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NITRATE NITROGEN AND PHOSPHATE CONCENTRATIONS IN DRAINFLOW: AN EXAMPLE OF CLAY SOIL*

Daniel Szejba[1], Ewa Papierowska[2], Ireneusz Cymes[3], Agnieszka Bańkowska[4]

[1]Chair of Environmental Improvement
[2]Laboratory – Water Center
Warsaw University of Life Sciences
[3]Chair of Water Resources, Climatology and Environmental Management
University of Warmia and Mazury in Olsztyn
[4]Chair of Hydraulic Engineering
Warsaw University of Life Sciences

Abstract

Nutrients dissolved in water and not taken by plants leach into deeper soil layers or flow out to surface water through pipe drainage systems, causing ground or surface water contamination. Thus, drainflow from agricultural areas has significant influence on surface water eutrophication. The objectives of this study were to evaluate nitrate nitrogen and phosphate concentrations and load changes in drainflow using as an example clay soil analyzed in period spanning the years 2010 and 2013. Field research was conducted at an experimental site in Lidzbark Warmiński, in the Province of Warmia and Mazury (*województwo warmińsko-mazurskie*) in Poland. Mollic Gleysols developed from loam and clay dominate in this area. The experimental field has a tile drainage system with 21 m drain spacing and average 0.9 m drain depth. Winter wheat (*Triticum* L.) and oilseed rape (*Brassica napus*) were cultivated in 2009-2012 and in 2012-2013, respectively. Chemical analysis of water samples was performed with a Hach Lange DR 3900 spectrophotometer. Annual rainfall ranged from 555 mm in 2013 to 814 mm in 2012. Average nitrate nitrogen daily loads ranged from 0.07 to 0.58 kg ha^{-1}, while the total annual nitrate load varied from 7.5 to 34.6 kg ha^{-1}. Daily loads of phosphate were about ten times lower than daily loads of nitrate and the total annual phosphate load ranged from 0.1 to 2.0 kg ha^{-1}. Neither nitrate nor phosphate concentrations are strongly depended on drainflow, but the nitrate nitrogen concentration indicates some relationship with the season. A substantial increase in the nitrate nitrogen concentration appears at snow melting (March) and continues until the end of May, peaking in the third decade of April, when the cultivated crops begin the vegetative growth. The phosphate concentration did not undergo significant changes during the investigated period.

Keywords: drainage system, outflow, loads of nutrients.

dr inż. Daniel Szejba, Chair of Environmental Improvement, Warsaw University of Life Sciences, Nowoursynowska Str. 159, 02-776 Warsaw, Poland, phone: (+48) 22 59 35 386, e-mail: daniel_szejba@sggw.pl

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INTRODUCTION

Surface water eutrophication is a global problem (Smith, Schindler 2009; Withers et al. 2014). Eutrophication can also be considered as a major environmental problem of the Baltic Sea, more serious than local environmental problems caused by metals and persistent organic substances (Enell, Fejes 1995). Thus, environmental conditions in waters around the coast of the Baltic Sea are currently the focus of research, monitoring, national and international measures (Vagstad et al. 2000, Bonsdorff et al. 2002, Rönnberg, Bonsdorff 2004, Sapek 2008, 2010). Agriculture is indicated as a main source for riverine loads of nutrients in the Gulf of Riga drainage basin and has therefore strong impact on the eutrophication of coastal waters (Vagstad et al. 2000). Seasonal increase in nitrogen and phosphorus concentrations stimulates algae blooms, thus interfering with the ecosystem's balance (Ilnicki 2014) and deteriorating water quality (Smith, Schindler 2009). Nitrogen transfer from the basin to surface water is a continuous, season-dependent process caused by precipitation. Temporality of this component's outflow is shaped mainly by soil texture, canopy and river flow quantity. The outflow of nitrogen mineral forms through rivers is significantly affected by the type and intensity of land use. The problem of maintaining right water quality parameters (including nitrogen and phosphorus content) in the Łyna River and its ox-bow lakes was presented by Glińska-Lewczuk and Burandt (2011). Nitrate concentrations in rivers change seasonally: they are 2- to 20-fold higher in winter than in summer because of biological sorption (Grabińska et al. 2005, Koc et al. 2009, Popek et al. 2014).

