUP2: SWAT Calibration and Uncertainty Programs – A User Manual*, Department of Systems Analysis, Integrated Assessment and Modelling, Eawag, Swiss Federal Institute of Aquatic Science and Technology, Duebendorf 2008.
- [2] BDL – Polish Local Database, http://stat.gov.pl/bdl/app/strona.html?p_name=indeks (access: 20.05.2015).
- [3] Bossard M., Feranec J., Otahel J., *CORINE land cover technical guide – Addendum 2000*, Technical report No. 40, European Environment Agency, Copenhagen 2000.
- [4] Burwell R.E., Timmons D.R., Holt R.F., *Nutrient Transport in Surface Runoff as Influenced by Soil Cover and Seasonal Periods I*, Soil Sci. Soc. Am. J., 39, 1975, 523-528.
- [5] Byczkowski A., *Hydrologia*, vol. I, Warsaw University of Life Sciences, Warszawa 1999.
- [6] Cai Y., Guo L., Douglas T., Whitledge T., *Seasonal variations in nutrient concentrations and speciation in the Chena River, Alaska*, Journal of Geophysical Research, Vol. 113, 2008.
- [7] Causse J., Baurès E., Mery Y., Jung A.V., Thomas O., *Variability of N export in water: a review*, Critical Reviews in Environmental Science and Technology, 2015.



- [8] Centralny Ośrodek Dokumentacji Geodezyjnej i Kartograficznej – national databases (Centre of Geodesic and Cartographic Documentation), www.codgik.gov.pl (access: 6.06.2015).
- [9] CORINE, CORINE LAND COVER, <http://www.eea.europa.eu/themes/landuse/interactive/clc-download>, July (access: 6.06.2015).
- [10] Dabrowska J., *Ocena zawartości związków azotu i fosforu w wodach rzeki Trzemny*, Infrastruktura i ekologia terenów wiejskich, (07) 2008.
- [11] Directive 2000/60/EC of the European Parliament and of the Council establishing a framework for Community action in the field of water policy, 2000.
- [12] Douglas C.L., King K.A., Zuzel J.F., *Nitrogen and Phosphorus in Surface Runoff and Sediment from a Wheat-Pea Rotation in Northeastern Oregon*, J. Environ. Qual., 27, 1998, 1170-1177.
- [13] Fal B., *Zmienność odpływu z obszaru Polski w bieżącym stuleciu*, Institute of Meteorology and Water Management – notifications, 3, 1993, 3-19.
- [14] Fotyma M., Kęsik K., Pietruch Cz., *Azot mineralny w glebach Polski*, Fertilizers and Fertilization, No. 38, Institute of Soil Science and Plant Cultivation – State Research Institute, Puławy 2010.
- [15] Gafur A., Jensen J., Borggaard O., Petersen L., *Runoff and losses of soil and nutrients from small watersheds under shifting cultivation (Jhum) in the Chittagong Hill Tracts of Bangladesh*, Journal of Hydrology, Vol. 274, 2003, 30-46.
- [16] Gawel E., *Rola roślin motylkowych drobnonasiennych w gospodarstwie rolnym*, Woda – Środowisko – Obszary Wiejskie, 11, 2011, 73-91.
- [17] Gębala J., Orlińska-Woźniak P., Wilk P., *Zanieczyszczenia związkami azotu pochodzenia rolniczego wód powierzchniowych w Polsce – wybrane problemy oceny jakości wód*, Gospodarka Wodna, 11, 2013.
- [18] Gębala J., *Method of assessing the impact of agricultural anthropopression on surface water quality on example of the Rega basin*, PhD thesis supervising by M. Ostojki, Institute of Meteorology and Water Management – National Research Institute, Warsaw 2015.
- [19] Grabińska B., Kuc J., Glińska-Lewczuk K., *Zanieczyszczenia obszarowe w zlewniach rolniczych i leśnych – możliwości ograniczania. Wpływ użytkowania zlewni Narwi na zagrożenie wód związkami azotu*, 2004, 164.
- [20] Gupta H.V., Sorooshian S., Yapo P.O., *Status of automatic calibration for hydrologic models: Comparison with multilevel expert calibration*, J. Hydrologic Eng., 4(2), 1999, 135-143.
- [21] HELCOM, Stakeholder Conference on the Baltic Sea Action Plan, Eutrophication in the Baltic Sea, Draft HELCOM Thematic Assessment in 2006, Helsinki 2006.
- [22] Hobot A., Banaszak K., Stolarska M., Serafin R., Stachura A., *Warunki korzystania z wód zlewni rzeki Redy – Etap 1 – Dynamiczny bilans zasobów wodnych*, The Regional Water Management Authority in Gdańsk, Gdańsk 2012.
- [23] IUNG 2009, *Mapy kategorii glebowych* Ministerstwa Rolnictwa i Rozwoju Wsi, Institute of Soil Science and Plant Cultivation – State Research Institute, <http://www.susza.iung.pulawy.pl/index.html?str=mapkat> (access: 1.06.2015).



