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CONTENTS

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SHARE OF PRECIPITATION NITROGEN IN THE RIVER DISCHARGE OF THE UPPER WIEPRZ RIVER (ROZTOCZE, SE POLAND)

UDZIAŁ AZOTU Z OPADÓW ATMOSFERYCZNYCH W ODPŁYWIE RZECZNYM GÓRNEGO WIEPRZA (ROZTOCZE, POLSKA)

Abstract: Based on hydrochemical, hydrometric and meteorological material, a nitrogen balance was made for the catchment of the upper Wieprz River, covering the years 2005–2006. The calculations showed that nitrogen discharged through the river system accounted for approx 4.1 % of the pool of nitrogen introduced into the Wieprz River catchment (1572.7 Mg · year^{-1}). The proportion of precipitation nitrogen in the total nitrogen discharge through the Wieprz River (64.4 Mg · year^{-1}) was estimated at 11.4 %. The main part of nitrogen discharged via the river system was nitrogen of agricultural origin (53.3 Mg · year^{-1}).

Keywords: water cycle, nitrogen, precipitation, agriculture

The water cycle in a river catchment is an important stage of nitrogen migration in the natural environment [1]. The importance of this element in the aquatic environment is emphasised by special legislation applicable in the EU and Poland, referred to as the Nitrates Directive. The overriding task of this Directive is to reduce the pollution of waters with nitrogen compounds and to prevent further such pollution from agricultural sources, since this element affects the intensity of eutrophication of waters and the possibility to use them for consumption purposes. The excessive nitrogen load to the aquatic environment usually results from human activity: the emissions of pollutants into the atmosphere, agricultural use of land (field fertilisation) and sewage discharge.

In order to make a quantitative evaluation of the nitrogen load to the environment, area balances of this element within an administrative unit or a hydrographic unit – catchment area – are made [2–5]. It allows the determination of the contribution of atmospheric and agricultural nitrogen reaching the catchment and discharged from it. Results of calculations can be used to prepare water management plans within

catchment areas, incorporating sustainable development principles, which are essential, in particular, in agriculturally used areas, valuable natural areas as well as areas being drinking water reservoirs or used for recreation purposes.

The study area

The present study on the nitrogen cycle within the hydrologic cycle was carried out on the example of the upper Wieprz River catchment, with an area of 300.3 km^2, closed with the Guciow river gauge (Fig. 1). In physiographic terms, the study site is located in Central Roztocze (the Tomaszów area), in the southern part of the Lublin province (regional administrative unit) (SE Poland). This area is partially included in the Roztocze National Park's buffer zone, the Kransobrod Landscape Park – the spa of Krasnobrod being situated within the catchment area.
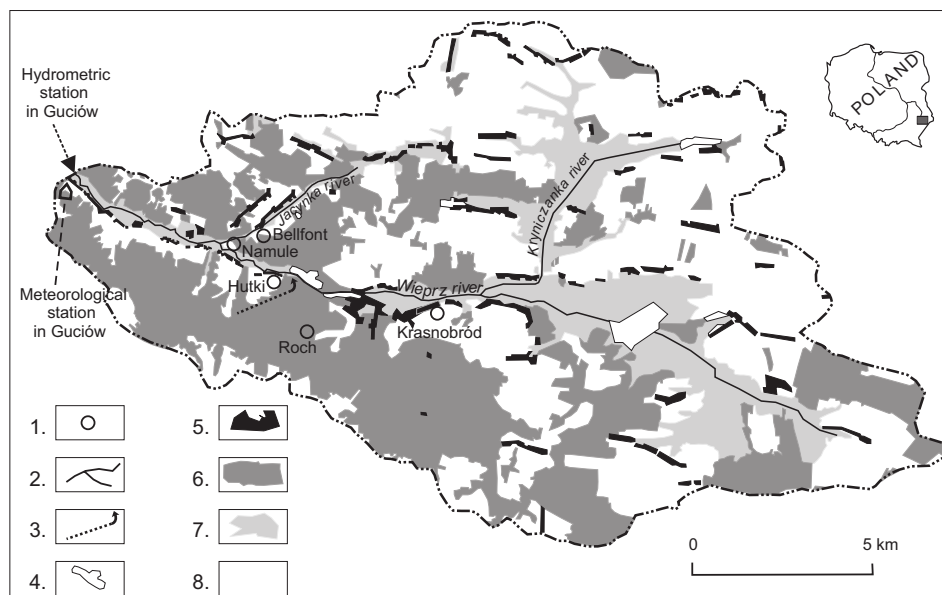
Fig. 1. The location of sampling sites against the background of land use within the Wieprz River catchment (1 – springs, 2 – rivers, 3 – municipal sewage, 4 – waters, 5 – built-up areas, 6 – forests, 7 – meadows and pastures, 8 – arable land areas)

As regards the land use structure within the catchment area, arable land occupies 47.8 %, meadows and pastures 12.4 %, forests 33.3 %, built-up areas and roads 3.6 % and waters 1 %. This area is characterised by low population density, low urbanisation, and as far as agriculture is concerned – by quite extensive farming, except for the loess catchment of a tributary of the Wieprz River – Kryniczanka. It results from the type of rocks composing cover deposits and soils formed on them. In the north-eastern part of the catchment, typical brown soils and grey-brown podzolic soils developed (7.1 % of

the catchment area), with favourable plant cultivation conditions, likewise rendzina soils formed from marl and marly rocks (4.9 % of the catchment area). Leached and acid brown soils, predominant within the catchment area (51.8 %), which developed on shallow calcareous-siliceous rocks as well as loess rocks, are characterised by a medium potential for plant cultivation. Rusty and podzolic soils, formed primarily from sand deposits, with unfavourable plant cultivation conditions, are found in a large area (22.8 % of the catchment area). At the bottoms of the river valleys, on alluvial soils, silts and peats as well as hydrogenic soils developed (11 % of the catchment area), used primarily as meadows and pastures [6, 7]. In the areas with fertile soils as well as within meadows and pastures, ca 60 kg N $\cdot$ ha^{-1} $\cdot$ year^{-1} is applied as fertiliser, on poorer soils ~40 kg N $\cdot$ ha^{-1} $\cdot$ year^{-1}.

The leaching of nitrogen from soil to groundwater is conditioned to a large extent by precipitation. In the upper Wieprz River catchment, average total precipitation is approx 680 mm, and the total discharge rate is 160 mm [8]; the share of groundwater inflow in the total river discharge is estimated at over 80 % [9]. The Wieprz River is fed by efficient springs and through direct channel drainage. The main and most abundant aquifer of this area, referred to as the Rotocze aquifer, occurs in tight Upper Cretaceous and Tertiary calcareous-siliceous rocks (eg gaizes). In the river valleys, the waters of the Rotocze aquifer merge with those filling Quaternary alluvia (mainly sands), forming a joint system [9].

Materials and methods

The aim of this study was to determine the share of the nitrogen load introduced into the substratum by precipitation and agricultural land use in the river discharge from the upper Wieprz River catchment. This task was carried out by measuring nitrogen concentrations at particular stages of the hydrologic cycle: in precipitation, surface runoff, groundwater and the river. Based on hydrometric and meteorological material, a nitrogen balance was made for the catchment of the upper Wieprz River, covering the years 2005–2006.

Water samples from precipitation events were collected on a daily basis, at the Guciow-based Roztocze Research Station of the Maria Curie-Sklodowska University, as total precipitation: dry + wet [10]; precipitation was recorded using Hellmann's standard rain gauge. Water samples from slope runoff were collected randomly after heavy rainfalls and during snowmelt. The nitrogen concentration in groundwater was determined based on periodic water sampling from 4 springs, including 3 springs from the main aquifer feeding the Wieprz River and 1 from the Quaternary aquifer located above it. 49 water samples were collected from the Wieprz River under different hydrometeorological conditions.

In the samples collected, total nitrogen (TN) and dissolved inorganic nitrogen (DIN) were determined as the sum of nitrogen: nitrate nitrogen(III, V) and the ammonium nitrogen, using an ion chromatograph (MIC 3 manufactured by Metrohm) with conductometric detection. Anion forms were determined by using an anion separation column Metrosep A Supp 5-250 for analyses with chemical suppression, whereas cation

forms by means of a cation separation column Metrosep C 2-150 for analyses without chemical suppression. Dissolved inorganic nitrogen forms were determined in water samples filtered through a 0.45 μm filter. Total nitrogen was determined from samples collected from the Wieprz River: unfiltered, acidified with H_2SO_4 to pH ~2 and subjected to UV oxidation with an addition of H_2O_2. During analytical procedures, Merck standard solutions and CMR RAIN-97 certified material were used.

Results and discussion

The nitrogen content in the hydrologic cycle

In rainwater, the weighted average content of dissolved inorganic nitrogen in the years 2005–2006 was 0.90 mgN $\cdot$ dm^{-3} (Table 1). From that pool, the largest amount of nitrogen reached the substratum in the form of ammonium ion (on the average 0.47 mgN $\cdot$ dm^{-3}) and nitrate(V) ion (on the average 0.42 mgN $\cdot$ dm^{-3}), much less in the form of nitrate(III) ion (0.01 mgN $\cdot$ dm^{-3}).

Table 1

The nitrogen content in the hydrologic cycle of the Wieprz River catchment downstream to the Guciow profile (2005–2006)

Hydrologic cycle phase	Number of samples	N-NO$_3$	N-NO$_2$	N-NH$_4$	DIN*	TN**
		min-max/average [mgN $\cdot$ dm^{-3}]				
Precipitation	156	0.05–.36/ 0.42	< 0.01–0.10/ 0.01	0.03–0.18/ 0.47	0.10–5.1/ 0.90	DIN ≈ TN
Surface runoff	16	0.1–12.9/ 1.81	< 0.01–0.35/ 0.09	0.09–2.14/ 0.96	0.35–14.6/ 2.26	—
Groundwater	20	0.23–3.1/ 1.75	< 0.01–0.01/ < 0.01	<0.01–0.1/ 0.02	0.23–3.07/ 1.77	DIN ≈ TN
Wieprz River – Guciow	49	0.51–2.47/ 1.22	< 0.01–0.06/ 0.03	0.01–0.88/ 0.30	0.86–2.81/ 1.55	1.04–3.2/ 1.89

* DIN – dissolved inorganic nitrogen; ** TN – total nitrogen; — not investigated.

In surface runoff water, the average concentration of dissolved inorganic nitrogen (DIN) was at a level of 0.5–3 mgN $\cdot$ dm^{-3}. The largest amount of nitrogen runoff flew to the river usually in the nitrate(V) and ammonium forms, the least amount in the nitrate(III) form. Water runoff from arable land and built-up areas had high nitrogen concentrations, much lower from meadows.

In the groundwater feeding the river, nitrogen in the nitrate(V) form was predominant. The concentration of nitrates(V) was dependent on the degree of anthropogenic changes in the environment and circulation conditions at the underground stage of the water cycle. In a spring with a forest catchment (St. Roch's spring), the concentration of nitrates(V) was within a range of 0.23–0.31 mgN $\cdot$ dm^{-3}. In the catchments of springs with a large nitrogen contribution of cropland, the nitrate(V)

nitrogen content was as follows: Krasnobrod spring – 2.9–3.2 mgN · dm^{-3}, Hutki spring – 1.1–1.4 mgN · dm^{-3} and Belfont spring – 0.9–1.3 mgN · dm^{-3}. The content of ammonium and nitrate(III) ions in the waters from the studied springs did not generally exceed 0.02 mgN · dm^{-3} and 0.01 mgN · dm^{-3}, respectively.

In the waters of the Wieprz River, the content of total nitrogen(TN) in the years 2005–2006 was 1.89 mgN · dm^{-3}; dissolved inorganic nitrogen accounted for ~82 % of total nitrogen. In the winter period, dissolved inorganic forms accounted for over 85 % of total nitrogen, whereas during the growing period the share of dissolved inorganic forms decreased. The content of total nitrogen changed within quite a wide range from ~1 mgN · dm^{-3} to over 3 mgN · dm^{-3}.

The nitrogen balance in the upper Wieprz River catchment

The amount of nitrogen introduced into the upper Wieprz River catchment in the years 2005–2006 was 1572.7 Mg · year^{-1} (523.7 kg · ha^{-1} · year^{-1}); out of this pool, precipitation nitrogen was 12.1 % (Table 2). Nitrogen deposition on the catchment surface, with averaged precipitation of 703 mm from the years 2005–2006, was 6.33 kg · ha^{-1} · year^{-1}. This level was almost three times lower than the values recorded for the Lublin province [11]. It indicates a relatively low nitrogen concentration in the rainwater of the upper Wieprz River catchment.

The level of nitrogen introduced into the catchment in the form of mineral and organic fertilisers was 1382.7 Mg · year^{-1}; hence, it was much higher than that from precipitation. The consumption of mineral fertilisers on arable land was calculated based on data of the Central Statistics Office in Warsaw, and it was, on the average, 55.2 kg · ha^{-1} · year^{-1} for the Lublin province in the years 2005–2006. In the case of nitrogen introduced into the catchment in the form of mineral fertilisers, an assumption was made that only arable land was fertilised at an amount of 28 kg · ha^{-1} · year^{-1}, which corresponds to the averaged value for the Lublin province [11].

The level of nitrogen discharged from the upper Wieprz River catchment was 1167.3 Mg · year^{-1} (38.9 kg · ha^{-1} · year^{-1}), including 64.4 Mg · year^{-1} which was carried away through the river system. The river transport of nitrogen was at a level defined for the Wieprz River downstream to the Zwierzyniec profile (55.75 Mg · year^{-1}) for the years 1992–1997 [12] based on dissolved inorganic nitrogen forms. The main pool of nitrogen discharged via the river system in the years 2005–2006 originated from agriculturally used areas – 61.7 Mg · year^{-1} (3.08 kg · ha^{-1} · year^{-1}). From forest areas, only 2.8 Mg · year^{-1} (0.28 kg · ha^{-1} · year^{-1}) was discharged. The outflow of nitrogen originating from the groundwater inflow to the Wieprz River was 48.6 Mg · year^{-1} (1.62 kg · ha^{-1} · year^{-1}). Together with water surface runoff, 13.1 Mg · year^{-1} of nitrogen (0.65 kg · ha^{-1} · year^{-1}) was discharged through the Wieprz River. The results of the calculations show that, on the average, 405.5 Mg · year^{-1} of nitrogen (13.5 kg · ha^{-1} · year^{-1}) remains within the Wieprz River catchment, with a major amount of nitrogen left remaining in agriculturally used soils.

Table 2

The annual nitrogen balance in the hydrologic cycle of the Wieprz River catchment downstream to the Guciow profile*
(averaged values from the years 2005–2006)

Balance area	Introduced into the catchment through [ton · year⁻¹/kg · ha⁻¹· year⁻¹]		Discharged from the catchment through [Mg · year⁻¹/kg · ha⁻¹· year⁻¹]					Net balance of the catchment Σ introduced – Σ discharged [Mg · year⁻¹/ kg · ha⁻¹· year⁻¹]
	Precipitation	Mineral; organic fertilisers	River discharge				Agriculture	
			Total	Originated from groundwater inflow	Municipal sewage	Surface runoff (nitrogen of agricultural + atmospheric origin + other)		
Wieprz catchment	190.0/6.33	980.9; 401.8 (55.2/28.0)	64.4/2.14	48.6/1.62	2.7 —	13.1/0.65	1103/61.5	405.3/13.5
Forests	63.3/6.33	0	2.8/0.28	2.8/0.28	—	0.0	0	60.5/6.05
Arable land, built-up areas, other areas	126.7/6.33	980.9; 401.8 (55.2/28.0)	69.9/2.94	45.8/2.29	—	13.1/0.65	1103/61.5	344.8/17.2

* In the calculations, the following water balance values were adopted:
 – upper Wieprz River catchment: precipitation 703 mm, total discharge – 113.4 mm; groundwater inflow to the river – 91.5 mm; surface runoff inflow to the river – 21.9 mm;
 – forests: precipitation 703 mm, total discharge – 113.4 mm; groundwater inflow to the river – 113.4 mm; surface runoff inflow to the river – 0 mm.

