

Mineral nitrogen content in hydrographic areas of Poland depending on land use**

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Received October 29, 2018; accepted May 7, 2019

Abstract. One unintended consequence of nitrogen use in agriculture is an increase in nitrate content in ground waters. Nitrogen content was evaluated in soil samples from specific hydrographic regions of Poland from the 60-90 cm soil layer, in which this nutrient is not readily available to the main root mass of crop plants and may negatively affect the environment. It was revealed that N_{\min} content in specific hydrographic regions was highly dependent on both the soil type and land use. Notably higher values of N_{\min} content were observed for organic soils. The highest N contents were found in the grasslands of the north-western area of Poland, while they were slightly lower in several regions of the main Odra River catchment and west of the Vistula River. The area with a high N_{\min} content in soils under maize was significantly larger compared to the grasslands area and primarily included the hydrographic regions of the Odra River basin in its south-western stretch, and of the Vistula River on its western and south-eastern side. With regard to the arable land under mixed cereals, the soils with the highest N_{\min} content in the non-root layer were predominantly located in hydrographic regions belonging to the main Odra catchment and to the catchment of the Vistula River in its upper course.

Key words: nitrogen, spatial distribution, hydrographic areas, land use, grassland

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**This work has been partly financed from the funds of the Polish National Centre for Research and Development in frame of the project BIO-FERTIL, contract number: BIOSTRATEG3/347464/5/NCBR/2017 (2018-2021).

INTRODUCTION

Nitrogen is the most yield-increasing nutrient of plants and the importance of its role in agricultural production is beyond question. Nevertheless, there are non-production consequences of nitrogen use in agriculture, among which the increase in nitrate content in crop plants as well as in ground and surface waters is the most important one. Mineral nitrogen leached from the topsoil layers to the 60-90 cm layer of the soil profile is considered to be unavailable for the main root mass of crop plants. Therefore, research into nitrogen migration to deeper layers of the soil profile is extremely important, both in terms of nitrogen loss estimation and potential groundwater pollution. Research is also being carried out concerning the possibility of phytoremediation of nitrates from the soil, for example Marecik *et al.* (2013) showed high nitrogen removal rates for the treatment of industrial wastewater with a high concentration of $N-NO_3$ using sweet flag (*Acorus calamus*), common reed (*Phragmites communis*) and broadleaf cattail (*Typha latifolia*). It should be noted that much attention is now being paid to nitrogen losses and the resultant problems of water pollution in the context of the document known as the Nitrate Directive and the Helsinki Convention (Directive, 91/676/CEE; Convention, 1992; Directive, 2000/60/EC). The main

assumptions of the Nitrate Directive are focused on preventing the causes of eutrophication as a serious threat to water quality (Directive, 91/676/CEE; Randal and Goss, 2008). Hence, the quantities of soil mineral nitrogen, which have been recorded for years, are an important indicator of the effects of nitrogen on water quality (Regulation, 2002; Fotyma *et al.*, 2010; Lipiński, 2010).

Apart from the environmental aspect, monitoring nutrient changes in various soil layers over the years and making an attempt to correlate these changes with the influence of various factors is significant both from a scientific and practical point of view. Such information is the basis for constructing simple empirical models based on, for example, multiple regression equations, that allow for the prediction of nutrient content in the studied soil and thus help farmers to plan the rational use of fertilizers in order to ensure an optimal nutrient supply for crop growth and to increase soil productivity using only a limited set of soil properties (Tkaczyk *et al.*, 2017; 2018a; 2018b). Knowledge concerning nutrient content, especially NPK balance, and their relationship with other soil physicochemical properties are important for agrophysical modelling (Walczak *et al.*, 1997; Lamorski *et al.*, 2013). All of these models need input data to run, therefore representative data, especially at a large scale, are sought by modellers using and developing crop growth and yield models. Detailed information put into agrophysical models may constitute a new quality in research on how crop production will change in the conditions of a changing climate (Pirttioja *et al.*, 2015; Fronzek *et al.*, 2018) and how different cultivation and fertilization methods will impact this production (Ruiz-Ramos *et al.*, 2018; Rodríguez *et al.*, 2018). The balance of NPK also depends on the root system of the plant species and the level of mineral and organic fertilization (Antonkiewicz *et al.*, 2018; Watros *et al.*, 2018). The content of mineral nitrogen in the soil is also impacted by the biological activity of the soil, which in turn may be influenced by soil moisture (Wnuk *et al.*, 2017) or N fertilization (Walkiewicz *et al.*, 2018), and by atmospheric conditions. For this reason, research concerning the spatio-temporal variability of meteorological series from different climate zones (Baranowski *et al.*, 2015; Hoffmann *et al.*, 2017; Krzyszczak *et al.*, 2017a; 2017b; 2019) and their prediction (Murat *et al.*, 2018) is extremely important. It allows for the assessment of the likely impact of climate change not only on agricultural production, but also on the content of macroelements (NPK) in the soil.