- [24] Kiryłuk A., Rauba M., *Zmienność stężenia związków azotu w różnie użytkowanej zlewni rolniczej rzeki Ślina*, Woda – Środowisko – Obszary Wiejskie, 9, 2009, 71-86.
- [25] Kuźniar A., Twardy S., Kowalczyk A., *Przyczyny zmian stężenia azotu i fosforu w wodach powierzchniowych górnej zlewni Sanu (po przekrój w Przemyślu) w latach 1990-2005*, Woda – Środowisko – Obszary wiejskie, 8, 2008, 185-196.
- [26] Li J., Okin G., Alvarez L., Epstein H., *Quantitative effects of vegetation cover on wind erosion and soil nutrient loss in a desert grassland of southern New Mexico*, Biogeochemistry, Volume 85, Issue 3, 2007, 317-332.
- [27] Maréchal D., Holman P., *Comparison of Hydrologic Simulations using Regionalised and Basin-Calibrated Parameter Sets for three Basins in England*, Institute of Water and Environment, Cranfield University, UK, 2004.
- [28] MPHP, *The Map of Hydrographical Divisions of Poland*, Institute of Meteorology and Water Management – National Research Institute, Warszawa 2009.
- [29] Moriasi D.N., Arnold J.G., *Model evaluation guidelines for systematic quantification of accuracy in watershed simulations*, American Society of Agricultural and Biological Engineers, 2007.
- [30] Neitsch S.L., Arnold J., Kiniry R., Srinivasan R., Williams J.R., *Soil and Water Assessments Tool Input/Output File Documentation*, Blackland Research Center Texas Agricultural Experiment Station, 2004.
- [31] Neitsch S.L., Arnold J., Kiniry R., Williams J.R., *Soil and Water Assessments Tool Theoretical documentation*, Blackland Research Center Texas Agricultural Experiment Station, 2005.
- [32] Ostojki M.S., *Modelowanie procesów odprowadzania do Bałtyku związków biogenych na przykładzie azotu i fosforu ogólnego*, Wydawnictwo Naukowe PWN, Warszawa 2012.
- [33] Ozga-Zielińska M., Brzeziński J., *Hydrologia stosowana*, Wydawnictwo Naukowe PWN, Warszawa 1994.
- [34] Pietrzak S., *Priorytetowe środki zaradcze w zakresie ograniczania strat azotu i fosforu z rolnictwa w aspekcie ochrony jakości wody*, Instytut Technologiczno-Przyrodniczy, 2012.
- [35] Przywara L., *Warunki i możliwości usuwania fosforanów i fosforu ogólnego ze ścieków przemysłowych*, Ph.D. desideration, Bielsko-Biała 2006.
- [36] Regulation of the Minister of Environment on the forms and manner of monitoring of surface water bodies and groundwater bodies, Journal of Laws, No. 258/1550, 2011.
- [37] Regulation of the Minister of the Environment on the classification of surface water bodies and environmental quality standards for priority substances, Journal of Laws, No. 257/1545, 2011.
- [38] Report on the state of the environment in Western Pomeranian in years 2006-2007.
- [39] Robinson H.T., Leydecker A., Keller A., Melack J.M., *Steps towards modeling nutrient export in coastal Californian streams with a Mediterranean climate*, Agricultural Water Management, 77, 2005, 144-158.
- [40] RZGW – The Regional Water Management Authority in Szczecin, Charakterystyka ogólna, 2010, http://www.rzgw.szczecin.pl/ogolna-charakterystyka/index/id/129/print_site/1 (access: 2.06.2015).

- [41] Sarma P.B., Delleur J.W., Rao A.R., *Comparison of rainfall-runoff models for urban areas*, Journal of Hydrology, Volume 18, Issues 3-4, 1973, 329-347.
- [42] Srinivasan R., Hadley J., Uhlenbrook S., Van Griensven A., Holvoet K., Bauwens W., European SWAT summer school, UNESCO – IHE, Institute for Water Education, 2006.
- [43] Srinivasan R., *Soil and Water Assessment Tool, Introductory Manual – teaching materials*, Texas, 2011.
- [44] Sullivan D.M., Hart J.M., Christensen N.W., *Nitrogen Uptake and Utilization*, A Pacific Northwest Extension Publication, Oregon–Idaho–Washington 1999.
- [45] Udawatta R.P., Motavalli P.P., Garrett H.E., Krstansky J.J., *Nitrogen losses in runoff from three adjacent agricultural watersheds with claypan soils*, Agriculture, Ecosystems & Environment, Elsevier, 2006.
- [46] Warric J.A., Washburn L., Brzezinski M., Siegel D., *Nutrient contributions to the Santa Barbara Channel, California, from the ephemeral Santa Clara River*, Estuarine Coastal and Shelf Science, 62, 2005, 559-574.
- [47] Watson C., Mills C., *Gross nitrogen transformations in grassland soils as affected by previous management intensity*, Soil Biology and Biochemistry, Vol. 30, 6, 1998, 743-753.
- [48] Wilk P., *The method of calculating the absorption rate of the river as a tool to evaluate the physico-chemical state of surface water flowing*, Ph.D thesis supervising by M. Ostojski, Institute of Meteorology and Water Management – National Research Institute, Warszawa 2015.
- [49] Youssef T., Skaggs M., Amatya R.D., *Temporal variations and controlling factors of nitrogen export from an artificially drained coastal forest*, Environmental Science & Technology, 46(18), 2012, 9956-9963.
- [50] Zhang G., Liu G., Wang G., Wang Y., *Effects of Vegetation Cover and Rainfall Intensity on Sediment-Bound Nutrient Loss, Size Composition and Volume Fractal Dimension of Sediment Particles*, Pedosphere, Vol. 21, 2011, 676-684.
- [51] Zwolsman J., *Seasonal Variability and Biogeochemistry of Phosphorus in the Scheldt Estuary, south-west Netherlands*, Estuarine, Coastal and Shelf Science, Vol. 39, Issue 3, September, 1994, 227-248.