Conclusions

The nitrogen balance made for the Wieprz River downstream to the Guciow profile shows that nearly 90 % of the pool of this element introduced into the catchment (1572.7 Mg · year^{-1}) was attributable to agriculture. Nitrogen reaching the substratum with precipitation made up the remaining part. A major amount of nitrogen discharged from the catchment (1167.4 Mg · year^{-1}) was also attributable to agriculture (approx 75 % of nitrogen introduced into the catchment), and it was associated with the discharge of nitrogen contained in plant crops.

Nitrogen discharged from the Wieprz River catchment through the river system accounted for approx 4.1 % of the pool of nitrogen introduced into the catchment area (from precipitation and agriculture). Nitrogen of agricultural origin made up the main pool of nitrogen discharged through the Wieprz River (53.3 Mg · year^{-1}), whereas nitrogen from municipal waste discharge accounted for approx 4 %. The share of precipitation nitrogen in the total nitrogen discharge via the Wieprz River was estimated at 11.4 %. At periods when the river was fed by surface runoff waters, the share of precipitation nitrogen in the river discharge increased up to ca 30 %.

The net balance of the Wieprz River catchment shows that approx. 25 % of nitrogen introduced into the catchment area remained in the soil and plants as well as it underwent denitrification processes.

References

[1] Berner E.K. and Berner R.: Global environmental: water, air and geochemical cycles. Prentice-Hall, Inc., New Jersey 1996, 376 pp.

[2] Żelazny M., Chełmicki W., Jaszczyńska B., Michno A., Pietrzak M., Raczak J. and Święchowicz J.: Dynamika związków biogennych w wodach opadowych, powierzchniowych podziemnych w zlewniach o różnym użytkowaniu na Pogórzu Wiśnickim. Inst. Geogr. i Gosp. Przestrz. UJ, Kraków 2005, 216 pp. (in Polish).

[3] Żurek A.: *The estimation of the level of nitrate leaching in to groundwater based on the example of small agricultural catchments at the foothills of the Carpathian Mountains*. Gaz Woda Technika Sanitar. 2006, (11) (in Polish).

[4] Sapek A., Sapek B. and Pietrzak S.: *The nitrogen cycle and balance in Polish agriculture.* Nawozy Nawoż. 2002, (1), 100–121.

[5] Igras J., Kopiński J. and Lipiński W.: *Nutrient balances in Polish agriculture.* Ann. Polish Chem. Soc. 2003, (2/II), 713–718.

[6] Dębicki R., Chodorowski J. and Gawrysiak L.: *Characteristics of the soil cover*, [in:] Natural conditions of the water cycle dynamics and fluvial transport rate in the upper Wieprz River catchment. Wyd. UMCS, Lublin 2004, 33–40 (in Polish).

[7] Maruszczak H. and Święca A.: *Geological and geomorphological characteristics*, [in:] Natural conditions of the water cycle dynamics and fluvial transport rate in the upper Wieprz River catchment. Wyd. UMCS, Lublin 2004, 23–32 (in Polish).

[8] Stępniewska S.: *Variability in the upper Wieprz River discharge*, [in:] The water cycle in the natural and transformed environment. Hydrographic research in environmental knowledge, vol. VIII, Wyd. UMCS, Lublin 2007, 513–520 (in Polish).

[9] Michalczyk Z.: *Characteristics of water relations*, [in:] Natural conditions of the water cycle dynamics and fluvial transport rate in the upper Wieprz River catchment. Wyd. UMCS, Lublin 2004, 50–64 (in Polish).

[10] Chmiel S. and Maciejewska E.: *Physicochemical features of rainwater at Guciów in the Roztocze region*, [in:] The water cycle in the natural and transformed environment. Hydrographic research in environmental knowledge, vol. VIII, Wyd. UMCS, Lublin 2007, 133–141 (in Polish).

[11] Kopiński J.: *The gross nitrogen balance on the surface of a field as an agro-environmental indicator of changes in the intensity of agricultural production in Poland.* IUNG-PIB, Puławy, Studia i raporty 2007, (4), 20–32 (in Polish).

[12] Świeca A., Krukowska R. and Tucki A.: *Spatial variations and variability in the concentration of occurrence of dissolved inorganic nitrogen forms in river waters of the Wieprz River basin.* Ann. UMCS, sec. B., 2002, **LVII**(8), 127–154 (in Polish).

UDZIAŁ AZOTU Z OPADÓW ATMOSFERYCZNYCH W ODPŁYWIE RZECZNYM GÓRNEGO WIEPRZA (ROZTOCZE, SE POLSKA)

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Abstrakt: Opierając się na materiałach hydrochemicznych, hydrometrycznych i meteorologicznych, sporządzono bilans azotu w zlewni górnego Wieprza obejmujący lata 2005–2006. Obliczenia wykazały, że azot wynoszony systemem rzecznym stanowił około 4,1 % puli azotu wprowadzanego do zlewni Wieprza (1572,7 Mg · rok^{-1}). W całkowitym odpływie azotu rzeką Wieprz (64,4 Mg · rok^{-1}) udział wyprowadzanego azotu pochodzącego z opadów atmosferycznych oszacowano na 13,1 % (8,4 Mg · rok^{-1}). Główną część azotu wyprowadzanego systemem rzecznym stanowił azot pochodzenia rolniczego (53,3 Mg · rok^{-1}).

Słowa kluczowe: obieg wody, azot, opady atmosferyczne, rolnictwo

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EFFECT OF THE CONCENTRATIONS AND QUALITY OF PROTEIN IN DIETS FOR GROWING-FINISHING PIGS ON NITROGEN EXCRETION TO THE ENVIRONMENT

WPŁYW POZIOMU I JAKOŚCI BIAŁKA W MIESZANKACH PASZOWYCH DLA TUCZNIKÓW NA WYDALANIE AZOTU DO ŚRODOWISKA

Abstract: The objective of this study was to determine the effect of the concentrations and quality of protein in diets for growing-finishing pigs on total protein digestibility, and on the levels of nitrogen retention, utilization and excretion to the environment. Digestibility and balance trials were conducted on 24 young hybrid (Polish Large White x Polish Landrace) x Duroc) boars, placed in individual metabolism cages equipped for quantitative collection of feces and urine. The boars were divided into three experimental groups, of 8 animals each, and were fed grower and finisher diets differing in the concentrations of total protein, lysine, methionine, threonine and tryptophan. Control diet 1 contained standard amounts of total protein and essential amino acids, diet 2 contained reduced amounts of total protein (by 15 % to the standard level) and essential amino acids, and diet 3 contained reduced amounts of total protein and standard (as in control diet 1) amounts of essential amino acids.

It was found that a decrease in the levels of total protein and essential amino acids (lysine, methionine, threonine and tryptophan) in grower diets negatively affected protein digestibility and nitrogen balance parameters. The analyzed experimental factor had a beneficial influence on urinary and fecal nitrogen excretion in pigs fed on finisher diets. The supplementation of diets with a decreased total protein content with essential amino acids had no statistically significant effect on nitrogen balance. It was estimated that a 15 % reduction to the standard level in total protein concentrations and a decrease in essential amino acid levels in grower and finisher diets reduced nitrogen excretion to the environment by 5.38 to 16.81 %.

Keywords: various concentrations of protein and amino acids, digestibility, nitrogen balance, nitrogen excretion, growing-finishing pigs

The conversion of plant products into foods of animal origin is accompanied by the emissions of unused metabolites to the environment. The growing demand for meat products leads to the intensification of animal production, and the consequent

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environmental pollution problems resulting primarily from increased nitrogen and phosphorus emissions. Animal excreta contain large amounts of pollutants which get into the air, soil and surface waters, thus contributing to the greenhouse effect, the formation of acid precipitation and to the depletion of the stratospheric ozone layer [1]. Biogenic nitrogen-containing compounds that come from animal excreta penetrate into the soil and inland waters, leading to gradual degradation of aquatic ecosystems.

The concentrations of total protein in feedstuffs and the quality of this nutrient in diets for pigs have a decisive effect on the amounts of nitrogen excreted in feces and urine. Müller [2] demonstrated that a decrease in the protein content of feed for pigs allows to reduce nitrogen excretion by up to 40 %. According to this author, environmental load from pig production can be effectively reduced by feeding high-quality protein sources and supplementing rations with synthetic amino acids, which are readily absorbed in the small intestine and used for protein accumulation in the body. Any excess protein supplied in feed, above the requirements of the animals, is metabolized to urea and excreted [3]. Urea nitrogen is broken down producing ammonia which is emitted into the atmosphere, posing a serious threat to soil and groundwater. According to Kirchgessner et al [4], the major environmental goal in pig production should be to reduce the amount of nitrogen in urine that is mixed with feces to form slurry.

The main criterion applied to determine the amount of protein in diets for pigs is the adequate provision of essential amino acids, with particular attention given to limiting amino acids, such as lysine, methionine, threonine and tryptophan. Other amino acids may be supplied in excess of the animals' needs. Lowering the protein content of feed and balancing the ration to meet the dietary requirements of pigs at particular stages of fattening enables to improve the utilization of this nutrient. However, complete diets have to be precisely balanced with respect to essential amino acids, by selecting appropriate feed components or supplementing low-protein diets with limiting amino acids.

The objective of this study was to determine the effect of the concentrations and quality of protein in diets for growing-finishing pigs on total protein digestibility, and on the levels of nitrogen retention, utilization and excretion to the environment.

Materials and methods

Total protein digestibility and nitrogen balance were determined twice during digestibility and balance trials conducted on 24 young hybrid (Polish Large White x Polish Landrace) x Duroc) boars with average body weight of approximately 30 kg at the beginning of experiment I, and approximately 85 kg at the beginning of experiment II. The animals were placed in individual metabolism cages equipped for quantitative collection of feces and urine. The boars were divided into three experimental groups, of 8 animals each, and were fed grower (experiment I) and finisher (experiment II) diets differing in the concentrations of total protein and amino acids (Table 1).

Table 1

Composition and nutritive value of protein in diets for growing-finishing pigs [%]

Specification	Diets for growing pigs			Diets for finishing pigs		
	1-k[1]	2	3	1-k[1]	2	3
	Standard[2]	Decreased about 15 % to the control group	Decreased about 15 % and supplemented in essential amino acids	Standard[2]	Decreased about 15 % to the control group	Decreased about 15 % and supplemented in essential amino acids
Concentration of protein and essential amino acids						
Crude protein	17.94	15.54	15.76	14.51	12.39	12.24
Lysine	0.95	0.84	0.95	0.75	0.65	0.75
Methionine + cystine	0.61	0.55	0.61	0.45	0.38	0.45
Threonine	0.61	0.55	0.61	0.45	0.38	0.45
Tryptophan	0.21	0.19	0.21	0.15	0.13	0.15
Components [%]						
Wheat	40	40	40	40	40	40
Barley	37.28	42.45	42.02	43.92	49.49	49.18
Soybean meal	15.00	9.00	9.00	6.00	8.00	8.00
Rapeseed meal "00"	5.00	5.00	5.00	8.00	8.00	8.00
Minerals[3]	1.80	1.80	1.80	1.35	1.35	1.35

Table 1 cont.

Specification	Diets for growing pigs			Diets for finishing pigs		
	1-k[1]	2	3	1-k[1]	2	3
Mineral – vitamin premix	0.70	0.70	0.70	0.50	0.50	0.50
L-lysine HCl (78 %)	0.22	0.25	0.41	0.23	0.23	0.23
Dl-methionine (99 %)	—	—	0.15	—	—	0.04
Threonine	—	—	0.09	—	—	0.08
Tryptophan	—	—	0.03	—	—	0.03
Rapeseed oil	—	0.80	0.80	—	0.40	0.40
Nutritive value						
Digestible protein [g/kg]	149.00	122.00	130.00	117.94	99.65	100.47
Metabolizable energy [MJ/kg]	12.80	12.80	12.80	12.80	12.80	12.80

[1] Control diet; [2] Value calculated based on Nutrition Requirement of Pigs (1993); [3] Limestone (0.8/0.7 %), dicalcium phosphate (0.7/0.4 %), salt (0.3/0.25 %).

The daily allowance of grower and finisher diets was 2.3 kg and 3.0 kg per pig, respectively. Feed was offered in wet form (feed to water ratio of 1:1), twice daily. The nutritional value of diets was consistent with the Pig Nutrient Requirements [5].

During the experimental period proper, the entire amounts of feces and urine were collected. 5 % samples of the total amount of feces excreted daily were collected for analysis and frozen, and their total nitrogen content was determined at the completion of the experimental period proper. Urine collected into containers was preserved with sulfuric acid, and 5 % samples were assayed for total nitrogen content [6].

The digestible protein content of grower and finisher diets was determined based on the digestibility coefficients calculated during digestibility trials. The levels of lysine, methionine, cystine, threonine and tryptophan in diets were calculated based on the concentrations of the above amino acids in feed raw materials used for diet formulation. Nitrogen losses to the environment were determined based on daily nitrogen balance and feed intake levels.

The results regarding protein digestibility and nitrogen balance were verified statistically using a one-factor analysis of variance (ANOVA) and Duncan's multiple range test [7].

Results and discussion

Protein digestibility, daily nitrogen balance and nitrogen utilization parameters are presented in Table 2.

Table 2

Digestibility of crude protein and nitrogen balance

Specification	Diets for growing pigs			Diets for finishing pigs		
	1-k[1]	2	3	1-k[1]	2	3
Digestibility coefficient [%]						
Crude protein	82.8[A]	78.6[B]	82.7[A]	81.27	80.43	82.09
Nitrogen balance [g day]						
N intake [g]	66.02[A]	57.18[B]	57.8[B]	69.65[A]	59.47[B]	58.75[C]
Fecal N excretion [g]	11.46	12.66	11.53	13.04[A]	11.64[b]	10.52[B]
Fecal N excretion / N intake [%]	17.36	22.14	19.94	18.72	19.57	17.91
N digested [g]	54.56[A]	44.52[B]	46.27[B]	56.61[A]	47.83[B]	48.23[B]
Urinary N excretion [g]	21.79[a]	18.8[b]	19.59[b]	29.37[A]	23.64[B]	24.78[B]
Urinary N excretion / N intake [%]	33.01	32.87	33.89	42.17	39.75	42.18
Retention [g]	32.77[A]	25.74[B]	26.68[B]	27.24[A]	24.19[B]	23.45[B]
Nitrogen utilization [%]						
Retention / intake	49.64	45.02	46.62	39.11	40.68	39.91
Retention / digested	60.06	57.78	57.66	48.19	50.57	48.62

[1] See Table 1.