Subsurface drainage is a common agricultural water management practice in areas with shallow groundwater or seasonally rising water tables. Dissolved compounds not absorbed by plants move below the crop's rhizosphere and reach deep into the soil profile or else travel into a drainage system, causing ground or surface water contamination (Lipiński 2003). In many areas, subsurface drains discharge agrichemicals, including nutrients, into surface ditches, streams or ponds (Kladivko et al. 1991, 1999). Main sources of nitrogen and phosphorus are mineral and organic fertilizers as well as soil organic matter. Mineralization processes are accelerated when soil aeration becomes improved by drainage. The result is the leaching of dissolved nutrients, mainly nitrate. Thus, an outflow from an agricultural drainage system is a important cause of surface water eutrophication. Compared with a ditch system, a pipeline drainage system carries away twice as much phosphate (Koc, Solarski 2006) and twice as much water with a five-fold higher nitrate concentrations and a twenty-fold higher nitrate load (Koc et al. 2007).

Amounts of phosphorus and nitrogen drained from an intensive crop production field by a drainage system depend on many factors, including meteorological conditions, season of the year, cropping system, fertilization (type and dose of fertilizer, time and way of application), drainage system (depth and spacing) and soil properties (flow pathways, nutrient concentrations). The mobility of phosphorus is also controlled by sorption–desorption processes in soil (determined mainly by soil composition, grain size and physicochemical conditions in the soil profile). The leaching of nitrogen is strongly dependent on its microbial metabolism (Liu et al. 2012, King et al. 2015). A high phosphorus concentration was found in winter and spring due to intensive precipitation and shortage of leaf canopy (Rafałowska 2007).

Because phosphorus is the main factor controlling primary production, much effort has been made to reduce its concentration in waters, for example by using reactive materials (Karczmarczyk, Bus 2014).

Changes in water quality in the examined drainage system, located in Lidzbark Warmiński, were analyzed in 1998-2000 and in 2009-2010, thus making a comparison of the situation after a ten-year interval, during which the type of local land use was changed (Cymes et al. 2014).

The objective of this study was to evaluate changes in the nitrate nitrogen and phosphate concentrations as well as loads of these elements in drainflow through clay soil. Another aim was to explore the dependency of nutrient concentrations on season and drainflow volume, using data from 2010-2013 for this purpose.

MATERIAL AND METHODS

A field research was conducted at an experimental site in Lidzbark Warmiński (54°08′ N, 20°35′ E), located in the Province of Warmia and Mazury (*województwo warmińsko-mazurskie),* in Poland. Mollic Gleysols developed from loam and clay dominate in this area. According to the USDA soil taxonomy, the representative soil profile can be divided into four soil layers: loam (0-26 cm), clay (26-45 cm), clay loam (45-90 cm) and clay (90-150 cm) (Table 1). This soil lies on hills with slope angles ranging between 2 and 4%. Until the autumn of 2009, the site was used as an unfertilized pasture. In the seasons 2009/10, 2010/11 and 2011/12 it was cropped with winter wheat (*Triticum* L.) and after that, in 2012/13, oilseed rape (*Brassica napus*) was

Table 1

Basic properties of the soil profile

Soil type	Depth (cm)	pH	$CaCO_3$ (%)	C_{org} (g kg^{-1})	N (g kg^{-1})
Loam	0 - 26	6.2	0.0	21.3	2.20
Clay	26 - 45	5.3	0.0	5.6	0.70
Clay Loam	45 - 90	5.6	0.0	2.2	0.30
Clay	90 - 150	8.0	1.3	2.2	0.35

grown at that site. Fertilization began in spring 2010. An amount of 250 kg ha^{-1} of ammonium nitrate (17% of N-NO_3 and 17% of N-NH_4), applied using a a fertilizer spreader, was divided into two doses, supplied at the end of March 2012 and in mid-April 2011. Moreover, doses of 250 kg ha^{-1} and 180 kg ha^{-1} of ammonium nitrate were applied at the end of March 2012 and in the last decade of May 2012, respectively. Additionally, 130 kg ha^{-1} of Saletrosan® 26 fertilizer (19% of N-NO_3, 7% of N-NH_4, 32.5% SO_3, Ca and Mg) was applied in March 2012. An average annual sum of precipitation for this region equals 624 mm and the highest rainfall is usually in July and August. The plant growing period lasts about 200 days. There is a tile drainage system with 21 m drain spacing and average 0.9 m drain depth in the experimental field. This drainage system consists of one collecting pipeline, 177 m long and 7.5 cm in diameter, as well as thirteen short pipes, 5 cm in diameter and 1218 m of total length (Figure 1). The collecting pipe slopes