About 1/5 of the total area of soil used for agriculture is occupied by grasslands (GUS, 2018). The location, area and shape of these grasslands are physiographically determined, which prevents arbitrary changes. This results in high grassland area stability (Wasilewski, 2010), also the location of grasslands among crop fields, water bodies and watercourses as well as the large variations in habitat conditions indicate their exceptional role in the natural

environment (Wasilewski, 2009). Despite a decrease in the area of both arable land and grasslands in the 21st century, the yields of plants obtained per surface unit are increasing, which is related to the intensity of plant production, and thus with the more pronounced impact of agricultural land on the natural environment. Therefore, it is necessary to search for solutions optimizing the management of macro- and microelements, including nitrogen, that will take into account the diversity of Polish soils and land use.

The results of previous research mainly concerned the scale of nitrogen outflow, as well as the impact of various factors on the migration of this nutrient into the soil profile, mainly on arable land. Grasslands, including those located on organic soils, have not been the subject of wider analyses. Thus far, the amount of mineral nitrogen in the soil layer 60-90 cm from grassland soils with regard to agricultural fodder crops has not been examined. Also, the potential impact of this form of nitrogen on water quality in the hydrographic regions of Poland has not been studied previously.

Therefore, taking into account the environmental effects, as well as production and economic considerations, this study attempted to evaluate the mineral nitrogen content in the 60-90 cm soil layer in grassland soils with regard to selected agricultural fodder crops in Poland's hydrographic regions.