The digestibility of total protein in experimental grower and finisher diets was found to vary depending on the experimental factor and diet type. A decrease in the content of protein and amino acids limiting the biological value of protein in grower diet 2 resulted in a significant decrease in the digestibility of this nutrient, from 82.8 % to 78.6 %. Compared with finisher diet 2, the analyzed experimental factor had a statistically non-significant effect. The supplementation of grower and finisher diets 3 with lysine, methionine, threonine and tryptophan significantly improved total protein digestibility, which increased from 78.6 % to 82.7 % in the grower diet, and from 80.43 % to 82.09 % in the finisher diet. Also in a study conducted by Więcek et al [8] on growing-finishing pigs, total protein digestibility was affected by the levels of protein and amino acids in mixed feed. The coefficient of protein digestibility was high, at 80 %.

Data concerning daily nitrogen balance (Table 2) show that nitrogen intake was substantially higher in control group animals fed grower and finisher diets with standard concentrations of protein and essential amino acids, in comparison with boars of experimental groups 2 and 3 (by 8.84 and 8.22 g and by 10.18 and 10.9 g/day, respectively). This resulted from a different total protein content of diets. An analysis of fecal nitrogen excretion revealed that it was higher in pigs fed grower diet 2, with decreased levels of protein and essential amino acids, and significantly lower in pigs receiving finisher diet 2. The addition of lysine, methionine, threonine and tryptophan to diets with a lower total protein content caused a further decrease in fecal nitrogen excretion. The experimental factor contributed also to a considerable reduction in urinary nitrogen excretion. This could indicate better balancing of the amino acid composition of protein in experimental diets than in control diets.

Shriver et al [9] reported that the supplementation of a low-protein diet with lysine, methionine, threonine, tryptophan, isoleucine and valine reduced fecal and urinary nitrogen excretion. Rohr [10] added synthetic amino acids (lysine, methionine and threonine) to diets for growing-finishing pigs, in which protein content was decreased from 17.5 to 14 %, and achieved an approximately 30 % reduction in nitrogen excretion.

The levels of nitrogen retention varied depending on the concentrations and quality of protein. Regardless of the fattening stage, the decrease in the protein content of diets lowered nitrogen retention in pigs of experimental groups 2 and 3. As regards the grower diet, the lowest nitrogen retention was noted in group 2 animals (25.74 g), while in the case of the finisher diet (with a decreased protein content, supplemented with essential amino acids) – in group 3 animals (23.45 g). The highest nitrogen retention was observed in pigs fed control diet 1 (32.77 and 27.24 g, respectively).

The best nitrogen utilization, in relation to nitrogen intake and digestion, was noted in pigs fed a grower diet with standard concentrations of total protein and essential amino acids (control diet 1). A decrease in the content of protein and amino acids in diets negatively affected the analyzed parameters. Diet supplementation with essential amino acids in group 3 slightly improved nitrogen utilization in relation to nitrogen intake. Group 2 animals fed a finisher diet with a decreased content of protein and amino acids were characterized by the best nitrogen utilization relative to nitrogen

intake and digestion. The lowest values of nitrogen utilization were observed in the control group.

Table 3 shows the amount of nitrogen excreted to the environment depending on the concentrations of protein and amino acids in diets.

Table 3

Nitrogen excretion levels as dependent on the concentrations of protein and amino acids in diets for growing-finishing pigs

Specification	Diets for growing pigs			Diets for finishing pigs		
	1-k[1]	2	3	1-k[1]	2	3
N intake [g]	924.28	800.52	809.20	975.10	832.58	822.50
Fecal N excretion [g]	160.44	177.24	161.26	182.56	162.96	147.28
Urinary N excretion [g]	305.06	263.20	274.26	411.18	330.96	346.92
Total N excretion [g]	465.5	440.44	435.68	593.74	493.92	494.20
Nitrogen excretion levels as dependent on the concentrations of protein and amino acids						
[g]	0	–25.06	–29.82	0	–99.82	–99.54
[%]	100	94.62	93.59	100	83.19	83.23
[g]		0.0	–4.76		–0.28	0
[%]		100	98.99		99.94	100

[1] See Table 1; [2] Analysis performed during digestibility and balance trials.

It was estimated that at the first stage of fattening, a boar fed a grower diet with reduced concentrations of protein and essential amino acids excreted by 25.06 g (5.38 %) nitrogen less than a boar fed a control diet. The addition of essential amino acids to a diet with a reduced protein content caused a further reduction in nitrogen excretion, to a level of 6.41 % in comparison with control feed, and by 1.01 % compared with diet 2. Among pigs fed finisher diets, the lowest amounts of nitrogen were excreted to the environment in group 2, where nitrogen excretion was by 99.82 g (16.81 %) lower than in the control group. The supplementation of diet 2 with essential amino acids had no beneficial effect on fecal and urinary nitrogen excretion.

The findings of Carter et al [11] and Sutton et al [12] show that feeding low-protein diets supplemented with lysine, methionine, threonine and tryptophan to pigs allows to reduce nitrogen excretion by approximately 28–35 %, in comparison with high--protein diets.

Conclusions

1. A decrease in the levels of total protein and essential amino acids (lysine, methionine, threonine and tryptophan) in grower diets negatively affected protein digestibility and nitrogen balance parameters.

2. A decrease in total protein content and dietary supplementation of essential amino acids had a beneficial influence on urinary and fecal nitrogen excretion in pigs fed finisher diets.

3. The supplementation of diets with a decreased total protein content with essential amino acids had no statistically significant effect on nitrogen balance.

4. It was estimated that a 15 % reduction to the standard level in total protein concentrations and a decrease in essential amino acid levels in grower and finisher diets reduced nitrogen excretion to the environment by 5.38 to 16.81 %.

References

[1] Wiliams P.E.V.: *Animal production and European pollution problems*, Anim. Feed Sci. and Techn. 1995, **53**, 135–144.

[2] Müller A.: *Zrównoważyć zawartość aminokwasów w paszy*, Top Agrar 1999, **1**, 23–24.

[3] Jamroz D.: *Zmniejszenie obciążeń środowiska poprzez modyfikację żywienia zwierząt*, Konf. Nauk.--Techn., CLPP "Pasze przemysłowe a ochrona środowiska", Puławy 19–20.05.1997, 19–32.

[4] Kirchgessner M., Windisch W. and Roth F.X.: Możliwość żywienia zwierząt w zmniejszaniu obciążenia środowiska przez rolnictwo, Akad. Roln, Wrocław 1994.

[5] Normy Żywienia Świń., Wartość pokarmowa pasz, Omnitech Press, Warszawa 1993.

[6] AOAC, Official Methods of Analysis, 16th ed. Assoc. Offic. Anal. Chem. 1998, Arlington, VA.

[7] Stanisz A.: Przystępny kurs statystyki z wykorzystaniem programu STATISTICA PL na przykładach z medycyny, Wyd. Statsoft Polska, Kraków 2000, 1–401.

[8] Więcek J., Skomiał J., Rekiel A. and Śliwiński M.: *Wpływ poziomu białka i aminokwasów w mieszankach dla tuczników na strawność składników pokarmowych*. LXX Zjazd Polskiego Towarzystwa Zootechnicznego we Wrocławiu. Komunikaty Naukowe PTZ, Warszawa 2005, 98.

[9] Shriver J.A., Carter S.D., Sutton A.I., Richert B.T., Senne B.W. and Pettey L.A.: *Effects of adding fiber sources to reduced crude protein, amino acids suplemented diets on nitrogen excretion, growth performance nd carcass traits of finishing pigs*, J. Anim. Sci. 2003, **81**, 492–502.

[10] Rohr K.: *Verringerung der Stickstoffausscheidung bei Rind, Schwein und Geflugel*, Landbauforschung, Volkenrode, Sonderheft 1992, **132**, 39–53.

[11] Carter S.D., Cromwell G.L., Lindemann M.D., Turner W. and Bridges T.C.: *Reducing N and P excretion by dietary manipulation in growing and finishing pigs*, J. Anim. Sci. 1996, **74 (Suppl. 1)**, 59. (Abstr.).

[12] Sutton A.L., Kephardt K.B., Patterson J.A., Mumma R., Kelly D.T., Bogus E., Jones D.D. and Heber A.: *Manipulating swine diets to reduce ammonia and odor emisions*, Proc. 1st Int.Conf. Air Pollution from Agric. Operations, Kansan City, MO 1996, 445–452.

WPŁYW POZIOMU I JAKOŚCI BIAŁKA W MIESZANKACH PASZOWYCH DLA TUCZNIKÓW NA WYDALANIE AZOTU DO ŚRODOWISKA

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Abstrakt: Celem pracy było określenie wpływu poziomu i jakości białka w mieszankach paszowych dla tuczników na strawność białka ogólnego, retencję azotu i jego wykorzystanie oraz na ilość wydalanego azotu do środowiska. Materiał doświadczalny w badaniach strawnościowo-bilansowych stanowiły 24 wieprzki, mieszańce ras (wbp x pbz) x Duroc. Tuczniki umieszczono w indywidualnych klatkach metabolicznych, przystosowanych do ilościowego zbierania kału i moczu. Zostały one podzielone na 3 grupy doświadczalne po 8 osobników w każdej i żywione mieszankami Grower/Finiszer o różnej koncentracji białka ogólnego, lizyny, metioniny, treoniny i tryptofanu. Mieszanka 1-K zawierała standardową ilość białka ogólnego i aminokwasów egzogennych; mieszanka 2 miała obniżony o 15 % w stosunku do standardu poziom białka ogólnego i aminokwasów egzogennych; w mieszance 3 zmniejszona ilość białka ogólnego została wzbogacona w aminokwasy egzogenne do poziomu jak w mieszance 1-K.

Stwierdzono, że obniżenie poziomu białka ogólnego i aminokwasów egzogennych (lizyny, metioniny, treoniny i tryptofanu) w mieszance paszowej Grower dla tuczników wpłynęło ujemnie na strawność białka i parametry bilansu azotu. Odnotowano korzystny wpływ analizowanego czynnika doświadczalnego na wydalanie azotu w kale i moczu u tuczników otrzymujących paszę Finiszer. Wzbogacenie ocenianych mieszanek paszowych o obniżonym poziomie białka ogólnego w aminokwasy egzogenne nie miało statystycznie istotnego wpływu na gospodarkę azotową w organizmie świń. Oszacowano, że redukcja poziomu białka ogólnego i aminokwasów egzogennych o 15 % w stosunku do ilości standardowej w mieszankach paszowych Grower/Finiszer zmniejsza wydalanie azotu do środowiska od 5,38 do 16,81 %.

Słowa kluczowe: różne poziomy białka i aminokwasów, strawność, bilans azotu, wydalanie azotu, tuczniki

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CONTENT OF NITRATES(V) IN POTATO TUBERS IN CONDITIONS OF APPLICATION OF NEW GENERATION INSECTICIDES

ZAWARTOŚĆ AZOTANÓW(V) W BULWACH ZIEMNIAKA W WARUNKACH STOSOWANIA INSEKTYCYDÓW NOWEJ GENERACJI

Abstract: Studies were carried out on the basis of a field experiment set upon the soil of the rye very good complex. The experiment was designed as randomized sub-blocks with three replications. Experimental factors included three cultivars of edible potato – Wiking, Mors, Zagiel, and six Colorado potato beetle control methods using the following insecticides: Actara 25 WG at the rate of 80 g/ha, Regent 200 SC at the rate of 0.1 dm^3/ha, Calypso 480 SC at three rates: 0.05, 0.075 and 0.1 dm^3/ha, and a control object without chemical protection. Nitrates(V) content in potato tubers was determined with ion-selective nitrate electrode and silver-sliver chloride reference electrode. The content nitrates(V) depended on the cultivars and weather conditions throughout the growing season. Tubers of Mors cultivar had the highest nitrates(V) content – on average 168.2 mg/kg.

Keywords: potato, nitrates(V), insecticides, Colorado potato beetle

Among other foodstuff potato play an important role as staple food in human nutrition in many countries, also in Poland [1–4]. The potato quality depends on chemical composition, which modifies its nutritional value. Potato tubers contain not only nutritional compounds but also substances adversely affecting our health [5]. From the point of view of a consumer's health, it is very important, that the tubers of potato include the smallest possible content of nitrates(V) [6–9]. These compounds, under the influence of the stomach's bacterial flora, may undergo reduction to nitrates(III) (nitrites), and these in turn are the precursors of nitrosamine, that may have carcinogenic and mutagenesis action [10–12]. Accumulation of nitrates(V) in potato tubers depending on many factors – cultivar properties [10, 12, 13], tillage, fertilization and protection against agrophages [7, 9, 14, 15] and environmental conditions [8, 16].

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The studies aimed at determining an impact of the newest generation insecticides (Actara 80 WG, Regent 200 SC, Calypso 480 SC) on nitrates(V) content in the tubers of three potato cultivars.

Material and methods

Studies were carried out on potato tubers obtained from a field experiment conducted in the years 2004–2006 at the Zawady Experimental Farm. The soil originading from strong clay sands and belongs to the rye very good complex. Selected soil chemical properties prior to the experiment are shown in Table 1. The experiment was a randomized sub-block design including two factors: factors I – three edible potato cultivars: Wiking, Mors, Zagiel and factor II – six methods of Colorado potato beetle control including the newest generation insecticides: 1. control object with no chemical protection, 2. Actara 80 WG (thiametoxam) at the rate 80 g/ha, 3. Regent 200 SC (fipronil) 0.1 dm^3/ha, 4. Calypso 480 SC (thiacloprid) 0.05 dm^3 /ha, 5. Calypso 480 SC (thiacloprid) 0.075 dm^3/ha, 6. Calypso 480 SC (thiacloprid) 0.1 dm^3/ha. At the start of the experiment the Calypso 480 SC rate was not provided, thus the amount applied was 0.05–0.1 dm^3/ha. At present the recommended rate is 0.075–0.1 dm^3/ha. Insecticides were applied only once during occurrence of Colorado potato beetle larvae.

Table 1

Chemical properties of the soil

Year	pH 1 mol KCl^{-3}	Macroelements content [mg/kg^{-1}]				Hh	S	T	V [%]
		N total	P	K	Mg	[mm(+)kg^{-1}]			
2004	5.35	0.91	42.8	87.3	159.0	7.60	81.30	88.90	91.45
2005	5.72	0.72	88.0	85.5	89.1	8.10	82.00	90.10	91.01
2006	5.06	0.68	50.4	179.3	99.6	6.40	58.80	65.20	90.18

Hh – hydrolitic acidity; S – total base exchangeable cations; T – sorptive complex exchange capacity; V – saturation with base cations.

Potato was cultivated following winter wheat. Each year the same organic and mineral fertilization was applied. The amount of farmyard manure was 25.0 Mg/ha, and the respective rates of N, P and K were as follows: N – 100.0; P – 44.0 (100 P$_2$O · 0.44) and K – 124.5 kg/ha (150 K$_2$O · 83). The area of one plot was 15 m^2, and the number of plants per one plot was 60. Potato tubers were planted manual in the third decade of April at the spacing of 67.5 × 37 cm. Potato were harvested in technological maturity phase in the first and second decade of September. Chemical analyses were performed using fresh material in three replications. Nitrates(V) content was determined with ion-selective nitrate electrode and silver-silver chloride reference electrode [17]. Results of the study were statistically analysed by means of variance analysis and means were compared by Tukey test at the significance level of p = 0.05. Climatic conditions varied over the growing periods of potato cultivation (Table 2).