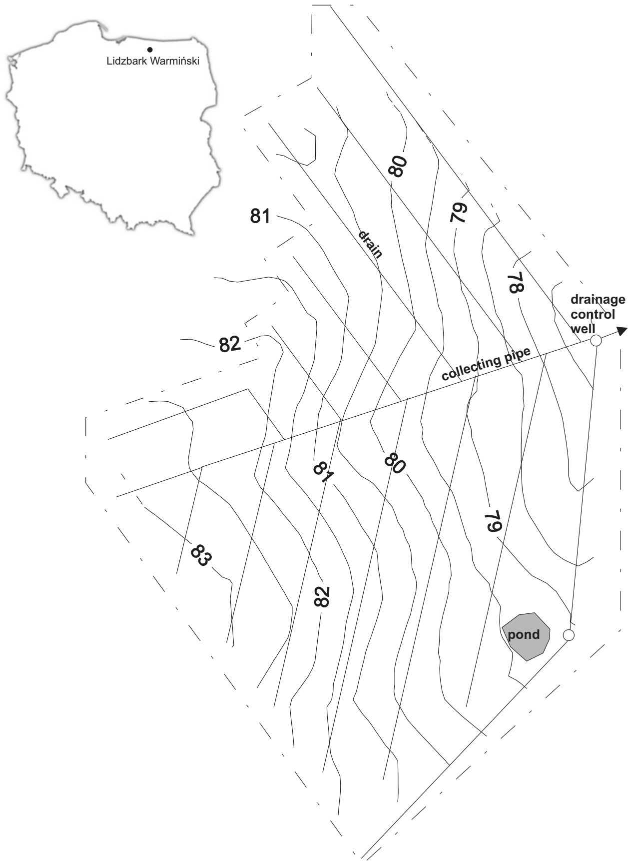

Fig. 1. The location and the scheme of the experimental site

down at an angle of 4 % at the most, and its catchment area equals 2.35 ha. An ultrasonic area velocity flow module ISCO 2150 was applied to measure drainflow, according to the guidlelines provided by Szejba et al. (2010, 2011). The flow meter was placed in a drainage control well, where an AV sensor was installed in a specially adapted outlet of the collecting pipe (Figure 2).

Fig. 2. An ultrasonic area velocity flow module ISCO 2150 with an AV sensor installed in a specially adapted outlet of the collecting pipe

Drainflow water samples were collected from 2010 to 2013, once a month on average, as long as there was some drainflow. Concentrations of nitrate and phosphate in water samples were determined spectrophotometrically (Hach Lange DR 3900 spectrophotometer) in the Laboratory of Porous Media Physic, Water Center, Warsaw University of Life Sciences. Nitrate concentrations were measured after reducing nitrate to nitrite with cadmium, using sulfanilic acid to form intermediate diazonium salt and gentisic acid to form amber coloured solution. The determinations were carried out at 500 nm wavelength (*Nitrate* ... 2014). The ortophosphate concentration was measured with the blue method at 880 nm wavelength, after reduction with ascorbic acid using molybdate as a complexing agent (*Phosphorus* ... 2014). All analyses were conducted under laboratory conditions, at constant temperature of 20°C.

Loads of nitrate and phosphate were calculated based on a drainflow rate and nutrient concentration, assuming that a nutrient concentration measured during a single drainflow wave was constant for the entire wave.

Vesper software was used to test correlations of nutrient concentrations with drainflow rates and seasons. The following log-normal function was chosen for the correlations of nutrient concentrations with drainflow:

$$y = a \cdot \exp\left\{-0.5 \cdot \left[\ln\left(\frac{Q}{b \cdot c}\right)\right]^2\right\}, \quad 1)$$

where:
y – compound concentration (g m^{-3}),
Q – drainflow (m^3 ha^{-1}),
a, b, c – log-normal function parameters.

To verify correlations between nutrient concentration in drainflow and the seasons, the following Gaussian equation was applied:

$$y = a + b \cdot \exp\left[-0.5 \cdot \left(\frac{n-c}{d}\right)^2\right], \quad (2)$$

where:
$a + b$ – parameters of maximum compound concentration (g m^{-3}),
c – number of day with maximum compound concentration,
d – shape of the parameter,
n – day of the year.
For calculations, each concentration value was assigned a number indicating the day of water sample collection.