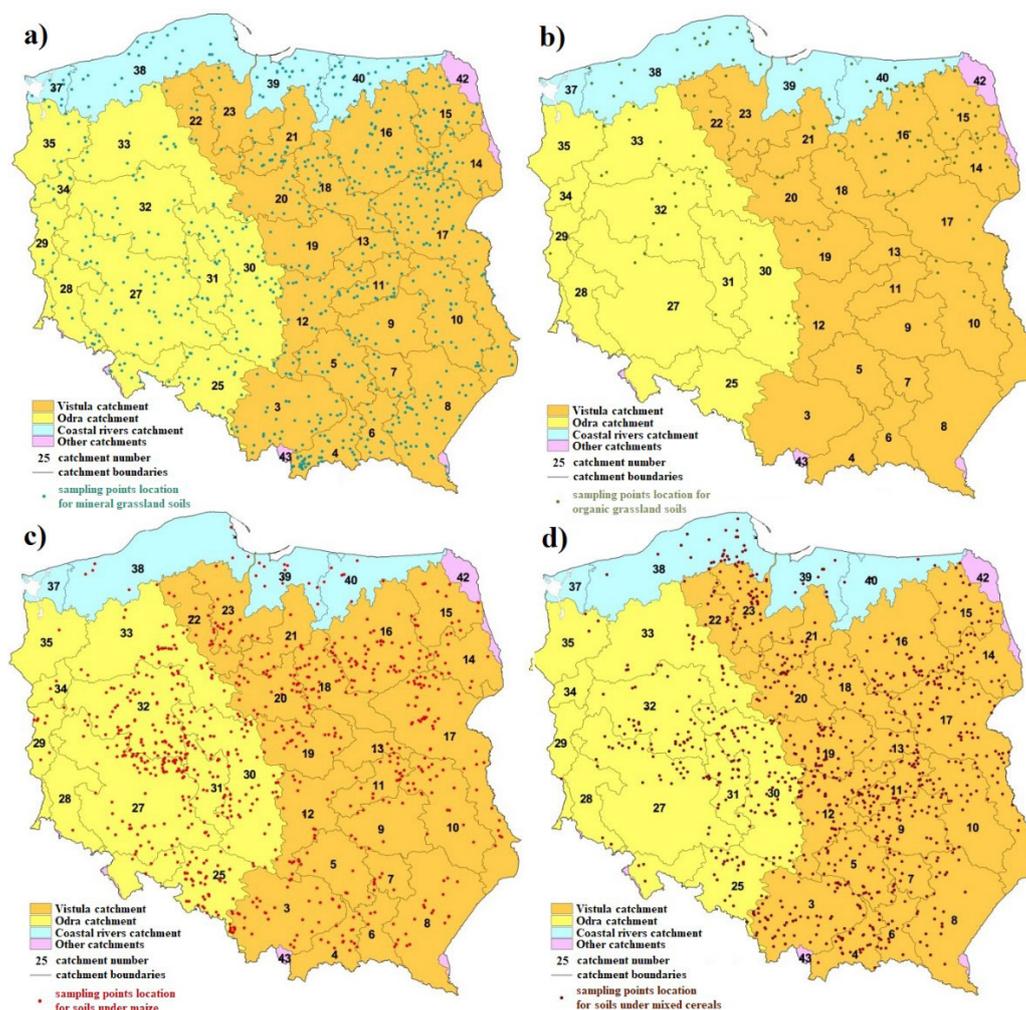
MATERIALS AND METHODS

The evaluation of the soil mineral nitrogen content was performed based on the results of environmental investigations conducted by the accredited Regional Chemical and Agricultural Stations in agricultural farms across Poland over the period 2010-2012. The sampling sites were divided between Poland's hydrographic regions (Table 1). The vector layer of Poland's division into hydrographic areas (second-order catchments) used in this study was developed based on the Institute of Meteorology and Water Management (IMGW) hydrological atlas of 1986 "Hydrographic division of Poland – Part II. A map series of the hydrographic division at a scale of 1:200000". The locations of the sites were characterized by geographical coordinates using a GPS tracker, which allowed for sampling to be carried out in the same places in successive years of the study. The location of the sampling sites, divided into soil type and land use, is presented in Fig. 1.

Soil samples were taken in spring and autumn from three soil profile layers, 0-30, 30-60, and 60-90 cm, from fields with a total area of not more than 4 ha. Each total sample (with a weight of about 100 g) consisted of 15-20 primary samples collected from an area of not more than 100 m². In this study only soil samples from the 60-90 cm layer were subjected to the analysis. Sites where the same land use was continued throughout the entire study period were selected

Table 1. Number of samples collected from the 60-90 cm soil layer in grasslands and soils under maize and mixed cereals in the selected hydrographic regions of Poland

Hydrographic region	Grassland on mineral soils	Grassland on organic soils	Maize	Mixed cereals
Poland (in total)	859	167	826	951
Vistula basin	553	95	431	685
Odra basin	223	36	370	227
Basin of coastal rivers	83	36	25	39

**Fig. 1.** Location of soil sampling points from a) grasslands on mineral soil, b) grasslands on organic soil, c) maize and d) mixed cereals.

from the grassland area. For comparison, sites where maize and mixed cereals were grown over the period 2010-2012 were also selected (if the same crop was grown during successive years, the average value from the respective years was taken into consideration). The number of soil samples collected for each soil type and land use is listed in Table 2. Additionally, information about the mineral nitrogen fertilization rate for each soil sampling point (land use) was acquired. The fields were classified according to the doses of nitrogen fertilization: 0 (without fertilization), 1-40, 41-80, 81-120 and >120 kg N ha⁻¹.

The soil samples were subjected to analyses of N_{min} in accordance with the PN-R-04028:1997 norm. The collected soil samples were used to determine the mineral nitrogen content in the 60-90 cm layer which were kept at a temperature of -18°C. The soil samples with a natural moisture content (after defrosting) were subjected to extraction with a 1% potassium sulphate solution at a ratio of 1:10. For the extracts obtained, both nitrate and ammonium nitrogen content were determined spectrophotometrically using a Skalar San Plus System auto-analyser. Dry matter content was also determined in the examined samples. Mineral

Table 2. Number of analysed samples taken from the 60-90 cm soil layer in grasslands and soils under maize and mixed cereals

Crop type/land use	Number of samples
Total	859
Grassland on mineral soils	
meadows	521
pastures	160
hay and pasture use	84
alternate use	98
Total	167
Grassland on organic soils	
meadows	111
pastures	17
hay and pasture use	39
alternate use	0
Maize	826
Mixed cereals	951

nitrogen content, in the form of total nitrate and ammonium nitrogen, was expressed in mg kg^{-1} of dry weight of the soil sample.

Based on the average mineral nitrogen content calculated for individual sites, its spatial distribution was shown in Poland's hydrographic areas and analysed in relation to specific land uses. Interpolation was performed using ArcView software which applied the IDW (inverse distance weighting) method, which is based on the assumption that the value of the trait being investigated at a given point is dependent on the value of this trait in the closest base points). The data from 12 adjacent base points were included. Interpolation was performed with a strength of 3 and without barriers. The generated 1000 m mesh grid was cropped using the contour of Poland.

RESULTS AND DISCUSSION

Many authors have drawn attention to the phenomenon of mineral nitrogen movement in soil profile layers, stressing nitrogen losses (Powlson, 1988; Trehan, 1996; Tremblay *et al.*, 2001; Coyne and Frye, 2005). In the opinion of Soon *et al.* (2001), almost half of mineral nitrogen located in the 0-30 cm layer may migrate to deeper layers due to leaching. Coyne and Frye (2005) also explain this phenomenon by the beneficial influence of biological processes occurring in the soil. The spatial distribution of mineral nitrogen content in the 60-90 cm layer in grassland soils presented in Fig. 2a shows that the highest values were recorded in the north-western area of Poland, both in spring and in autumn, especially in the basin of western coastal rivers belonging to the basin of the Vistula; in the Warta region from the conflux with the Prosna to the mouth of the Noteć; in the Noteć basin, and also in the regions of the main Vistula catchment (the Vistula from the conflux with the Drwęca to the conflux of the Brda and the Vistula