Table 2

Characteristics of weather conditions in the period of potato vegetation

Year	Months						Sum IV–IX
	IV	V	VI	VII	VIII	IX	
Rainfall [mm]							
2004	35.9	97.0	52.8	49.0	66.7	19.5	320.9
2005	12.3	64.7	44.1	86.5	45.4	15.8	268.8
2006	29.8	39.6	24.0	16.2	228.1	20.9	358.6
Multiyear average 1981–1995	52.3	50.0	68.2	45.7	66.8	60.7	343.7
Temperature [$^{\circ}$C]							
2004	8.0	11.7	15.5	17.5	18.9	13.0	14.1
2005	8.7	13.0	15.9	20.2	17.5	15.0	15.0
2006	8.4	13.6	17.2	22.3	18.0	15.4	15.8
Multiyear average 1981–1995	7.7	10.0	16.1	19.3	18.0	13.0	14.0

Results and discussion

The average nitrates(V) content in potato tubers fresh matter amounted to 165.3 mg/kg (Table 3) and was similar to the values reported by other authors [4, 7, 15, 16].

Table 3

Content of nitrates(V) in potato tubers [mg/kg fresh matter]

Objects	Cultivars			Years			Average
	Wiking	Mors	Zagiel	2004	2005	2006	
1. Control object	163.1	166.6	162.7	158.7	164.3	169.4	164.1
2. Actara 25 WG 0.08 kg/ha	165.6	168.3	163.1	159.8	164.8	172.5	165.7
3. Regent 200 SC 0.1 dm^3/ha	164.6	168.1	163.2	160.1	164.9	170.8	165.3
4. Calypso 480 SC 0.5 dm^3/ha	163.8	168.5	162.9	159.9	165.6	169.7	165.1
5. Calypso 480 SC 0.75 dm^3/ha	164.0	169.2	163.8	160.4	165.3	171.3	165.7
6. Calypso 480 SC 0.1 dm^3/ha	164.6	168.6	165.3	161.2	165.4	171.8	166.2
Average	164.3	168.2	163.5	160.0	165.1	170.9	165.3
LSD$_{0.05}$ objects							n.s.
cultivars							1.5
years							1.5
interaction: objects × cultivars							n.s.
objects × years							n.s.

n.s. – no significant difference.

The insecticides applied to control the Colorado potato beetle not caused changes significant in nitrates(V) content in the potato tubers. In the available literature lacks information on an impact of insecticides on accumulation of nitrates(V) in potatoes. Hamouz et al [7] claimed that the conventional way of cultivation increased nitrates content in tubers comparing with the tubers cultivated ecologically. In the studies by Sawicka and Kus [16] concentration the element did not depend on the production system (integrated and ecological). Zarzecka and Gugala [15] did not show the influence of herbicides on nitrates(V) content in tubers. The cultivars studied contained different nitrates(V) amounts, the largest amount accumulated by Mors – on average 168.2 mg/kg, and the lowest amount accumulated by Zagiel – on average 163.5 mg/kg. The differences between Wiking and Zagiel were not statistically confirmed. Many authors found that potato tuber chemical composition was in the first place determined by the cultivar [4, 12, 16].

Table 4

Content of nitrates(V) in potato tubers depending on the cultivars [mg/kg fresh matter]

Years	Cultivars			Mean
	Wiking	Mors	Zagiel	
2004	159.1	166.3	154.7	160.0
2005	165.3	165.9	163.9	165.1
2006	168.4	172.5	171.9	170.9
Average	164.3	168.2	163.5	165.3
$LSD_{0.05}$ years				1.5
cultivars				1.5
interaction: cultivars × years				2.7

Potato tubers harvested in individual years differed in respect of nitrates(V) content (Table 3, 4). Weather condition in 2006 favoured the element accumulation because rainfalls were heavy and unequally distributed. The lowest content nitrates(V) was in 2004 when there temperature and rainfall record revealed even distribution of both characteristics. An impact of weather conditions on this characteristic has also been confirmed in the works by Hluska et al [10], Zarzecka and Gugala [15], and Zgorska and Grudzinska [12].

Conclusion

1. The content of the nitrates(V) determined in potato tubers, depended significantly on the cultivars and weather conditions over the years of study.

2. The insecticides applied control the Colorado potato beetle not caused significant changes in nitrates(V) content in the potato.

References

[1] Leszczyński W.: Żywność, Supl. 2000, **4**, 5–27.
[2] McLaughlin M.J., Palmer L.T., Tiller K.G. and Beech T.A.: J. Environ. Qual. 1994, **23**, 1013–1018.

[3] Prośba-Białczyk U.: Sci. Agricult. Bohem. 2004, **35**, 154–157.

[4] Rogozińska I., Pawelzik E., Pobereżny J. and Delgado E.: Potato Res. 2005, **48**, 167– 180.

[5] Lisińska G.: Zesz. Probl. Post. Nauk Roln. 2006, **511**, 81–94.

[6] Cieślik E.: Przem. Spożywczy 1992, **46**(92), 266–267.

[7] Hamouz K., Lachman J., Dvořák P. and Pivec V.: Plant Soil Environ. 2005, **51**(9), 397–402.

[8] Pobereżny J.: Polish J. Natur. Sci. 2008, **23**(2), 336–346.

[9] Rogozińska I., Wojdyła T. and Pobereżny J.: Polish J. Environ. Stud. 2000, **10**, I Eco-med. Supl., 38–41.

[10] Hlušek j., Zrůst J. and Jůzl M.: Rostl. Vyroba 2000, **46**(1), 17–21.

[11] Rembiałkowska E.: Jakość żywności a rolnictwo ekologiczne. Warsztaty zorganizowane w ramach projektu "Accompying Measure" do projektu "Flair-Flow Europe IV". Kraków 2002, 13–28.

[12] Zgórska K. and Grudzińska M.: Zesz. Probl. Post. Nauk Roln. 2004, **500**, 475–481.

[13] Kołodziejczyk M., Szmigiel A. and Kiełbasa S.: Fragm. Agron. 2007, **2**(94), 142–150.

[14] Rębarz K. and Borówczak F.: Zesz. Probl. Post. Nauk Roln. 2006, **511**, 287–299.

[15] Zarzecka K. and Gugała M.: Zesz. Probl. Post. Nauk Roln. 2006, **513,** 575–582.

[16] Sawicka B. and Kuś J.: Zesz. Probl. Post. Nauk Roln. 2002, **489**, 273–282.

[17] Kolbe H. and Müller K.: Potato Res. 1987, **29**, 333–334.

ZAWARTOŚĆ AZOTANÓW (V) W BULWACH ZIEMNIAKA W WARUNKACH STOSOWANIA INSEKTYCYDÓW NOWEJ GENERACJI

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Abstrakt: Badania przeprowadzono na podstawie doświadczenia polowego założonego na glebie kompleksu żytniego bardzo dobrego. Doświadczenie założono metodą losowanych podbloków w trzech powtórzeniach. Czynnikami eksperymentu były trzy odmiany ziemniaka jadalnego (Wiking, Mors, Żagiel), sześć sposobów zwalczania stonki ziemniaczanej z udziałem insektycydów (Actara 25 WG w dawce 80 g/ha, Regent 200 SC w dawce 0,1 dm³/ha, Calypso 480 SC w dawkach 0,05; 0,075 i 0,1dm³/ha) i obiekt kontrolny bez ochrony chemicznej. Zawartość azotanów(V) w bulwach ziemniaka oznaczono za pomocą jonoselektywnej elektrody azotanowej oraz chlorosrebrowej elektrody odniesienia. Zawartość azotanów(V) zależała od uprawianych odmian i warunków pogodowych w okresie wegetacji. Bulwy odmiany Mors cechowały się największą zawartością azotanów(V) – średnio 168,2 mg/kg.

Słowa kluczowe: ziemniak, azotany(V), insektycydy, stonka ziemniaczana

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NITROGEN CONTENT AND AMINO-ACID PROTEIN COMPOSITION OF GRAIN OF RAPE FOLIAR FERTILIZED WITH UREA AND MICROELEMENTS

ZAWARTOŚĆ AZOTU I SKŁAD AMINOKWASOWY BIAŁKA NASION RZEPAKU JAREGO DOKARMIANEGO DOLISTNIE MOCZNIKIEM I MIKROELEMENTAMI

Abstract: The field experiment was carried out over 2003–2005 on the lessive soil (Haplic Luvisols), defective wheat complex, with a randomized block method in four random replications. The soil was characterised with an acid reaction (pH_{KCl} – 5.3) and a natural content of trace elements (characteristic for the geochemical background). Licosmos "00" spring variety of rape was used as a test crop. The aim of this study was to determine the effect of feeding urea and foliar nickel chelate EDTA-Ni(II) and Plonvit R on the content of total nitrogen and amino acid composition of spring rape seeds. Nickel chelate influenced an increase in the amount of amino acids in the seeds, but reduced the amount of protein.

Keywords: nitrogen, amino acids, rape, foliar application, urea, microelements

In the intensive agricultural production, foliar fertilization is one of the essential technology of plants cultivation [1–3]. This form of fertilization concerns mainly the microelements (Zn, Cu, Mn, Fe, B, Mo, and relatively recently nickel – Ni), and sometimes also macroelements, especially nitrogen and magnesium. Oilseed rape (*Brassica napus oleifera*) is an important crop for oil production and feed because of its high fat content (40–50 %) and protein (20–30 %) content in seed [4]. The nutritional value of each protein is determined by the amino acid composition, in particular by the number of necessary amino acids [5]. A shortage of even one essential amino acid in the diet, immediately affects the body as a negative balance of nitric eg total excreted nitrogen exceeds the amount of nitrogen intaken. This indicates that the tissue protein is degraded and is used to provide the missing amino acid for these proteins on a "high-priority" that must be continuously synthesized [6]. The oil seed-meal, because of its high protein content and its well-balanced composition of amino acids, may be

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used as a substitute for soybean pellets after extraction for farm animals, and contains more sulphur amino acids (methionine and cystine), but slightly less lysine [7, 8]. Lysine in rapeseed pellets have to be especially protected with the highest seed processing technology [9]. In 1991, nickel next to Fe, Mn, Cl, B, Zn, Cu, Co and Mo was included into microelements [10]. Research shows that plants fed with urea with no nickel access, can accumulate large amounts of urea due to reduced urease activity [11]. The addition of nickel increases the activity of urease located in leaves and prevents the accumulation of urea [12, 13].

The aim of this study was to determine the influence of foliar feeding with urea and nickel chelate EDTA-Ni(II) and Plonvit R for the total nitrogen content and endogenous amino acid composition of spring rape seeds.

Materials and methods

The field experiment was carried out over 2003–2005 on the lessive soil (Haplic Luvisols), defective wheat complex, with a randomized block method in four random replications. Size of plots: 6×5 m = 30 m^2 gross, including 5.2×3 m = 15.6 m^2 to harvest.

The soil was characterised with an acid reaction (pH$_{KCl}$ – 5.3) and a natural content of trace elements (characteristic for the geochemical background). Licosmos "00" spring variety of rape was used as a test crop. The following fertilization per one hectare was used: soil application per 1 ha: pre-sowing, 75 kg N in ammonium nitrate (solid form), 40 kg P in the form of triple superphosphate and 140 kg K in the form of potassium salt; 60 kg N in the form of $CO(NH_2)_2$ (3×20 kg) according to the experiment scheme (foliar application). Times of foliar feeding: (stage of development of the crop according to BBA): I. Steam elongation (KD 33); II. inflorescence emergence (KD 55); III. after flowering (KD 71).

Experimental objects:

1. urea (3×20 kg N $\cdot$ ha^{-1}) soil application in solid form + MgSO$_4$ $\cdot$ H$_2$O + water (spray 3×);

2. urea (3×20 kg N $\cdot$ ha^{-1}) in a solution + MgSO$_4$ $\cdot$ H$_2$O;

3. urea (3×20 kg N $\cdot$ ha^{-1}) in a solution + chelate nickel + MgSO$_4$ $\cdot$ H$_2$O;

4. urea (3×19.9 kg N $\cdot$ ha^{-1}) in a solution + Plonvit R + MgSO$_4$ $\cdot$ H$_2$O;

5. urea (3×19.9 kg N $\cdot$ ha^{-1}) in a solution + Plonvit R + chelate nickel + + MgSO$_4$ $\cdot$ H$_2$O.

The concentration of urea solution used in all phases of plant development was 12 %. Magnesium sulphate was used only in the spring period (3 % solution of magnesium sulphate monohydrate). Plonvit R was used in quantities of $2 \times$ dm^3 ha^{-1}, and the Ni chelate $2 \times$ dm^3 ha^{-1} (5 g Ni $\times$ 1 dm^{-3}). The content of elements [g $\cdot$ kg^{-1}] in Plonvit R was as follows:

N	Mg	S	Mn	Fe	Zn	Cu	B	Ti	Mo	Na
100	18	16	5	5	6	1	5	0.3	0.05	10

Plant protection products Butisan Star 415 SC (metazachlor 333 g/dm^3, chinomerak 83 g/dm^3), Decis 2,5 EC (deltametryna 2.5 %), Owadofos 540 EC (fenitrotion 540 g/dm^3), Karate Zeon 050 CS (lambda-cyhalotryna 50 g/dm^3) were used.

The weather conditions in the years of experiments were variable. The rainfalls were quite diverse, and the air temperature in both years was similar to average from perennial. The spring (except from May) and the first half of the summer year 2004 was characterized by higher precipitation than perennial average. The emergence of rape was good, plant development in this conditions was proper. High rainfalls which occurred in July made the vegetative period longer and has the beneficial effect on rape. In April of 2005 high precipitation deficiencies took place, and the second decade of this month was cold with ground freeze up to –8 $^{\circ}$C occurred. The emergence of rape was irregular. Higher rainfalls took place in May but due to periodical cold the vegetation was not getting better as expected. However, June was quite hot with heavy rains which made the harvest delayed.

The rape seed was harvested 26.08.2004 and 20.08.2005. In the rape seeds were determined the total protein content with Kjel-Tec Auto Plus 1030 apparatus, using its 6.25 version. Moreover, the composition and content of amino acids was measured using an ion exchange chromatography Microtechna 339 M apparatus in the Central Apparatus Laboratory of Life Sciences University in Lublin. The results were statistically analysed with variance analysis method with a level of significance equalling 0.05. To compare the statistical significant differences the Tukey test was used.

Results and discussion

Protein content in the seeds of rape is more diverse than the content of fat. The amount of this component is mainly dependent on the level of fertilization as well as on variety and weather. The higher accumulation of protein in seeds results from dry years [14, 15]. Protein from immature seeds will be less rich in exogenous amino acids (lysine), resulting in lower quality of pellets and pressed residues [16].

The average protein content of spring rape Licosmos variety was similar in all objects apart of the third (Table 1), where nickel chelate was used in combination with urea affect of the protein content reduction in seeds by 19.65 g $\cdot$ kg^{-1} in relation to object with foliar used urea. Taking into account the fact that the object with Ni chelate, but additionally fed with Plonvit R, there was no decrease, it can be supposed that the plant took microelements (including nickel) in a more balanced way, and their interaction influenced the larger protein content compared with the object where Plonvit R was applied with urea by foliar application.

In examining the effects of different microelement fertilizers supplied by foliar application to the plant, Palka et al [17] found that there was no significant variation in protein content under the influence of foliar feeding. A factor that was influencing the protein content was a variety, including the Licosmos variety, which was characterised with the lowest at 22.41 %. The same result was reached in own studies (the average of the experiment from two years).