RESULTS AND DISCUSSION

Hydrology and nutrients loads

The annual rainfall in the analyzed period ranged from 555 mm in 2013 to 814 mm in 2012. (Table 2), which corresponds to 89% and 130% of average annual precipitation, respectively. According to Kaczorowska (after Szejba et al. 2009), 2013 was a dry year and 2012 was a very wet year. The years 2010 and 2011, with 106% and 102% of average rainfall, were classified as intermediate (Table 2). The length of each season investigated depended on the presence of drainflow and meteorological conditions, because the AV sensor applied was not frost-resistant. The highest drainflow (195 mm) was recorded in 2010 (Table 2) and equalled 29.5% of annual rainfall and 42.4% of seasonal rainfall. This was mostly due to severe rainstorms rather than an unusual outpour in July (Figure 3*a*,*b*). The 2011-year drainflow (105 mm) was almost half of that in the previous year. It was 16.5% of the annual and 21.5% of seasonal rainfall (Figure 3*e*,*f*). the year 2012 was very wet (814 mm); even seasonal rainfall (658 mm) was higher than the annual aver-

Table 2

Annual and seasonal rainfall, drainflow and N-NO_3, P-PO_4 loads in seasons

Season	Annual rainfall (mm)	% of average (%)	Seasonal rainfall (mm)	Drainflow (mm)	N-NO_3 load (kg ha^{-1})	P-PO_4 load (kg ha^{-1})
12.05 – 27.09. 2010	660	106	460	195	34.6	2.0
01.04 – 19.10.2011	636	102	487	105	8.5	0.2
04.04 – 04.12.2012	814	130	658	140	23.0	0.1
05.03 – 31.12.2013	555	89	492	181	7.5	1.0

age (624 mm). However, drainflow was relatively low (140 mm). It was just 17.2% of the annual and 21.3% of seasonal precipitation. No drainflow was observed from mid-May to the end of June (Figure 4*a*,*b*). The explanation can be soil water retention and high evapotranspiration. Very intensive drainflows appeared in October and November as a result of the evapotranspiration value close to zero and soil saturation caused by high groundwater level. Relatively high drainflow (181 mm) was registered in 2013, where the annual rainfall was just 555 mm. It was only 32.6% of the annual and 36.7% of seasonal rainfall. However, it has to be noted that it was the "continuation" of drainflow from the very wet 2012 year. The drainflow, which started in December 2012, lasted to about mid-May 2013 (Figure 4*b*,*f*). Next, the drainflow did not appear until October. The highest drainflow took place in December. Nitrate nitrogen and phosphate loads for the 2010-2013 period are presented in Figures 3 and 4 (*c*, *d*, *g*, *h*). The highest daily nitrate nitrogen loads with the maximum value (7.8 kg ha^{-1}) appeared during August 2010. This was caused by an instant and very intensive drainflow after a few weeks without drainflow. Average daily loads ranged from 0.07 kg ha^{-1} in 2013 to 0.58 kg ha^{-1} in 2010. Unfortunately, the data for 2012 are incomplete because sporadically water samples were not taken during drainflow appearance or ion concentrations were below the detecable range. However, due to low values at neighbouring points and values below the measurable range, it can be assumed that these missing data were not significant. The total annual nitrate nitrogen load ranged from 7.5 to 34.6 kg ha^{-1} (Table 2). These results are comparable with those presented by Koc et al. (2007) for the same region. High nitrate loss with drainflows (22 kg ha^{-1} yearly) distributes uniformly during a year, with maximum peaks in March and June. However, our results are higher than the values for Olsztyn Lake District (from 1.13 to 11.66 kg ha^{-1}) presented by Szymczyk (2010). According to this author, nitrate leaching to a drainage system continues throughout an entire year, with the highest intensity in March and April, and depends on meteorological conditions and the type of a drainage system. Pulikowski et al. (2012) analyzed the results of research on the nitrate and total nitrogen content in drainage