from the conflux with the Brda to the estuary leading to the Baltic). The highest contents of N_{\min} (more than 13 mg kg^{-1} DM) were also found in the north-eastern area, in the regions belonging to the Vistula river basin (the Narew from its sources to the mouth of the Biebrza, the Biebrza basin and the Narew from the conflux with the Biebrza to the mouth of the Bug). High N_{\min} contents ranging from 7.1 to more than 13 mg kg^{-1} DM of this form of nitrogen were found in many regions of the main Odra catchment, with a greater value recorded in spring than in autumn. It results from the fact that in organic soils a mineral nitrogen content was noted to be much higher. This is evident from an analysis of the spatial distribution of mineral nitrogen content in the 60-90 cm layer in mineral grassland soils presented in Fig. 2b. It shows that the highest content values, which ranged from 7.1 to more than 13 mg kg^{-1} DM of N has been observed in numerous areas belonging to the Odra main catchment, with a higher number of them recorded in autumn rather than in spring. With regard to the area of the other main catchments, *i.e.* the catchments of the Vistula River and of the rivers of the coastal regions, the above-mentioned mineral nitrogen contents were only found in some hydrographic regions, with values of less than 5.0 mg kg^{-1} DM being predominant.

When comparing the spatial distribution of mineral nitrogen in grassland soils and soils under maize (Fig. 2c) and mixed cereal crops (Fig. 2d), attention should be paid to a large area, being more than half of the territory studied, where the contents of this nutrient range from 7.0 to more than 13 mg kg^{-1} DM. This trend was particularly visible in the area under maize crops (Fig. 2c). Similarly, as in the case of grasslands, the highest mineral nitrogen contents were found in hydrographic regions belonging to the Odra basin and in the south-eastern part of Poland, in regions which are part of the Vistula catchment. With regard to soils on which mixed cereals were grown, high mineral nitrogen contents were noted in a slightly smaller area compared to the area under maize, but larger than in the case of grasslands (Fig. 2d). As far as cereal crops are concerned, the highest contents, ranging from 11.1 to more than 13.0 mg kg^{-1} DM, occurred in hydrographic regions within the Odra basin (especially in spring) and in regions within the Vistula basin in the south of Poland.

It has already been stated that the mineral nitrogen content N in the soil layer 60-90 cm varied significantly depending on the soil type. In all of the assessed catchments higher N contents were observed for organic soils than for mineral soils (Fig. 3). The average N content for the entire Polish area was 7.4 mg kg^{-1} DM in mineral soils and 34.2 mg kg^{-1} DM in organic soils. Significantly higher mineral nitrogen contents in mineral soils than the Polish averages were observed in 10 sub-basins, with the highest value found in catchment no. 26 (the Nysa Kłodzka basin) in the Odra basin - 14.6 mg kg^{-1} DM, and in the Odra basin in the hydrographic region No. 31 (the Prosna River basin)