Table 1

The share of amino acids protein composition of grain of rape seed [%]

Amino acids		Experimental objects				
		1	2	3	4	5
		Amino acids percentage in protein				
		Endogenous				
Asparagine	*Asp*	6.43	6.80	6.67	7.04	7.71
Tyrosine	*Tyr*	3.81	4.19	4.52	4.38	4.19
Arginine	*Arg*	6.95	6.42	6.95	6.71	6.28
Serine	*Ser*	4.15	4.24	4.05	4.25	4.18
Glutamine	*Glu*	15.21	15.36	14.96	15.17	15.95
Proline	*Pro*	3.13	3.02	3.19	2.95	3.13
Glycine	*Gly*	4.66	4.86	4.70	3.72	4.62
Alanine	*Ala*	4.08	4.11	3.86	3.88	3.91
		Exogeneous				
Threonine	*Thr*	4.88	5.12	5.17	5.47	5.35
Valine	*Val*	4.72	4.96	5.02	4.95	5.08
Isoleucine	*Ile*	3.78	3.95	3.82	3.59	3.84
Leucine	*Leu*	8.49	8.67	8.85	8.47	8.29
Phenylalanine	*Phe*	5.44	5.15	5.90	5.33	5.47
Histidine	*His*	3.38	3.58	3.79	3.40	3.36
Lysine	*Lys*	5.49	5.50	5.62	5.27	5.60
		Sulphur (exogeneous)				
Cysteine sulphonic acid $CySO_3H$		4.78	4.42	4.18	3.80	4.08
Methionine sulphone $MeSO_3$		4.20	4.15	4.46	4.20	4.37
The sum of amino acids		93.48	94.43	95.64	93.50	95.44
Total protein [g · kg^{-1} d.m.]		227.95	228.95	209.30	226.40	227.70
$LSD_{(0.05)}$ between objects – n. s.						

An analysis of the average over two years (Fig. 1) shows that in sites where Ni was used, seeds accumulated most amino acids in the protein. Identical results were obtained by Gerendás and Sattelmacher [18], examining the impact of Ni on the development and transformation of nitrogen in spring rape, where urea was an N source. This reaction explained by the authors as a high urease activity resulting from nickel additive. Urease catalyses the hydrolysis of urea to ammonia and carbon dioxide, so that nitrogen becomes available to plants [19].

The fertilizers used did not have a significant impact on the content of total nitrogen and amino acid composition of spring rape seeds. An addition of nickel chelate to urea had the effect of increasing the total amount of amino acids, mainly by increasing the content of essential amino acids like phenylalanine and histidine (Table 1); however, in this object the lowest (209.3 g · kg^{-1} d.m.) total protein content was obtained.
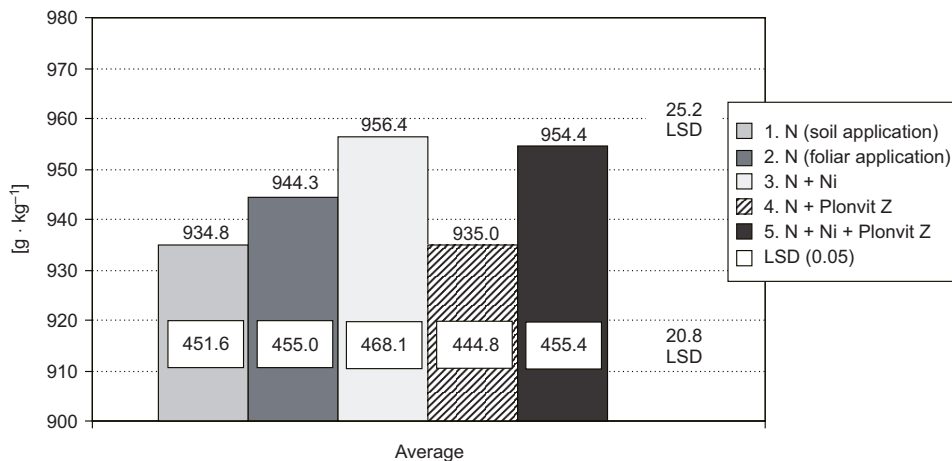
Fig. 1. The total sums of amino acids in protein of rape seed (in white squares are exogenous sums)

Application of Plonvit R with urea had positive effect on threonine content but negative on glycine, lysine and CySO$_3$H content. The content of sum of exogenous amino acids in protein was significantly different only between objects with Ni chelate and Plonvit R (Fig. 1). Comparing with other objects soil application of urea was characterized by lowest sum of amino acids mainly due to low asparagine, tyrosine and valine contents.

Conclusions

1. The foliar application of Ni chelate with urea affected an increase in the amount of amino acids in seeds, mainly by increasing the participation of essential amino acid, while reducing the amount of protein.

2. Exogenous amino acids sum was significantly higher where Ni chelate was used in comparison with found in object with Plonvit R.

3. Microelement fertilizer Plonvit R applied together with urea and Ni chelate prevented the reduction of protein content caused by Ni chelate impact.

References

[1] Czuba R.: Zesz. Probl. Post. Nauk Roln. 1996, **434**, 55–64.

[2] Warechowska M., Domska D. and Bobrzecka D.: Zesz. Probl. Post. Nauk Roln. 2002, **484**, 725–732.

[3] Szewczuk C. and Michałojć Z.: Acta Agrophys. 2003, **85**, 19–29.

[4] Tilsner J. and Lohaus G.: N use efficiency and amino acid transport in rape (*Brassica napus* L.) W.J. Horst et al. (eds.). Plant nutrition – Food security and sustainability of agro-ecosystems, 2001, 28–29.

[5] Rakowska M., Szkiłądziowa W. and Kunachowicz H.: Biologiczna wartość białka żywności. Wyd. Naukowo-Techniczne, Warszawa 1978, 11–208.

[6] Ferreira R.M.B. and Teixeira A.R.N.: Metabolism of amino acids, [in:] Encyclopedia of Food Science, Food Technology and Nutrition. Macrae R., Robinson R.K. and Sadler M.J. (eds.), Academic Press, London 1993, **1**, 158–166.

[7] Tys J., Piekarski W., Jackowska I., Kaczor A., Zając G. and Starobrat P.: Acta Agrophys. 2003, **99**, 1–153.

[8] Bell J.M.: J. Animal. Sci. 1984, **58**, 996–1010.

[9] Bartkowiak-Broda I., Wałkowski T. and Ogrodowczyk M.: Pamięt. Puław. 2005, **139**, 7–25.

[10] Mahler R.L.: USDA Forest Service Proc. 2004, RMRS-P-**33**, 26–29.

[11] Gerendás J., Zhu Z. and Sattelmacher B.: J. Exp. Bot. 1998, **326**(49), 1545–1554.

[12] Shimada N., Ando T., Tomiyama M. and Kaku H.: Jap. J. Soil Sci. Plant Nutr. 1980, **51**, 493–496.

[13] Tan X.W., Ikeda H. and Oda M.: Sci. Hortcult. 2000, **84**, 265–273.

[14] Kotecki A., Kozak M. and Malarz W.: Rośl. Oleis. 2004, **25**, 97–107.

[15] Muśnicki C., Toboła P. and Muśnicki B.: Rośl. Oleis. 1999, **20**(2), 457–469.

[16] Tys J. and Rybacki R.: Acta Agrophys. 2001, **44**, 1–75.

[17] Pałka M., Bobrecka-Jamro D. and Jarecki W.: Acta Agrophys. 2003, **85**, 277–287.

[18] Gerendás J. and Sattelmacher B.: Ann. Bot. 1999, **83**, 65–71.

[19] Sirko A. and Brodzik R.: Acta Biochem. Polon. 2000, **47**(4), 1189–1195.

ZAWARTOŚĆ AZOTU I SKŁAD AMINOKWASOWY BIAŁKA NASION RZEPAKU JAREGO DOKARMIANEGO DOLISTNIE MOCZNIKIEM I MIKROELEMENTAMI

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Abstrakt: Doświadczenie polowe przeprowadzono w latach 2003–2005 na glebie płowej (Haplic Luvisols), kompleks pszenny wadliwy, metodą bloków losowych w 4 powtórzeniach. Gleba miała odczyn kwaśny (pH$_{KCl}$ – 5,3) i naturalną (charakterystyczną dla tła geochemicznego) zawartość pierwiastków śladowych. Rośliną testową był rzepak jary odmiana "00" – Licosmos. Celem badań było określenie wpływu dokarmiania dolistnego mocznikiem oraz chelatem niklu EDTA-Ni(II) i Plonvitem R na zawartość azotu ogółem i skład aminokwasowy nasion rzepaku jarego. Chelat niklu wpływał na zwiększenie sumy aminokwasów w nasionach, ale redukował ilość białka.

Słowa kluczowe: azot, aminokwasy, rzepak jary, dokarmianie dolistnie, mocznik, mikroelementy

Andrzej JAGUŚ[1]

INFLUENCE OF REED-BED TREATMENT PLANT
ON THE ENVIRONMENT PROTECTION
FROM NITROGEN CONTAMINATION

SKUTECZNOŚĆ TRZCINOWEJ OCZYSZCZALNI ŚCIEKÓW
W OCHRONIE ŚRODOWISKA
PRZED ZANIECZYSZCZENIEM ZWIĄZKAMI AZOTU

Abstract: The paper presents efficiency of removal of nitrogen compounds in the reed-bed treatment plant in Inwald (southern Poland) and the influence of discharge of purified sewage on the water quality of the receiving watercourse (the Stawki stream). The research was carried out between 1998 and 2007. Average yearly loads of nitrogen entering the treatment plant with raw sewage were: 650 kg N_{org}, 2156 kg $N-NH_4$, 2.2 kg $N-NO_2$ and 74 kg $N-NO_3$. In purified sewage at the outflow, in turn, the amounts were: 234 kg N_{org}, 1867 kg $N-NH_4$, 5.8 kg $N-NO_2$ and 84 kg $N-NO_3$. Organic nitrogen compounds were broken down efficiently in the treatment plant, which was expressed by an average reduction of the N_{org} load in the inflow-outflow relation at 58 %. At the same time, absorption of ammonium compounds was inefficient – reduction of $N-NH_4$ load was below 20 % on average. The treatment plant showed practically no capabilities of absorption of nitrates(III and V). Average concentrations of $N-NH_4$ in the water of the Stawki stream were 0.25 mg/dm^3 above the point of discharge from the treatment plant, and 1.42 mg/dm^3 below. Average concentrations of $N-NO_3$ were 2.42 mg/dm^3 above the discharge point, and 2.52 mg/dm^3 below. Discharge of purified sewage caused contamination of the receiving stream with ammonia. The results of the research show the need to reduce the load of sewage coming to the treatment plant or improve the treatment technology.

Keywords: rural areas, reed-bed treatment plant, nutrients, nitrogen, quality of water

Hydrophyte sewage treatment technology has been in the point of interest in many regions of Poland since the early 1990s, mainly due to its relatively low costs of treatment plant construction and almost manless operation throughout the year. Sanitation systems comprising hydrophyte treatment plants are mainly operated in rural areas, both in individual households and in the form of sewage collectors. A wider use of the technology is restricted by the need of a definite size of hydrobotanic beds, at about 2–5 m^2 per 1 equivalent person (E.P.). With poorly developed sewerage of rural

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regions in Poland, hydrophyte treatment plants operating in these areas are an important element of protection of the soil-water environment.

The hydrobotanic beds in hydrophyte treatment plant are created by planting vegetation of swampy ecosystems, most frequently *Phragmites australis* (Cav.) Trin. ex Steud or *Salix viminalis* L., on processed filter aggregate [1–3]. So created environment is continuously supplied with sewage which has been preliminarily treated in the settlement tank (stage I of treatment). The flow of sewage through the bed provides at least stage II of treatment, which is mainly associated with mineralization of organic matter [4]. Due to the fact that sewage purified in hydrophyte treatment plants is discharged directly to the environment, these treatment plants should also feature efficient absorption of biogenic substances, that is nitrogen and phosphorus compounds (stage III of treatment).

Objects and methods of research

Sewage treatment using the hydrophyte technology (in a reed-bed treatment plant) was applied in the collective sanitation system of the village of Inwald, situated in the town of Andrychow (southern Poland). In geographic terms, the area covered by the sewage system stretches at the foothill of the northern slopes of the Beskid Mały Mountains, while the treatment plant itself was located at the bottom of the valley of the Stawki stream, which hydrographically belongs to the catchment area of the Skawa. The plant has been operating since mid-1997 and is administered by Water Supply System and Sewage Company in Andrychow. It collected increasing volumes of sewage as more household sanitary systems were connected. The current inflow has stabilized at about 113 m^3 of sewage per day, with maximum flow capacity, according to the technical specification, at 116 m^3/day. In terms of standards for water use [5], the plant may be described as designed for 1160 E.P., which translates to 2.6 m^2 of the bed for E.P. The administrator's resources and the author's own calculations show, however, that the load of BOD_5 flowing to the plant currently refers to a higher number of equivalent persons, which was estimated at about 1600 E.P. in 2007.

The following describes the operation of the technological sequence of a plant:
– large fraction of sewage is stopped on the floor drain;
– sewage flows through a three-chamber settlement tank with a volume of 200 m^3;
– sewage is evenly distributed over 4 reed fields of 750 m^2 each;
– there is a horizontal subsurface flow of sewage through the hydrobotanic bed constructed according to the Danish technology;
– treated sewage is discharged to the reservoir (the Stawki stream);
– retained sludge from the settlement tank is collected in a drying field with an area of 375 m^2.

The research was carried out between 1998 and 2007. Its objective was to assess the efficiency of absorption of nitrogen compounds in the analyzed treatment plant and to determine the changes in the water quality in the receiving stream caused by discharge of purified sewage. Samples of raw and purified sewage were taken every month and concentrations were measured of organic nitrogen (N_{org}), ammonium-nitrogen ($N-NH_4$),

nitrate(III)-nitrogen (N-NO$_2$) and nitrate(V)-nitrogen (N-NO$_3$). The total of the mentioned compounds amounts to total nitrogen (TN = N$_{org}$ + N-NH$_4$ + N-NO$_2$ + N-NO$_3$). Due to continuous measurement of sewage flowing through the plant, which was carried out by electromagnetic flow meters being an integral part of the technological line, it was possible to calculate monthly and annual loads of nitrogen in their inflow–outflow relation. Chemical analyses also concerned water from the Stawki stream – both above and below the discharge point of purified sewage, where concentrations of N-NH$_4$ and N-NO$_3$ were measured. A total of 120 measuring series were carried out.

Physiochemical analyses of sewage and water were made in the laboratory of the Water Supply System and Sewage Company in Andrychow. Organic nitrogen was mineralized to ammonium ions, concentrations of which were determined using the method of direct nesslerization. Nitrates(III and V) were determined using the sulphanilic acid method [6].