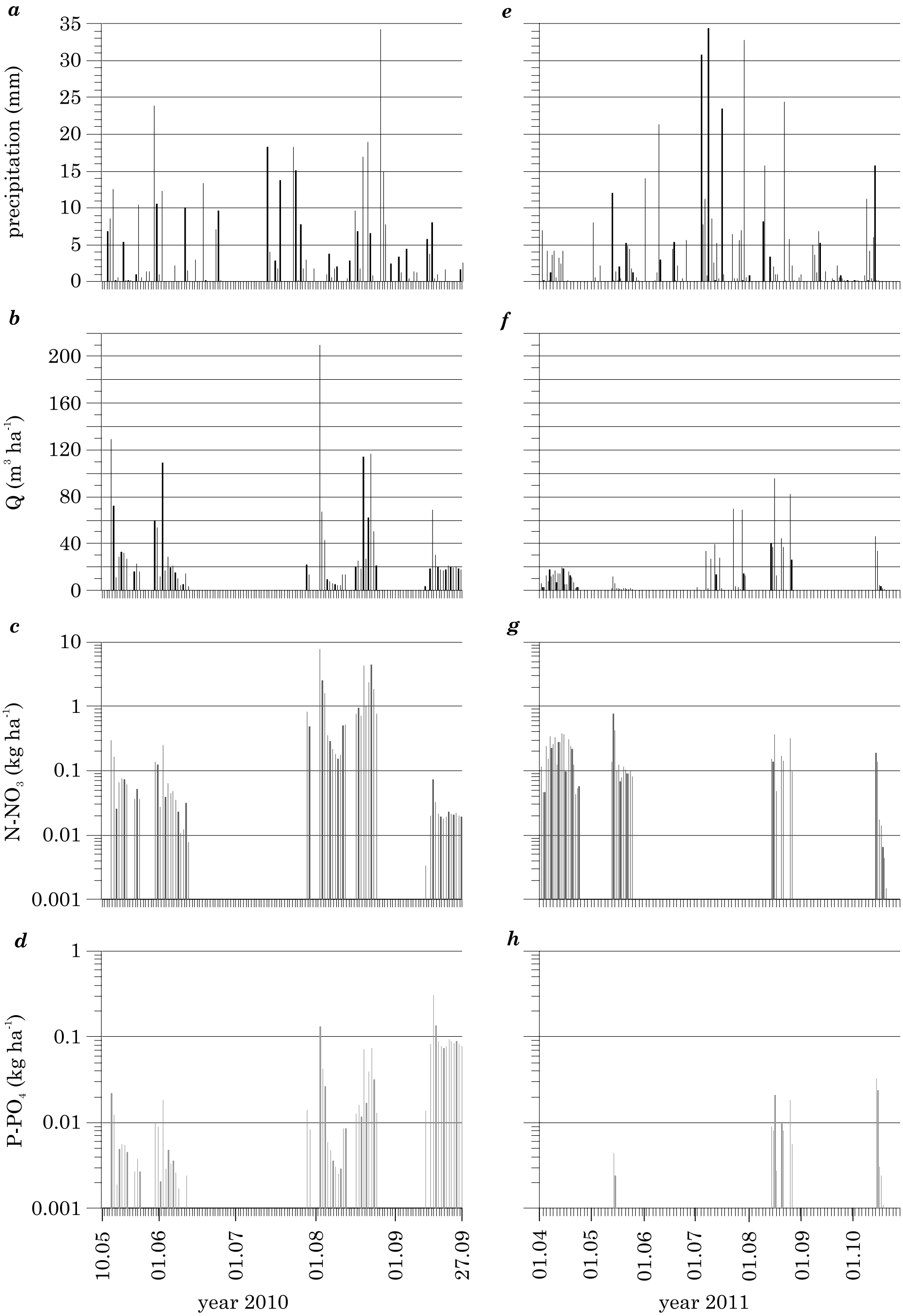

Fig. 3. Precipitation (*a*, *e*), drainflow (*b*, *f*), nitrate nitrogen (*c*, *g*) and phosphate loads (*d*, *h*) in 2010 and 2011