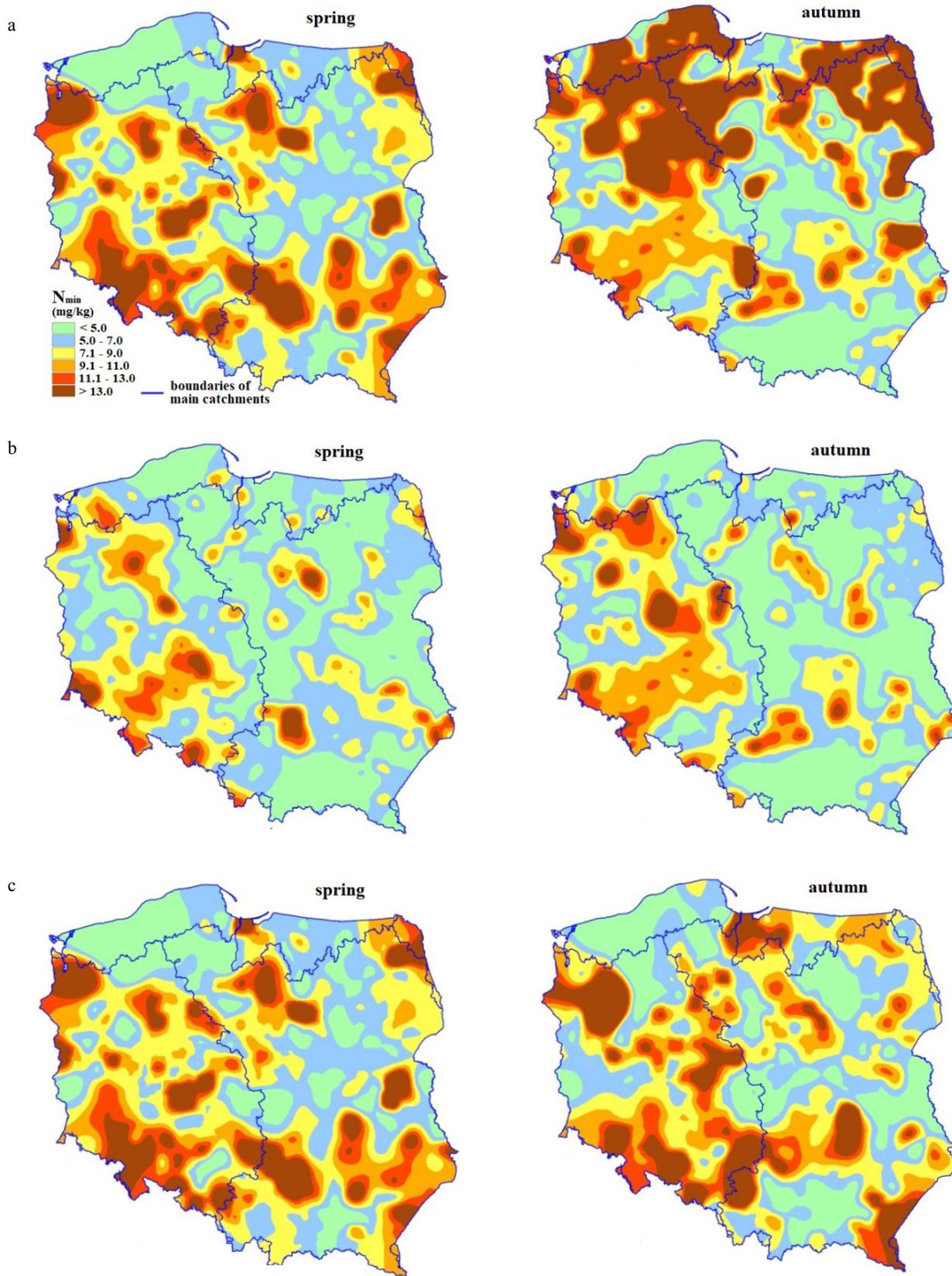


Fig. 2. Spatial distribution of N_{min} content in the 60-90 cm layer of: a – grassland soils (mineral and organic), b – mineral grassland soil, c – mineral soil under maize, d – mineral soil under mixed cereals; during the spring and autumn period in Poland’s selected hydrographic areas.

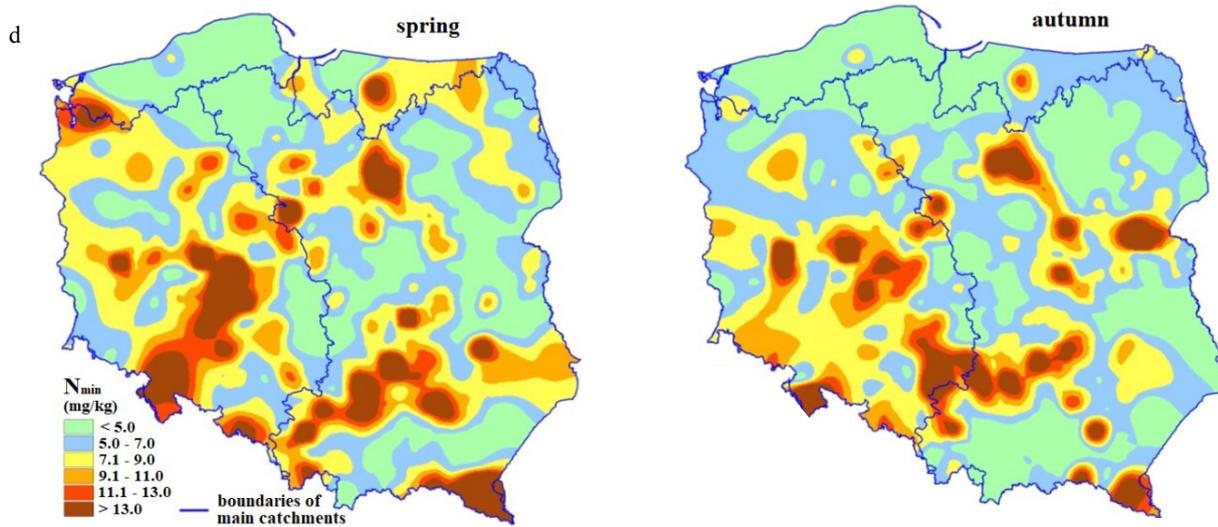


Fig. 2. Continuation.