Results and discussion

Efficiency of removing nitrogen from sewage

The changes in concentrations of total nitrogen (TN) in raw sewage ranged between 36.4 and 198.7 mg/dm^3 with the average value at 91.4 mg/dm^3, while in treated sewage between 24.9 and 131.6 mg/dm^3, with the average value at 67.8 mg/dm^3 (Fig. 1). Hence, the decrease in concentrations of total nitrogen during treatment was little efficient. Sewage discharge did not meet the limit of the maximum allowed con-
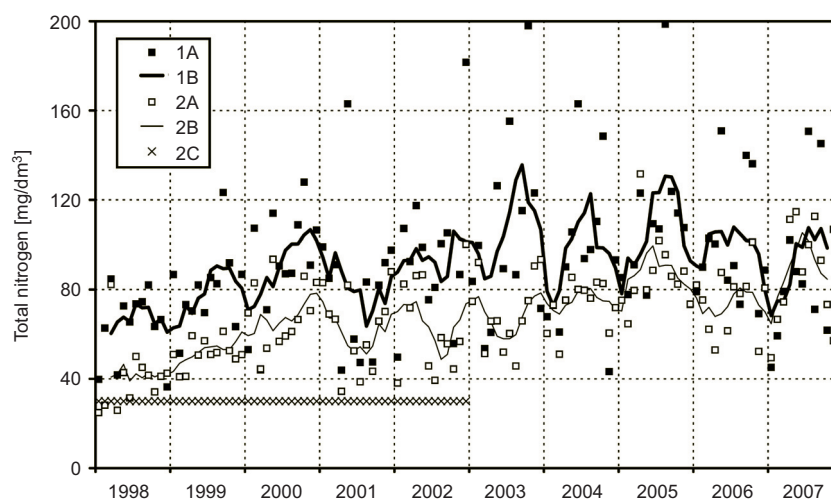
Fig. 1. Concentration of total nitrogen in sewage flowing through the reed-bed treatment plant in Inwald in the years 1998–2007: 1A – concentration in raw sewage (monthly); 1B – consecutive mean values in raw sewage (five month period); 2A – concentration in treated sewage (monthly); 2B – consecutive mean values in treated sewage (five month' period); 2C – maximal permissible concentration for discharge sewage

centration of 30 mg/dm^3 TN, which was in force until December 31, 2002 (Fig. 1). In next years, no limits were, or have been until the present, established for concentrations of total nitrogen in treatment plants with less than 2,000 E.P. discharging sewage to running waters. It is worth mentioning that the variability of total nitrogen concentrations in treated sewage was characterized by an increasing tendency, with fluctuations showing higher effectiveness in summer seasons (Fig. 1). That should be associated with intensified process of assimilation during the vegetative season of the reed.

Loads of nitrogen discharged with raw sewage into the treatment plant, as well as amounts of sewage, increased in consecutive years of research. In 1998, the inflowing load of total nitrogen was nearly 1100 kg, while in years 2005–2007 it was about 4000 kg/year. Increased loads were accompanied by a drop in efficiency of removing nitrogen from sewage. Reduction of the total nitrogen load was low and amounted to 26 % on average. Only 6.7 % of the inflowing load was removed in the treatment process in the last year of the research (2007). Such poor efficiency of nitrogen removal is featured by many hydrophyte treatment plants in Poland [4, 7], especially those with horizontal subsurface flow of sewage, as it is in Inwald. Performance of treatment plants with vertical flow is usually higher [8, 9].

The substance that was removed from sewage most efficiently was nitrogen contained in organic compounds (Table 1).

Table 1

Nitrogen removal effectiveness in the reed-bed treatment plant in Inwald – annual loads of nitrogen in raw sewage (inflow) and in treated sewage (outflow)

Year	Organic nitrogen N_{org}		Ammonium-nitrogen $N-NH_4$		Nitrate(III)-nitrogen $N-NO_2$		Nitrate(V)-nitrogen $N-NO_3$	
	inflow load [kg]	outflow load [%]*	inflow load [kg]	outflow load [%]*	inflow load [kg]	outflow load [%]*	inflow load [kg]	outflow load [%]*
1998	150	64.1	904	63.6	1.31	32.1	37.1	70.5
1999	173	54.9	1123	66.2	0.58	127.6	36.0	63.0
2000	266	58.1	1735	79.8	1.73	112.7	54.3	108.2
2001	313	36.5	1768	80.3	2.25	160.0	54.5	163.3
2002	650	26.4	2126	73.3	0.43	1051.2	57.2	226.2
2003	679	37.5	2641	72.1	1.29	327.1	81.9	129.9
2004	922	33.7	2685	90.6	4.25	197.9	110.1	107.0
2005	1124	38.6	3127	95.1	1.96	611.7	107.8	101.5
2006	1410	22.5	2590	101.9	2.41	473.0	98.2	97.1
2007	814	48.8	2863	106.2	5.54	187.5	107.8	82.2

* Inflow load value [kg] = 100%.

The average yearly reduction of the N_{org} load was 58 %. Only in the initial stage of operation of the treatment plant (1998–2000) was it noticeably lower – at about 35–45 %. Analyses of monthly loads showed that only in few cases was the load of N_{org} discharged into the receiving stream higher than that inflowing with raw sewage. This

occurred in winter seasons, among other factors, the reason was the increased volume of organic matter coming from decayed vegetation. In spite of that, that fact is hydrophyte treatment plants are efficient in mineralization of organic master, which is determined by a significant decrease in BOD_5 and COD in sewage in the process of purification [4, 10].

Removal of ammonium-nitrogen from sewage was very poor in the treatment plant (Table 1). The average reduction of N-NH_4 load in the inflow–outflow relation was at 18 % and was decreasing during the research period. The treatment plant did not reduce the load of ammonium-nitrogen in years 2006–2007. The situation was even worse concerning nitrate(III)-nitrogen. The loads of N-NO_2 that left the plant were higher than those inflowing (Table 1). These results prove very poor intensity of the nitrification process and, indirectly, possibly low oxygenation of the hydrobotanic bed. Insufficient oxidation of ammonia and nitrates(III) is reported in many hydrophyte treatment plants in Poland [4, 9].

The analyzed plant was also incapable of absorbing nitrate(V)-nitrogen from inflowing sewage (Table 1). The loads were reduced at 30–40 % only in the initial stage of the research (1998–1999). Generally, sewage was subject to an increased burden of nitrate(V)-nitrogen coming among others from nitrification. Hence, not only the process of nitrification was little efficient in the treatment plant. That was also the case of the process of denitrification, that is reduction of nitrates(V) to N_2O and N_2. It was no sooner than the last year of research that the load of nitrate-nitrogen was reduced to 82.2 % of the inflowing load (the reduction rate was at 17.8 %).

Contamination of the receiving stream

The receiving watercourse for sewage purified in the Inwald treatment plant is the Stawki stream – discharge takes place at the outlet section. The catchment area of the stream is typically agricultural. According to the information from the technical-legal documentation of the treatment plant [11], contamination of water in the Stawki stream with organic substances improved as the result of connecting about 30 % buildings in the catchment area to the sewerage system. It should be assumed, however, that discharge of purified sewage influences the water quality in the stream below the treatment plant.

The average low flow in the stream above the sewage discharge zone is estimated at 1898 m^3/day [11], whereas the amount of discharged sewage did not exceed 113 m^3/day during the research. In years 1998–2007, the average yearly amount of nitrogen inflowing with purified sewage to the stream was: 234 kg N_{org}, 1867 kg N-NH_4, 5.8 kg N-NO_2 and 84 kg N-NO_3. These amounts were inflowing as a solution which contained, on average, 7.18 mg/dm^3 N_{org}, 57.7 mg/dm^3 N-NH_4, 0.16 mg/dm^3 N-NO_2 and 2.7 mg/dm^3 N-NO_3.

During the research, concentrations of ammonium-nitrogen (N-NH_4) in the Stawki stream above the sewage discharge point ranges from 0.02 to 2.28 mg/dm^3 and was 0.25 mg/dm^3 on average. In most measurements, concentrations were typical of clean waters [12]. In consecutive years, average yearly concentrations ranged between 0.15 and 0.54 mg/dm^3 (Fig. 2). As the result of inflow of purified sewage, where the concentration of

N-NH$_4$ ranged between 19.7–113.0 mg/dm^3, the concentration of ammonium-nitrogen in the water of the stream increased noticeably. The concentration measured in water below the sewage discharge point was 0.04–9.8 mg/dm^3, and average yearly values were between 0.4 and 3.4 mg/dm^3 (Fig. 2). Hence, these were often contaminated waters [12].
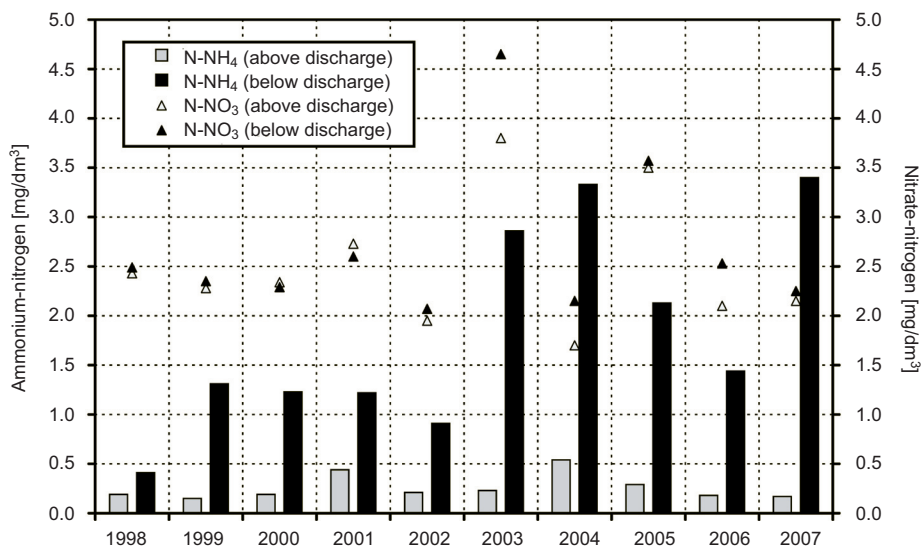
Fig. 2. Average annual ammonium- and nitrate(V)-nitrogen concentration in Stawki stream – above and below discharge point from reed-bed treatment plant in Inwald

The amounts of nitrate-nitrogen (N-NO$_3$) in waters of the Stawki stream above the plant ranged between 0.1 and 8.5 mg/dm^3 (average 2.4 mg/dm^3). Periodically, the concentrations were very high, which results from agricultural activities in the catchment. Average yearly concentrations were between 1.7 and 3.8 mg/dm^3 (Fig. 2). Sewage discharge had little effect on changes in the water quality of the stream, as concentrations of N-NO$_3$ were not significantly higher (0.5–11.8 mg/dm^3) in purified sewage than those in water of the stream. Below the discharge point, water of the stream averagely contained 2.5 mg/dm^3 of N-NO$_3$ – measurements showed results ranging between 0.6 and 7.8 mg/dm^3, and average yearly values were between 2.1 and 4.7 mg/dm^3 (Fig. 2). Occasionally, concentrations of N-NO$_3$ in water were lower after collecting purified sewage. The reported concentrations of nitrate-nitrogen in water of the Stawki stream often suggested its eutrophication. Running waters are regarded as eutrophicated if the average yearly concentration of N-NO$_3$ exceeds 2.2 mg/dm^3 [13].

Conclusions

The studies carried out in years 1998–2007 show that the reed-bed treatment plant in Inwald with horizontal subsurface flow of sewage through the hydrobotanic bed was

little efficient in terms of environmental protection from contamination with nitrogen compounds. Only organic nitrogen compounds were efficiently removed from sewage. Nitrification was not very intense, so the reduction rate of the load of ammonium-nitrogen in sewage was low, and in case of nitrate(III)-nitrogen, an increase of its load in sewage was observed in the process of purification. The plant was also incapable of removing nitrate(V)-nitrogen – assimilation by vegetation and denitrification did not result in a decreased load of $N-NO_3$ in purified sewage. As the result, discharge of purified sewage had a negative impact on the water quality of the receiving stream – an influence on contamination of water with ammonium-nitrogen was reported during the research.

The above results show that it is necessary to decrease the load of contaminants flowing into the plant (by reducing the volume of sewage) or improve the technological line of the plant regarding stage III of treatment. In spite of that, the discussed treatment plant and other objects of that type should be regarded as an important element of protection of the rural environment, especially in areas completely lacking any sewerage system.

References

[1] Obarska-Pempkowiak H.: Oczyszczalnie hydrofitowe, Gdańsk 2002.
[2] Scholz M. and Jing Xu: Bioresource Technol. 2002, **83**, 71–79.
[3] Vymazal J.: Ecol. Eng. 2002, **18**, 633–646.
[4] Sikorski M.: Gospodarka ściekami bytowymi na wsi jako czynnik ochrony środowiska. Falenty 1998.
[5] Rozporządzenie Ministra Infrastruktury w sprawie określenia przeciętnych norm zużycia wody, DzU 2002, nr 8, poz. 70.
[6] Hermanowicz W., Dojlido J., Dożańska W., Koziorowski B. and Zerbe J.: Fizyczno-chemiczne badanie wody i ścieków, Warszawa 1999.
[7] Biernacka E. and Obarska-Pempkowiak H.: Zesz. Nauk. Akad. Roln. we Wrocławiu 1996, **13**(1), 133–144.
[8] Kowalik P.: Wiadomości Melioracyjne i Łąkarskie 1996, **1**, 15–20.
[9] Soroko M.: Woda – Środowisko – Obszary Wiejskie 2001, **1**(1), 173–186.
[10] Jaguś A. and Rzętała M.: Regional aspects of land use, Chernivtsy–Sosnowiec 2002, 73–86.
[11] Nawieśniak T. and Waluś E.: Operat wodno-prawny na odprowadzanie ścieków oczyszczonych z hydrobotanicznej oczyszczalni ścieków w Inwałdzie, Bielsko-Biała 2005.
[12] Dojlido J.: Chemia wód powierzchniowych, Białystok 1995.
[13] Rozporządzenie Ministra Środowiska w sprawie kryteriów wyznaczania wód wrażliwych na zanieczyszczenie związkami azotu ze źródeł rolniczych, DzU 2002, nr 241, poz. 2093.

SKUTECZNOŚĆ TRZCINOWEJ OCZYSZCZALNI ŚCIEKÓW W OCHRONIE ŚRODOWISKA PRZED ZANIECZYSZCZENIEM ZWIĄZKAMI AZOTU

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Abstrakt: W artykule przedstawiono efektywność zatrzymywania związków azotu w trzcinowej oczyszczalni ścieków w Inwałdzie (południowa Polska) i jednocześnie wpływ zrzutu oczyszczonych ścieków na jakość wód odbiornika (potok Stawki). Badania prowadzono w latach 1998–2007. Średnie roczne ładunki azotu dopływające do oczyszczalni w ściekach surowych wynosiły: 650 kg N_{org}, 2156 kg $N-NH_4$, 2,2 kg $N-NO_2$ i 74 kg $N-NO_3$. W ściekach oczyszczonych średniorocznie odpływało natomiast: 234 kg N_{org}, 1867 kg $N-NH_4$, 5,8

kg N-NO$_2$ i 84 kg N-NO$_3$. W oczyszczalni następował efektywny rozkład azotowych związków organicznych, co wyrażała przeciętna 58 % redukcja ładunku N$_{org}$ w relacji dopływ–odpływ. Równocześnie zatrzymywanie związków amonowych było mało skuteczne – średnia redukcja ładunku N-NH$_4$ mniej niż 20 %. Oczyszczalnia praktycznie nie wykazywała zdolności akumulowania związków azotanowych(III i V). Stężenie N-NH$_4$ w wodzie potoku Stawki powyżej miejsca zrzutu z oczyszczalni wynosiło średnio 0,25 mg/dm^3, a poniżej 1,42 mg/dm^3. Z kolei średnie stężenie N-NO$_3$ powyżej zrzutu było równe 2,42 mg/dm^3, a poniżej 2,52 mg/dm^3. Zrzut oczyszczonych ścieków powodował zanieczyszczenie wód odbiornika amoniakiem. Wyniki badań wskazują na potrzebę zmniejszenia obciążenia oczyszczalni lub udoskonalenia technologii oczyszczania.