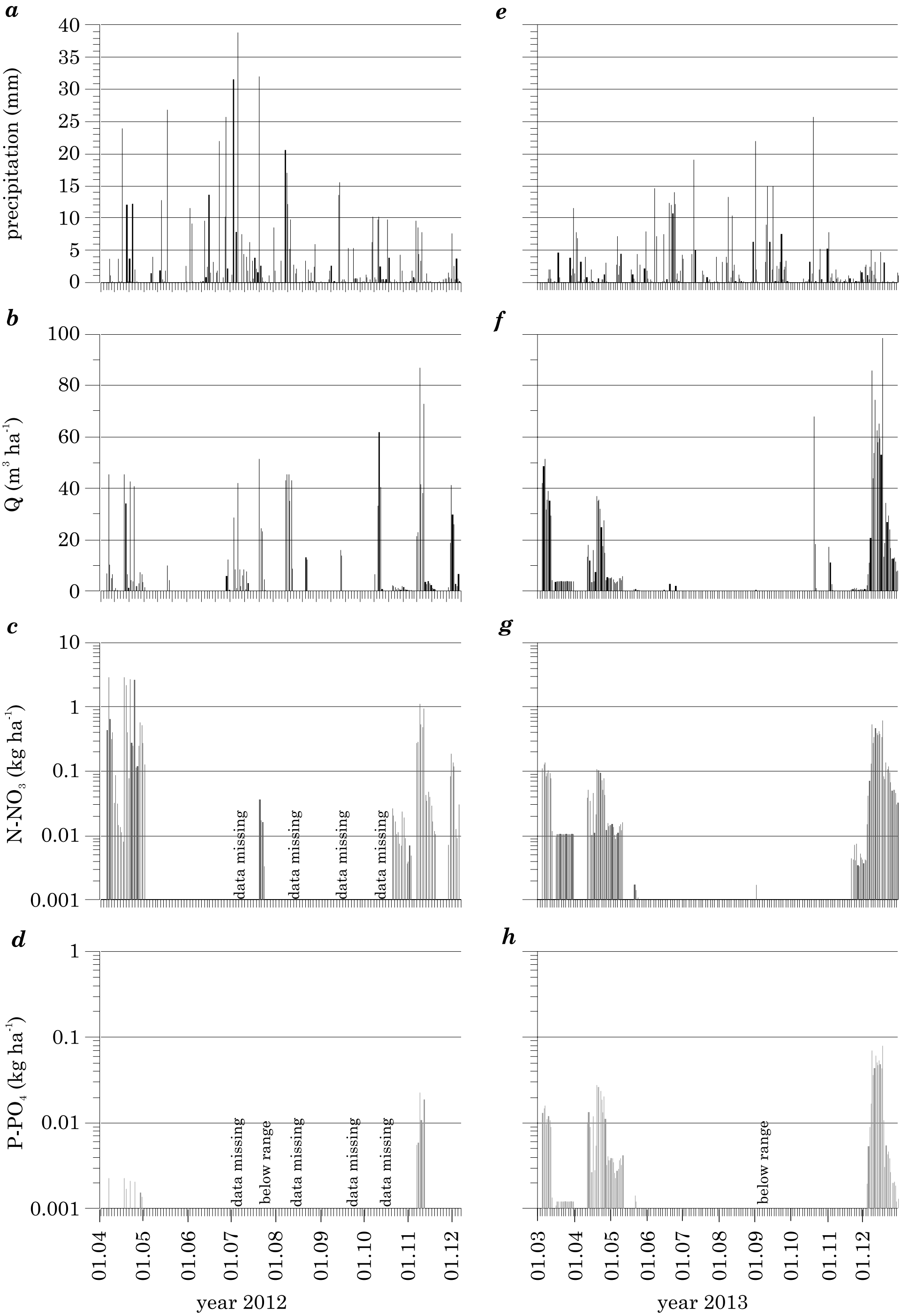

Fig. 4. Precipitation (*a*, *e*), drainflow (*b*, *f*), nitrate nitrogen (*c*, *g*) and phosphate loads (*d*, *h*) in 2012 and 2013

effluents for clay soils located in a rural area of Lower Silesia. An average nitrogen concentration in drainage outflow ranged from 22.4 to 36.9 mg N dm^{-3}. Thus, the maximum values of nitrate nitrogen loads of drainflow for clay soil near Lidzbark Warmiński are comparable with values for clay soils in Lower Silesia. Nonetheless, our results are are still lower than the values presented by KLADIVKO et al. (2004) for Indiana State (USA) conditions, where the loads ranged from 15.4 to 45.0 kg ha^{-1}. The combination of reduction in N fertilizer doses, change in rotation and tillage systems and cultivation of winter cover crop as a "trap crop" after maize led to a decrease in the nitrate concentration and load from 28 mg dm^{-3} and 38 kg ha^{-1} yr^{-1} to 8 mg dm^{-3} and 15 kg ha^{-1} yr^{-1} for the 1986-1999 investigation period. Most of the N loads occurs in the fallow season. About 63% of the annual N load occurs from November through March, and 78% appears from November through April. Concentrations did not vary greatly by month within a year, but loads *did* vary due to the seasonal distribution of drainflow (KLADIVKO et al. 2004).