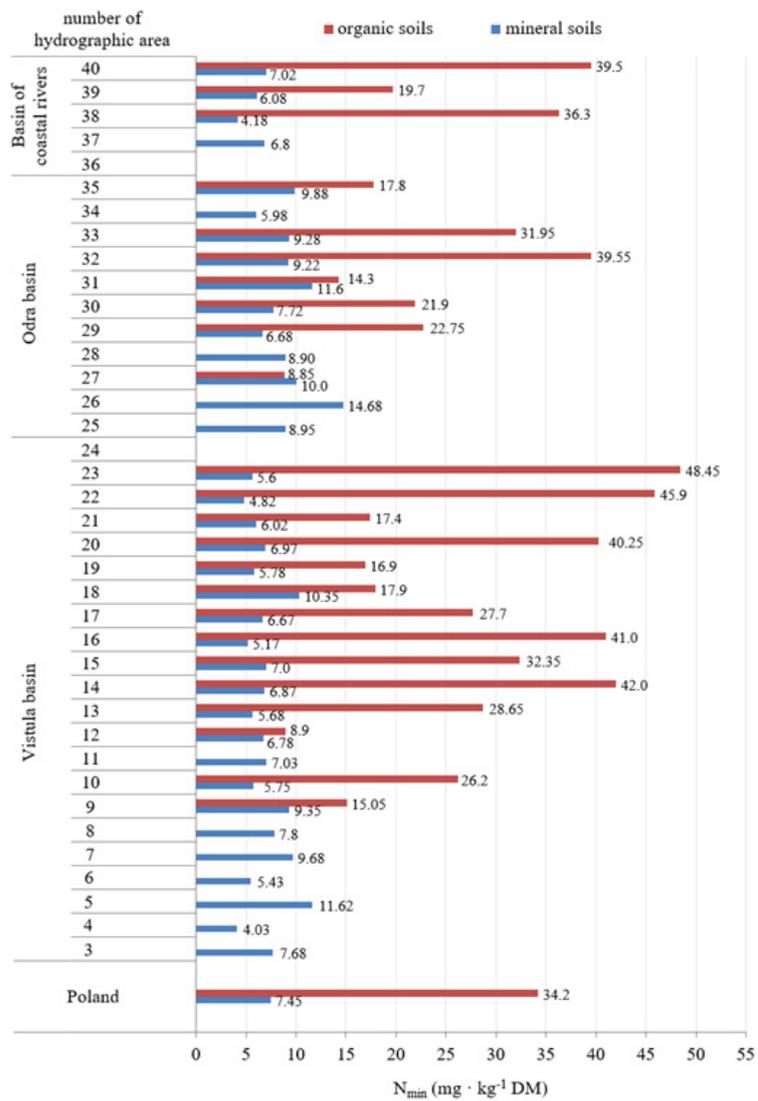


Fig. 3. Average mineral nitrogen content N_{min} in the 60-90 cm soil layer in the selected hydrographic areas of Poland depending on the soil type.

- 11.6 mg kg⁻¹ DM. As for organic soils, higher contents of N_{min} than the Polish average were observed for 7 subcatchments, with the highest value being recorded in region No. 23 (the Vistula from the mouth of the Brda to the estuary leading to the Baltic) and No. 22 (the Vistula from the conflux with the Drwęca to the conflux with the Brda) in the Vistula basin (48.4 and 45.9 mg kg⁻¹ DM, respectively). The lowest content of mineral nitrogen in mineral soils in the 60-90 cm layer was recorded in hydrographic region No. 4 (the Dunajec basin) in the Vistula basin (4.0 mg kg⁻¹ DM) and in region No. 38 (the basin of the western coastal rivers to the conflux with the Vistula River) belonging to the main catchment – the basin of the coastal rivers (4.2 mg kg⁻¹ DM). On the other hand, in organic soils, the lowest content was found in region No. 27 (the Odra from the conflux with the Nysa Kłodzka to the mouth of the Bóbr) in the Odra basin (8.8 mg kg⁻¹ DM) and in region No. 12 (Pilica river basin) in the basin of the Vistula (8.9 mg kg⁻¹ DM). Higher amounts of N_{min} in organic soils were observed compared to mineral soils, both for the spring and autumn sampling dates. These findings confirmed the studies of Sapek and Sapek (2007) and Pietrzak *et al.* (2006). Larger values of N_{min} content in the 60-90 cm soil layer in organic soils may be due to weaker mineralization in mineral soils as a result of limited C content. Sapek (2010) stated that the soil's abundance in organic matter may affect the efficiency of nitrogen mineralization. This was confirmed by the recent studies of Tian *et al.* (2017), who showed that net N mineralization in subsoil is limited by low amounts of a labile C source (which provides energy) and degradable organic N (which provides material). Additionally, Hatch *et al.* (2002) demonstrated that nitrogen immobilization is a result of the increased activity of soil microorganisms.

The mineral nitrogen content in the 60-90 cm soil layer in Poland's main catchments (Fig. 4) varied on average from 12.6 mg kg⁻¹ DM in the basin of the coastal rivers during the spring period to 14.4 mg kg⁻¹ DM in the Odra basin during autumn. The average content of this nutrient in the soil layer, which was beyond the reach of the root system, was respectively 14.3 (in spring) and 14.0 mg kg⁻¹ DM (in autumn) for the entire area of Poland. In spring, higher values were only found in the Vistula basin, whereas during the autumn months such values were found in the Odra basin and in the basin of the coastal rivers (Fig. 4). Compared to the averages for the entire area of Poland in spring, significantly lower N_{min} contents were found in soil samples collected from the basin of the coastal rivers, while in autumn – those from the Vistula basin were lower.