Słowa kluczowe: obszary wiejskie, trzcinowa oczyszczalnia ścieków, substancje biogenne, azot, jakość wód

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EFFECT OF SOIL CONTAMINATION WITH HERBICIDES ON THE NITRIFICATION PROCESS

WPŁYW ZANIECZYSZCZENIA GLEBY HERBICYDAMI NA PRZEBIEG PROCESU NITRYFIKACJI

Abstract: The objective of this study was to determine the effect of soil contamination with herbicides on the course of the nitrification process. The experiment was carried out in nine replications, on typical brown soil developed from loamy sand with pH 6.5, hydrolytic acidity of 8.25 mmol(+) kg^{-1}, total exchangeable alkaline cations of 78 mmol(+) kg^{-1} and organic carbon content of 6.3 g kg^{-1}. The experimental variables were: type of herbicide (Harpun 500 SC, Faworyt 300 SL, Akord 180 OF and Mocarz 75 WG), herbicide application dose expressed as a multiple of the dose recommended by the manufacturer (0 – control, 1 – dose recommended by the manufacturer, and doses 50, 100, 150 and 200 higher than recommended by the manufacturer), dose of nitrogen in the form of (NH$_4$)$_2$SO$_4$ (0 and 300 mg N kg^{-1} soil) and soil incubation time (14, 28, 42, 56 and 70 days). Soil samples weighing 50 g were incubated in a thermostat at a temperature of 25 $^{\circ}$C throughout the experiment. Soil moisture content was maintained constant at 60 % capillary water capacity.

The study showed that the nitrification process was affected by the type and dose of the applied herbicide as well as the time of the analysis. Lower levels of nitrified nitrogen were observed in soil contaminated with Harpun 500 SC, Akord 180 OF and Mocarz 75 WG herbicides, while Faworyt 300 SL increased the rate of nitrification. The inhibitory effect of the tested herbicides was significantly minimized over time.

Keywords: nitrification, soil pollution, herbicides

Herbicides are one of the main anthropogenic factors that substantially contribute to the degradation of the soil environment. Excessive herbicide use poses an immense environmental threat which may inhibit the growth of plants and living organisms [1–3]. By reacting with soil colonized by microbial communities, herbicides may modify nitrogen transformation in soil [4]. Nitrification is a very important process in the natural circulation of nitrogen [5, 6]. As the result of the above processes involving microbes, ammonia nitrogen is oxidized to nitrate nitrogen. This process may increase the levels of nitrogen easily available to plants and soil organisms [7, 8]. Produced by nitrification NO$_3^-$ ions are characterized by high mobility in the soil environment, and they may contribute to considerable nitrogen loss and environmental pollution [7,

9–12]. The transformation of nitrogen compounds is determined by: soil type, soil moisture content, soil pH, organic substance content, soil microbiological and enzymatic activity [13, 14]. According to reference data [7, 15, 16], the nitrification process is highly sensitive to soil pollution, and it is particularly influenced by biocides. For this reason, nitrification rate is a good indicator of soil pollution with chemical compounds [17, 18].

The objective of this study was to determine the effect of soil contamination with Harpun 500 SC, Faworyt 300 SL, Akord 180 OF and Mocarz 75 WG herbicides on the nitrification process.

Materials and methods

A laboratory experiment was performed with samples of typical brown soil with a granulometric composition of loamy sand with pH 6.5, hydrolytic acidity of 8.25 mmol(+) kg^{-1}, total exchangeable alkaline cations of 78 mmol(+) kg^{-1} and organic carbon content of 6.3 g kg^{-1}. The experimental variables were:

1) type of herbicide: Harpun 500 SC, Faworyt 300 SL, Akord 180 OF and Mocarz 75 WG;

2) herbicide application dose expressed as a multiple of the dose recommended by the manufacturer: 0 – control, 1 – dose recommended by the manufacturer, and doses 50, 100, 150 and 200 higher than recommended by the manufacturer;

3) dose of nitrogen in the form of $(NH_4)_2SO_4$ in mg N kg^{-1} soil: 0, 300;

4) soil incubation time in days: 14, 28, 42, 56, 70.

The applied herbicides comprised the following active substances: Harpun 500 SC – isoproturon (urea derivative – 500 g dm^{-3}), Faworyt 300 SL – chlopyralid (mono-ethanolamine salt – 300 g dm^{-3}), Akord 180 OF – phenmedipham, desmedipham (phenylcarbamate group compounds – each 60 g dm^{-3}) and ethofumesate (benzofuran derivative – 60 g dm^{-3}), Mocarz 75 WG – tritosulfuron (sulfonylurea derivative – 25 %) and dicamba (benzoic acid derivative – 50 %).

The experiment was conducted in 9 replications. 50 g of air-dried soil was placed in each in 100 cm^3 beakers. Herbicides (variables 1 and 2) and an aqueous solution of $(NH_4)_2SO_4$ (variable 3) were added, and all components were thoroughly mixed with soil. The moisture content of soil was brought to 60 % maximum water capacity, and the beakers were incubated in a thermostat at a temperature of 25 ^{o}C. Soil moisture levels were monitored throughout the experiment and losses were supplemented with distilled water. The incubation process was interrupted on different days of the experiment (variable 4) and $N\text{-}NH_4^+$ and $N\text{-}NO_3^-$ levels were determined in the soil. Mineral nitrogen was extracted with the use of a 1 % aqueous solution of K_2SO_4. The soil to extractor ratio was 1:5. The content of $N\text{-}NH_4^+$ ions was determined with the application of Nessler's reagent, and $N\text{-}NO_3^-$ levels – with the use of phenoldisulfonic acid.

In this study, only the concentrations of nitrate(V) nitrogen were determined, as ammonia nitrogen content was inversely proportional to nitrate nitrogen levels. The quantity of nitrified nitrogen was calculated based on the following formula [19]:

$$N = \left(\frac{N_1 - N_0}{D} \right) \cdot 100 \%$$

where: N – % nitrified nitrogen,
N_1 – N-NO_3^- levels in the experimental treatment [mg],
N_0 – N-NO_3^- levels in the control treatment [mg],
D – nitrogen dose [mg N kg^{-1}].

The results were processed statistically with the use of Duncan's multiple range test. Statistical analyses were performed in the Statistica application [20].

Results and discussion

Nitrification is one of the most important processes taking place in the soil and an effective indicator of changes caused by various environmental factors. In this experiment, the tested herbicides had a varied effect on the nitrification process (Fig. 1). When applied at the highest dose (200-fold higher than the recommended dose), Harpun 500 SC slowed down nitrification 2.1-fold, Mocarz 75 WG – 1.8-fold, Akord 180 OF – by 8 %, while Faworyt 300 SL enhanced the process by 22 %.

Nitrification rate in soil was relatively high, as shown by the levels of nitrified nitrogen in non-contaminated treatments on experimental days 42 and 56 (Table 1).
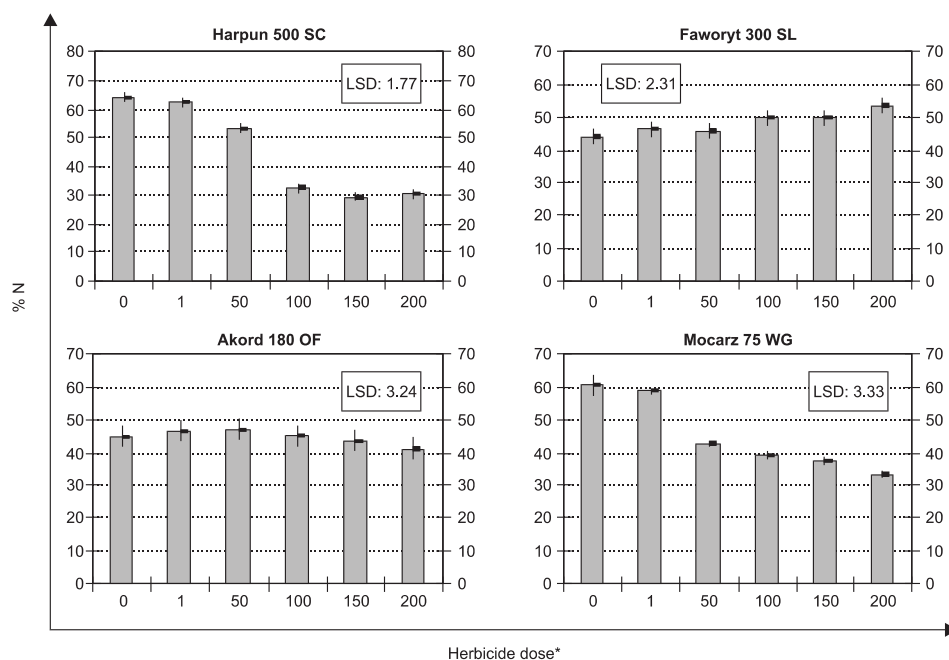
Fig. 1. Percentage content of nitrified nitrogen in soil contaminated with herbicides, regardless of incubation time [in average values]: * 0 – control not contaminated with herbicide; 1 – dose recommended by the manufacturer; doses 50, 100, 150 and 200 higher than recommended by the manufacturer

Table 1

Percentage content of nitrified nitrogen in soil contaminated with herbicides,
as dependent on incubation time

Herbicide dose*	Soil incubation time in days				
	14	28	42	56	70
Harpun 500 SC					
0	30.97 ± 0.58	29.49 ± 0.54	84.79 ± 1.34	86.02 ± 1.87	88.48 ± 1.86
1	31.44 ± 0.85	27.67 ± 0.50	87.66 ± 2.41	75.17 ± 0.87	88.69 ± 1.41
50	34.93 ± 1.47	18.79 ± 1.62	71.89 ± 1.55	60.93 ± 1.66	78.04 ± 1.37
100	11.79 ± 1.05	17.85 ± 0.90	32.56 ± 0.83	34.41 ± 0.98	65.44 ± 1.04
150	6.19 ± 0.81	16.18 ± 0.48	29.19 ± 0.72	28.27 ± 1.87	67.28 ± 0.44
200	4.09 ± 0.21	13.02 ± 0.80	26.73 ± 0.47	28.16 ± 1.30	79.26 ± 1.45
r	−0.92	−0.93	−0.94	−0.94	−0.62
Faworyt 300 SL					
0	10.44 ± 0.58	35.92 ± 0.54	44.94 ± 1.34	64.51 ± 1.87	73.23 ± 1.86
1	1.94 ± 0.93	36.82 ± 0.92	45.52 ± 2.16	70.83 ± 1.02	77.37 ± 1.22
50	2.47 ± 0.82	37.01 ± 1.39	43.01 ± 1.40	68.86 ± 0.53	77.23 ± 0.49
100	2.81 ± 1,04	36.68 ± 1.68	49.84 ± 1.30	66.39 ± 1.37	93.30 ± 1.52
150	2.23 ± 0.20	35.00 ± 1.24	48.19 ± 0.69	72.65 ± 1.38	90.83 ± 1.40
200	4.32 ± 0.46	36.48 ± 2.19	50.66 ± 0.51	80.00 ± 1.28	95.63 ± 1.53
r	−0.43	−0.31	0.80	0.77	0.92
Akord 180 OF					
0	12.47 ± 0.58	24.73 ± 0.54	25.52 ±1.34	73.10 ± 1.87	86.94 ± 1.86
1	6.45 ± 0.77	29.77 ± 2.60	29.60 ± 1.84	82.34 ± 1.55	84.66 ± 5.95
50	9.27 ± 1.12	31.06 ± 2.62	27.98 ± 2,35	81.96 ± 4.25	85.24 ± 2.98
100	3.23 ± 0.83	26.40 ± 2.55	33.82 ± 1.64	80.96 ± 1.65	80.26 ± 0.96
150	3.08 ± 1.06	26.72 ± 2.31	30.30 ± 2.51	78.82 ± 1.86	77.97 ± 3.65
200	3.01 ± 0.38	29.13 ± 4.28	31.53 ± 0.98	80.96 ± 2.54	60.90 ± 0.85
r	−0.80	0.05	0.63	0.26	−0.89
Mocarz 75 WG					
0	24.08 ± 0.58	51.48 ± 0.54	51.61 ± 1.34	88.22 ± 1.87	85.87 ± 1.86
1	22.01 ± 0.65	49.13 ± 0.47	52.45 ± 2.49	85.17 ± 1.58	83.56 ± 1.83
50	19.04 ± 0.78	47.31 ± 0.22	26.56 ± 1.43	54.96 ± 0.65	64.21 ± 1.09
100	14.99 ± 0.87	45.77 ± 0.74	22.32 ± 1.29	53.53 ± 1.46	59.93 ± 1.43
150	18.86 ± 0.76	44.94 ± 0.40	18.38 ± 0.52	48.90 ± 0.80	56.83 ± 0.60
200	13.02 ± 0.43	44.88 ± 0.78	12.95 ± 0.37	42.18 ± 1.52	52.77 ± 0.71
r	−0.86	−0.90	−0.92	−0.90	−0.92
LSD$_{0.01}$**	$a - 0.62, b - 0.76, c - 0.76, a \cdot b - 1.50, a \cdot c - 1.50, b \cdot c - 1.84, a \cdot b \cdot c - 3.68$				

* 0 – control not contaminated with herbicide; 1 – dose recommended by the manufacturer; doses 50, 100, 150 and 200 higher than recommended by the manufacturer; **LSD for: a – herbicide type; b – herbicide dose; c – soil incubation time; r – correlation coefficient.

Harpun 500 SC and Mocarz 75 WG did not have a lasting, negative effect on nitrification because on day 14, the highest dose of Harpun 500 SC slowed down the nitrification process nearly 8-fold, on day 70 – only 1.1-fold, while the highest dose of Mocarz 75 WG inhibited the process 1.8-fold on day 14 and 1.6-fold on day 70. Akord 180 OF had a similar effect on the nitrification process as the above herbicides in the first 14 days of the experiment. During that time, when applied at the highest dose, Akord 180 OF slowed down the nitrification process 4-fold. The product's adverse effect on nitrification ceased on day 28, and it continued to have a stimulating effect on the process toward the end of the experiment, except for day 70. Faworyt 300 SL had a completely different effect as it stimulated the nitrification process throughout the entire experiment (70 days).

Soil pollution with chemicals often disturbs the nitrification process [18, 21–24]. The results of this experiment indicate that the application of increasing doses of Harpun 500 SC, Akord 180 OF and Mocarz 75 WG had an adverse impact on the analyzed process. According to Kinney et al [25], soil pollution with biocides may inhibit nitrification. The above authors studied two fungicides (mancozeb and chlorothalonil) and one herbicide (prosulfuron) which were applied at 0.02 and 10-fold the recommended dose. They observed that growing biocide doses reduced nitrification rate by 20 % to 98 %. The lowest dose inhibited the process in a range of 10–62 %. The above is indicative of the toxic effect of herbicides on nitrifying bacteria. Different results were reported by Stratton and Stewart [26] in whose study glyphosat did not have an adverse effect on the nitrification process. The results of this experiment also indicate that not all herbicides are capable of slowing down nitrification. In this study, Faworyt 300 SL did not affect the investigated process.