Daily loads of phosphate were about ten times lower than daily loads of nitrate. The average value of daily loads ranged from 0.03 in 2010 to less than 0.01 kg ha^{-1} for the remaining years, whereas the total yearly phosphate load ranged from 0.1 to 2.0 kg ha^{-1} (Table 2). The average value is equal to 0.83 kg ha^{-1} and is lower than presented by VAGSTAD et al. (2000) (1.7 kg ha^{-1}) for some small agricultural catchments in the Gulf of Riga drainage basin. However, yearly loads registered in 2010 and 2013 (2 kg ha^{-1} and 1 kg ha^{-1}, respectively) can be considered as high (SVENBÄCK et al. 2014). An average annual load from the investigated area is three times higher than 0.26 kg ha^{-1} reported by KOC and SOLARSKI (2006).

Concentration and drainflow

Nitrate nitrogen as well as phosphate concentration versus drainflow are shown in Figure 5. The log-normal function (1) parameters are presented in Table 3. Measured nitrate concentration dependents are very scattered and

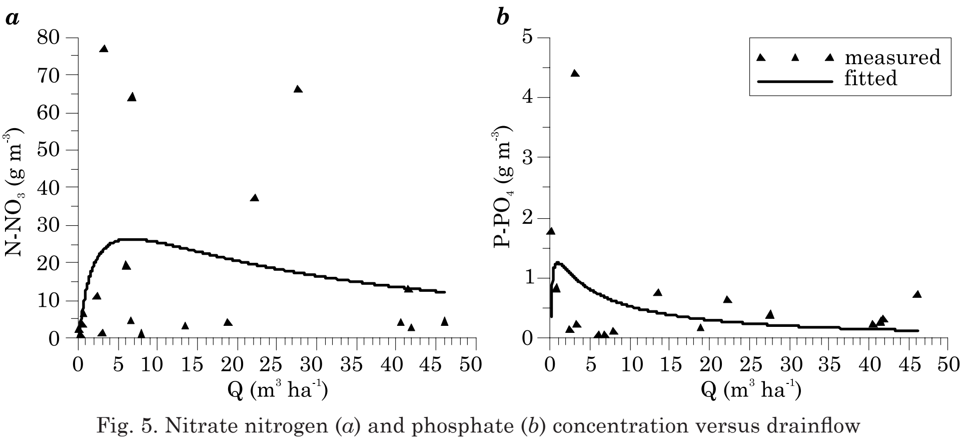

Fig. 5. Nitrate nitrogen (*a*) and phosphate (*b*) concentration versus drainflow

Table 3

The log-normal function parameters and coefficient of determination

y (g m^{-3})	Parameter			r^2
	a	b	c	
N-NO_3	26.32	6.69	1.56	0.12
P-PO_4	1.25	0.91	1.83	0.04

rather not related to drainflow rate. The same function (1) was used for phosphate concentration versus drainflow. The log-normal function parameters are presented in Table 3. There was observed very weak correlation for nitrate nitrogen function (r^2 = 0.12, p = 20) and even no correlation for phosphate function (r^2 = 0.04, p = 17).

Seasonal effects on concentration

Another problem was the relationship of nutrient concentrations in drainflow with the season. The Gaussian equation (2) parameters as well as a coefficient of determination are presented in Table 4. The measured and fitted concentration values are shown in Figure 6. The nitrate nitrogen concentration indicates some relationship with the season (r^2 = 0.36, p = 20),

Table 4

The Gaussian function parameters and coefficient of determination

y (g m^{-3})	Parameter				r^2
	a	b	c	D	
N-NO_3	7.29	48.0	112.82	16.04	0.36
P-PO_4	0.40	5.16	252.09	5.44	0.84