When comparing the average mineral nitrogen content in the 60-90 cm layer in grassland soils and soils under selected agricultural fodder crops, the lowest values were found in grassland soils in the area of almost all the main river catchments studied, regardless of the sampling date (Fig. 5). An exception to this trend were the catchments within the basin of the coastal rivers where lower N_{min} con-

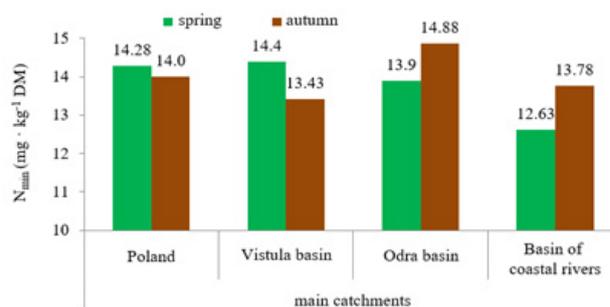


Fig. 4. Average mineral nitrogen content N_{min} in the 60-90 cm soil layer in the spring and autumn period in the main selected hydrographic regions of Poland.

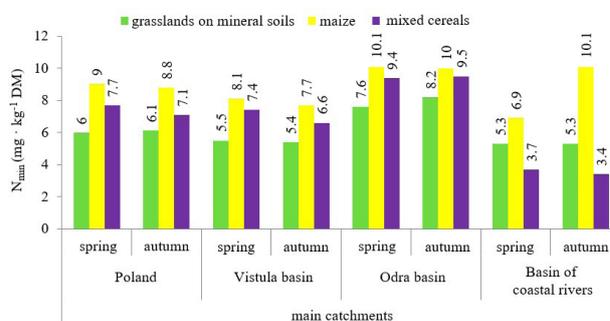


Fig. 5. Average mineral nitrogen content N_{min} in the 60-90 cm soil layer in the main selected hydrographic regions of Poland depending on agricultural land use and sampling date.

tents were recorded in soil material collected from soils under mixed cereals as compared to grassland soils. In all of the locations studied, the highest contents of this nutrient were found in soils under maize. Regardless of agricultural land use and the sampling date, the highest mineral nitrogen contents were determined for soils in the Odra basin, whereas the lowest ones were found in the basin of the coastal rivers, except for soils under maize sampled in the autumn period when one of the highest contents of the studied nutrient was noted (10.1 mg kg⁻¹ DM). García-Díaz *et al.* (2017) noted for vineyards that vegetation cover had a significant impact on runoff and dissolved mineral nitrogen losses, and as a result, a differentiation of the N_{min} content in the deeper soil layers. Also, De Notaris *et al.* (2017) showed that vegetation cover influences N leaching, with spring wheat and potatoes having the highest rate of nitrogen leaching.

When evaluating the mineral nitrogen content in the 60-90 cm layer of mineral grassland soils, depending on land use and the sampling date, the highest values were found in meadows in each of the main catchments evaluated, while the lowest ones were found in hay and pasture grasslands, as well as in alternating grasslands (Fig. 6). With the exception of grasslands used variably (hay and pasture use), for which these values reached their lowest level, in the case of the other grassland use types, the highest contents of the mineral form of nitrogen were found in

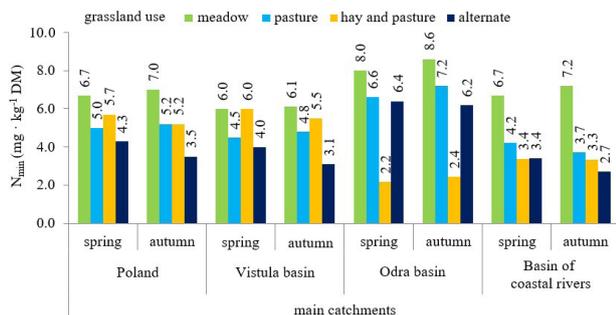


Fig. 6. Average mineral nitrogen content N_{\min} in the 60-90 cm soil layer in the main selected hydrographic regions of Poland depending on grassland use and sampling date.

the Odra basin. Taking into account the average values for the main catchments, the largest differences in the content of the evaluated nutrients in spring and autumn were noted in alternating grasslands (in arable land), with the highest values found in the Vistula basin. Bałuch-Małecka *et al.* (2004) showed that the most effective organic mass mineralization process was ensured by grass mixtures with a significant share of meadow clover and alfalfa.

In order to determine the factors that have the greatest influence over the spatial soil N_{\min} distribution in Poland, the determination coefficients (R^2) were calculated (Table 3). They reflect the relationship between mineral nitrogen content N_{\min} in the 60-90 cm soil layer under grasslands, maize, mixed cereals and the levels of N fertilization, soil pH and livestock density. Determination coefficients were calculated for both spring and autumn sampling dates, in addition to those values calculated on an annual basis. It transpired that livestock density mainly affected mineral nitrogen content N_{\min} in the 60-90 cm soil layer in grassland soils, regardless of the carbon content (mineral or organic soils) or the sampling date (spring or autumn), with R^2 even reaching 0.99 for grassland mineral soils for the spring sampling date. As was shown by Baryła and Kulik (2006) the livestock density may significantly influence the nitrogen supply to the soil. N_{\min} content in grassland mineral soils was also strongly influenced by the pH of the soil, in contrast to grassland organic soils. In soils under maize

crops the greatest influence over the spatial distribution of N_{\min} content in the 60-90 cm soil layer had pH value of the soil, whereas the dose of N fertilization did not have a significant effect over this distribution. It may be hypothesized with some justification that maize is able to assimilate more N from fertilizers, thus preventing it from migrating into the deeper soil profile layers. On the contrary, for soils under mixed cereals, not only soil pH has a strong influence over the distribution of N_{\min} content in the 60-90 cm soil layer, but also the dose of N fertilization greatly influences this distribution. Grover *et al.* (2017) observed that increases in pH values lead to changes in the availability of resources for microbes, thus altering their community structure, with the final result of modifying their activity and C-use efficiency. The relative abundance and diversity of bacteria were positively related to pH (Rousk *et al.*, 2010). This effect has an influence over the mineralization process, leading to positive correlations between the mineral nitrogen content N_{\min} in the 60-90 cm soil layer and soil pH. Similar correlations were also found in the studies of Sapek and Kalińska (2004, 2007) and Sapek (2010). In their opinion, lower acidity levels reduce the rate of release of the ammonium form of nitrogen and at the same time promotes the nitrification and the release of the nitrate form of nitrogen.

CONCLUSIONS

1. Soil mineral nitrogen content, particularly in the 60-90 cm layer, is a serious threat to water quality (especially outside the growing season). During the assessment (both in the spring and autumn dates of sampling) of mineral nitrogen content in the 60-90 cm layer of grassland soils relative to other selected agricultural crops in Poland's hydrographic regions, it was confirmed that there are observable differences in the content of this form of nitrogen depending on the type of soil and land use.

2. The N_{\min} content in the 60-90 cm soil layer in specific hydrographic regions was particularly diversified depending on the content of organic carbon in the soil samples and varied according to land use.

Table 3. Determination coefficients (R^2) between mineral nitrogen content N_{\min} in the 60-90 cm soil layer in grasslands and soils under maize and mixed cereals during spring and autumn sampling dates and the dose of N fertilization, soil pH and livestock density

Land use	Dose of N fertilization		Soil pH		Livestock density	
	spring	autumn	spring	autumn	spring	autumn
Grasslands on mineral soils	0.45	0.69	0.94	0.85	0.99	0.94
Grasslands on organic soils	0.23	0.07	0.23	0.23	0.48	0.90
Maize	0.28	0.01	0.96	0.83	0.01	0.74
Mixed cereals	0.69	0.85	0.92	0.96	0.62	0.20
Total mineral soils	0.69	0.81	0.98	0.92	0.86	0.04
Soils in total	0.19	0.20	0.59	0.81	0.14	0.74
Soils in total – annualized		0.01		0.72		0.05
Mineral soils in total – annualized		0.76		0.98		0.96
Organic soils in total – annualized		0.05		0.03		0.01

3. For grasslands, the highest contents of nitrogen were found in the north-western area, while slightly lower N contents were observed in several regions of the main Odra catchment and west of the Vistula River.

4. In soils under maize crops, the mineral nitrogen content was significantly higher than it was in the case of grasslands and primarily included the hydrographic regions of the basin of the Odra River, in particular in its south-western stretch, and the Vistula River on its western and south-eastern side. Substantially high levels of mineral nitrogen content were also found in the north-eastern area of Poland.

5. Areas of soil from arable land under mixed cereals, with the highest N_{min} content in the layer beyond the reach of the main mass of roots were predominantly located in hydrographic regions belonging to the main Odra catchment and to the catchment of the Vistula River in its upper course. This content was higher than the values found in grassland soils but lower than those in soils under maize.

6. Among the factors with the greatest influence over the spatial soil N_{min} distribution in Poland is soil pH. In grassland soils, regardless of the carbon content, livestock density has a significant effect over the N_{min} content in the 60-90 cm soil layer, whereas for soils under mixed cereals the dose of N fertilization has a strong influence on N_{min} content.

7. The results obtained have both an environmental and practical significance. They may help to identify regions (catchments) where agriculture has a more substantial impact (potential groundwater pollution) on the natural environment and facilitate the search for solutions leading to the sustainable management of nitrogen fertilization taking into account the diversity of Polish soils, organic carbon content and land use.

Conflict of interest: The Authors do not declare any conflict of interest.

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