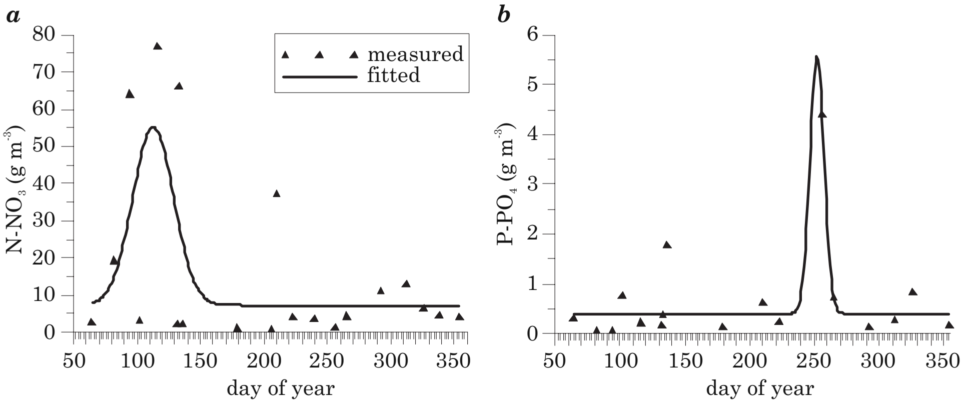

Fig. 6. Nitrate nitrogen (a) and phosphate (b) concentration versus day of the year

with the maximum values occurring in spring, e.g. the maximum of a fitted concentration (55.3 g m^{-3}) appeared in the third decade of April. The measured concentrations of nitrate during this season were high and exceeded 4- to 5-fold the standard of 15 g N-NO_3 m^{-3} (50 g NO_3 m^{-3}) defined in The Nitrates Directive (91/676/EEC) for groundwater. The highest concentration of nitrate in drainflow during spring can be an effect of recent fertilization, carried out from March until May, and of snow melting in March. Gentry et al. (2007) stress that substantial amounts of nitrate can be leached from soil during first flushing events following an application of fertilizers.

The calculated phosphate concentration curve has a quite good relationship with the measured values (r^2 = 0.84, p = 17). The maximum concentration (5.6 g m^{-3}) was predicted for the first decade of September. This was a period with a very high phosphate content in drainflow, exceeding 4 g m^{-3}. A similar pattern of phosphorus transport in a drain system was observed by Svenbäck et al. (2014) in Sweden, on an experimental site with clay soil. These researchers recorded the highest losses of phosphorus in September until November. It was considered to be an effect of autumn tillage carried out under wet conditions. Wet conditions in soil, irrespective of agricultural practices, accelerate water flow and thus intensify the transport of dissolved compounds (Kramers et al. 2012). A similar effect is produced by high precipitation (Köhne, Horts 2005). This can explain a substantial increase in the phosphorus concentration in the first decade of September, as it was recorded after a high precipitation period at the end of August (Figure 3a).

However, it had to be noted that the measured phosphate concentrations are close to each other (from 0 to 2 g m^{-3} in general) and just one point determines the peak of the fitting curve. Thus, it would be rather risky to base on just one value a hypothesis that phosphate concentrations increase in the first decade of September.

CONCLUSIONS

1. Total annual nitrate nitrogen loads ranged from 7.5 to 34.6 kg ha^{-1} and were comparable to values obtained by other researchers for different sites in Poland.

2. Nitrate nitrogen as well as phosphate concentrations do not strongly depend on drainflow. There was a very weak correlation for the nitrate nitrogen function (r^2 = 0.12) and no correlation for the phosphate function (r^2 = 0.04).

3. The nitrate nitrogen concentration indicates some relationship with the season (r^2 = 0.36). The maximum of the fitted concentration (55.3 g m^{-3}) appeared in the last decade of April. A significant increase in the N-NO_3 concentration appears at snow melting (March) and continues until the end

of May, with the maximum value in the third decade of April, which coincides with the onset of the plant vegetative growth period.

4. The phosphate concentration curve has quite a good relationship with the measured values (r^2 = 0.84). However, the measured values of phosphate have a very narrow range and just one point determines the peak of the fitting curve.

5. The high N-NO_3 concentration indicates that nitrates in drainflow can be a source of surface water eutrophication.

6. The total annual phosphate load ranged from 0.1 to 2.0 kg ha^{-1}. High loads exceeding 1.0 kg ha^{-1} were registered in two of the investigated years. Thus, it can be noted that phosphate loads can pose a risk of eutrophication in some years, but in general they are not a significant contributor to this problem.

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