Conclusions

1. Soil contamination with Harpun 500 SC, Akord 180 OF, Mocarz 75 WG and Faworyt 300 SL herbicides had a significant effect on the nitrification process. Harpun 500 SC, Akord 180 OF and Mocarz 75 WG inhibited nitrification, while Faworyt 300 SL stimulated the process.

2. The changes in the nitrification process induced by herbicides were not permanent and they were gradually minimized towards the end of the experiment.

References

[1] Menon P., Gopol M. and Parsad R.: Agric. Ecosyst. Environ. 2005, **108**, 73–83.
[2] Österreicher-Cunha P., Langenbach T., Torres J.P.M., Lima A.L.C., De Campos T.M.P., Vargas E.A. and Wagener A.R.: Environ. Res. 2003, **93**, 316–327.
[3] Sánchez M.E., Estrada I.B., Martinez O., Martin-Villacorta J., Aller A. and Morán A.: Chemosphere 2004, **57**, 673–679.
[4] Kara E.E., Aril M. and Uygur v.: Biol. Fertil. Soils 2004, **39**, 474–478.
[5] Drazkiewicz M.: Folia Mikrobiol. 1996, **41**(1), 76–80.
[6] Zhu W. and Carreiro M.M.: Soil Biol. Biochem. 1999, **31**, 1091–1100.
[7] Chao W.L., Gan K.D. and Chao C.C.: Biol. Fertil. Soils. 1993, **15,** 87–90.

[8] Sauveŕa S., Dumestrea A., Mcbridea M., Gillettc J.W., Berthelinb J. and Hendershotd W.: Appl. Soil Ecol. 1999, **12**, 29–39.

[9] Barth G., Tucher S. and Schmidhalter U.: Biol. Fertil. Soils 2001, **34**, 98–102.

[10] Kostov O. and Cleemput O.: Biol. Fertil. Soils 2001, **33**, 10–16.

[11] Dollhopf S.L., Hyun J., Smith A.C., Adams H.J., O'Brien S. and Kostka J.E.: Amer. Soc. Microbiol. 2005, **71**(1), 240–246.

[12] Subbarao G.V., Ishikawa T., Ito O., Nakahara K., Wang H.Y. and Berry W.L.: Plant Soil 2006, **288**, 101–112.

[13] Castaldi S., Carfora A., Fiorentino A., Natale A., Messere A., Miglietta F. and Cotrufo M.F.: Plant Soil 2009, **315**, 273–283.

[14] Qian C. and Cai Z.: Plant Soil 2007, **300**, 197–205.

[15] Martens D.A. and Bremner J.M.: Biol. Fertil. Soils 1994, **17**, 309–313.

[16] Pietril J.C.A. and Brookes P.C.: Soil Biol. Biochem. 2008, **40**, 797–802.

[17] Barabasz W.: Post. Mikrobiol. 1992, **31**(1), 3–29.

[18] Wyszkowska J., Kucharski J. and Kucharski M.: Zesz. Probl. Post. Nauk Roln. 2006, **515**, 439–445.

[19] Wyszkowska J.: Wyd. UWM., Rozprawy i Monografie 2002, **65**, 134 pp.

[20] Statsoft. Inc. 2006. Statistica (data analysis software), ver. 6.0. www.statsoft.com.

[21] Wyszkowska J., Kucharski M., Kucharski J. and Borowik A.: Acta Agric. Silv. ser. Agr. 2006, **49**, 507–515.

[22] Barabasz W., Albińska D., Jaskowska M. and Lipiec J.: Polish J. Environ. Stud. 2002, **11**(3), 193–198.

[23] Bottomley P.J., Taylor A.E., Boyle S.A., McMahon S.K., Rich J.J., Cromack Jr. K. and Myrold D.D.: Microb. Ecol. 2004, **48**, 500–508.

[24] Brierley E.D., Wood M. and Shaw P.J.A.: Plant Soil 2001, **229**, 97–104.

[25] Kinney C.A., Mandernack K.W. and Mosier A.R.: Soil Biol. Biochem. 2005, **37**, 837–850.

[26] Stratton G.W. and Stawart K.E.: Water, Air Soil Pollut. 1991, **60**, 231–247.

WPŁYW ZANIECZYSZCZENIA GLEBY HERBICYDAMI NA PRZEBIEG PROCESU NITRYFIKACJI

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Abstrakt: Celem badań było określenie wpływu zanieczyszczenia gleby herbicydami na przebieg procesu nitryfikacji. Doświadczenie przeprowadzono w dziewięciu powtórzeniach na glebie brunatnej właściwej wytworzonej z piasku gliniastego o pH 6,5, kwasowości hydrolitycznej – 8,25 mmol(+) kg^{-1}, sumie zasadowych kationów wymiennych – 78 mmol(+) kg^{-1}, zawartości węgla organicznego – 6,3 g kg^{-1}.

Czynnikami zmiennymi były: rodzaj herbicydu (Harpun 500 SC, Faworyt 300 SL, Akord 180 OF i Mocarz 75 WG); dawki herbicydów wyrażone jako wielokrotność dawki zalecanej przez producenta (0 – kontrola, 1 – dawka zalecana przez producenta, dawki 50-, 100-, 150- i 200-krotnie większe od zalecanej przez producenta); dawka azotu w postaci (NH$_4$)$_2$SO$_4$ (0 i 300 mg N kg^{-1} gleby) oraz czas inkubacji gleby (14, 28, 42, 56 i 70 dni). Przez cały okres trwania doświadczenia próbki glebowe o masie 50 g inkubowano w termostacie w temperaturze 25 $^{\circ}$C, utrzymując stałą wilgotność gleby na poziomie 60 % kapilarnej pojemności wodnej.

Z przeprowadzonych badań wynika, że proces nitryfikacji uzależniony był od rodzaju herbicydu i jego dawki, a także od terminu wykonanych analiz. Zmniejszenie ilości znitryfikowanego azotu odnotowano w glebie zanieczyszczonej herbicydami: Harpun 500 SC, Akord 180 OF i Mocarz 75 WG, natomiast Faworyt 300 SL spowodował zwiększenie tempa nitryfikacji. Wraz z upływem czasu trwania doświadczenia inhibicyjny wpływ testowanych preparatów istotnie ulegał zmniejszeniu.

Słowa kluczowe: nitryfikacja, zanieczyszczenie gleby, herbicydy

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NITRIFICATION PROCESS AS AN INDICATOR
OF SOIL CONTAMINATION WITH HEAVY METALS

PROCES NITRYFIKACJI WSKAŹNIKIEM ZANIECZYSZCZENIA GLEB
METALAMI CIĘŻKIMI

Abstract: The effect of soil contamination with heavy metals on the nitrification process was determined in a laboratory experiment. The study involved samples of typical brown soil with a granulometric composition of loamy sand, collected from the arable and humus horizon. The experiment was performed in three replications. Soil samples were contaminated with the following amounts of nickel chloride, copper chloride and zinc chloride: 0, 100, 300, 600 mg Me kg^{-1} soil. Nitrogen was supplied in the form of ammonium sulfate at a dose of 0, 250 mg N kg^{-1} soil. The pollutants were thoroughly mixed with the samples, and soil moisture content was brought to 50 % capillary water capacity. Samples were incubated in a thermostat at a temperature of 25 °C for 42 days. $N-NH_4^+$ and $N-NO_3^-$ levels in the soil were determined on experimental days 1, 14, 28 and 42.

Soil contamination with heavy metals (Ni^{2+}, Cu^{2+}, Zn^{2+}) significantly reduced the rate of nitrification. On the 42nd day of the experiment, the tested metals inhibited nitrification by 1 % to 15 % when the administered dose was 100 mg kg^{-1} soil, and by 14 % to 40 % when the pollutant dose reached 300 mg kg^{-1} soil. The highest level of contamination at 600 mg kg^{-1} inhibited nitrification by 70 % to 72 %. The process was most adversely affected by nickel, it was less influenced by copper, while zinc had the least effect on nitrification. A close correlation between the nitrification process and the degree and type of soil pollution with heavy metals renders nitrification rate a highly objective parameter in the evaluation of soil contamination.

Keywords: heavy metals, soil, nitrification, nickel, copper, zinc

When released to the natural environment, heavy metals are accumulated in the soil and they affect its biological activity [1, 2]. The availability of nutrients for plants is determined – mainly by microorganisms. Nitrogen-transforming microbes play a particularly important role in this process from the agricultural point of view [3–5]. Most relevant studies focus on nitrogen mineralization activity and nitrification [6–8]. Nitrification is a process taking place in soil, water and effluents. During this process, ammonium nitrogen (NH_4^+) is oxidized to nitrate nitrogen (NO_3^-) [9–11]. The micro-

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biological transformation of nitrogen is the most important biogeochemical cycle next to the carbon cycle. The intensity of the process in which reduced forms of mineral nitrogen are oxidized by nitrifying bacteria is determined by: the quantity of the oxidized substrate, environmental pH, oxygen content, organic C:N ratio, soil contamination with xenobiotics including heavy metals, temperature and moisture content [12–14].

According to Abramovitch et al [15], heavy metals are a primary source of industrial pollution in the soil environment. Antil et al [1] noted that excessive quantities of heavy metals may have a detrimental effect on all components of the soil ecosystem, including microbes, plants and animals. The above observations prompted the authors of this study to investigate the effect of soil contamination with nickel, copper and zinc on the rate of nitrification, and to determine whether soil nitrification activity is a good indicator of heavy metal contamination.

Materials and methods

The experiment was conducted in 150 cm^3 beakers. 100 g of air-dried soil was placed in each beaker. Under natural condition, this was typical brown soil developed from loamy sand with pH 6.6 in 1 M KCl, hydrolytic acidity (Hh) of 11.38 mmol$^+$ kg^{-1} d.m., total exchangeable alkaline cations (S) of 77.67 mmol$^+$ kg^{-1} and organic carbon content of 8.50 g kg^{-1} d.m. All samples were fertilized with ammonium sulfate (AS) in the amount of 0 and 250 mg N kg^{-1}. Soil was thoroughly mixed with AS, and the following heavy metals were added: nickel, copper and zinc at a dose of 0 100, 300 and 600 mg Me kg^{-1} soil. Heavy metals were administered in the form of NiCl$_2 \cdot$ 6H$_2$O, CuCl$_2$ and ZnCl$_2$. The soil was mixed again and brought to a moisture content of 50 % capillary water capacity. Samples were incubated in a thermostat at a temperature of 25 ^{o}C.

The content of mineral nitrogen (N-NH$_4^+$ and N-NO$_3^-$) was determined on the 1st, 14th, 28th and 42nd day of the experiment with the use of the Orion 720A ionometer. The levels of N-NH$_4^+$ were determined using an ammonium electrode (type 9300BNWP), and N-NO$_3^-$ – a nitrate electrode (type 9300BN). Nitrogen was extracted with a 0.03 % aqueous solution of acetic acid. The extract to soil ratio was 10:1. The experiment was carried out in three replications. The percentage of nitrified nitrogen (1) and percent nitrification inhibition (2) were calculated by the formula of Wyszkowska [16].

$$N = \left(\frac{N_1 - N_0}{D} \right) \cdot 100 \%$$ (1)

where: N – % nitrified nitrogen,
  N_1 – N-NO$_3^-$ concentration in soil fertilized with ammonium sulfate [mg],
  N_0 – N-NO$_3^-$ concentration in soil not fertilized with ammonium sulfate [mg],
  D – nitrogen dose [250 mg N kg^{-1}].

$$H = \left(1 - \frac{a}{b}\right) \cdot 100\,\% \qquad\qquad (2)$$

where: H – % nitrification inhibition,
$\quad\quad a$ – $N\text{-}NO_3^-$ concentration in soil containing Me [mg],
$\quad\quad b$ – $N\text{-}NO_3^-$ concentration in soil not containing Me [mg].

The results were processed statistically with the use of Duncan's multiple range test and a four-factor analysis of variance. Statistical analyses were performed in the Statistica application (17).

Results and discussion

The heavy metals applied in the study (Ni^{2+}, Cu^{2+}, Zn^{2+}) modified the nitrification process in all experimental treatments. $N\text{-}NH_4^+$ concentrations in contaminated soil were higher than in soil not polluted with heavy metals, and they decreased over time (Table 1). $N\text{-}NH_4^+$ levels were always higher in soil fertilized with ammonium sulfate than in non-fertilized samples. A reverse trend was noted as regards $N\text{-}NO_3^-$ concentrations (Table 2) which increased over time. The rate of increase in nitrate nitrogen levels grew with a decrease in heavy metal contamination of the soil. Nickel-contaminated soil contained significantly lower levels of nitrate nitrogen than soil samples polluted with copper and zinc. On average, the nitrified nitrogen content of soil contaminated with nickel was only 41 %, of soil contaminated with copper – 61 % and with zinc – 65 % (Table 3).

In this study, nickel inhibited the nitrification process by 31 % on average, copper – by 26 % and zinc – by 22 % (Table 4). On the 42nd day of the experiment, a nickel dose of 100 mg kg^{-1} soil inhibited nitrification in soil fertilized by ammonium sulfate by 15 %, copper – by 4 %, while zinc – by only 1 %. When the above dose was increased to 300 mg kg^{-1} soil, nickel decreased the rate of nitrification by 40 %, copper – by 21 % and zinc – by 14 %. Regardless of heavy metal type, higher levels of pollution, at 600 mg kg^{-1} soil, slowed down the nitrification process by 70–72 % in the course of 42 days of the experiment. The rate of inhibition was significantly higher in soil fertilized with ammonium sulfate than in non-fertilized soil. The most intensive nitrification was noted between experimental day 14 and 28.

Similar results were observed by Wyszkowska et al [18]. In their study, the nitrification process was significantly inhibited when soil samples were contaminated with copper in the form of $CuSO_4 \cdot 5H_2O$ at a dose of 300 and 600 mg Cu^{2+} kg^{-1}. The adverse effect of copper and lead on nitrification was also noted by Sauvé et al [19] who argued that the assessment of the nitrification process should account for soil contamination with heavy metals as well as for the soil organic matter content and pH. According to many researchers [19–22], pH is the main determinant of nitrogen transformations in the soil environment. Heavy metal contamination (Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}) modifies the soil pH, usually by lowering it. The above leads to changes in the soil biological activity which indirectly affects the rate of the nitrification process.

Table 1

The effect of heavy metal contamination on the $N\text{-}NH_4^+$ content
of soil [mg N kg^{-1} d.m. soil]

Metal dose [mg kg^{-1} d.m. soil]	Soil incubation time in days			
	0	14	28	42
0 mg N kg^{-1} d.m. soil				
0	33.80 ± 0.72	21.63 ± 0.12	20.73 ± 0.29	19.97 ± 0.49
100 Ni^{2+}	40.03 ± 1.64	26.13 ± 1.14	24.83 ± 0.49	23.33 ± 0.40
300 Ni^{2+}	39.83 ± 1.85	39.53 ± 0.25	30.73 ± 1.79	28.77 ± 0.35
600 Ni^{2+}	40.23 ± 0.76	52.47 ± 0.35	51.47 ± 0.21	49.27 ± 0.35
100 Cu^{2+}	40.57 ± 0.58	22.63 ± 0.06	22.23 ± 0.21	21.13 ± 0.32
300 Cu^{2+}	45.87 ± 0.45	32.87 ± 0.25	24.60 ± 0.10	23.23 ± 0.51
600 Cu^{2+}	41.90 ± 0.50	47.00 ± 0.10	43.07 ± 0.12	42.20 ± 0.30
100 Zn^{2+}	39.93 ± 0.15	20.07 ± 0.64	18.60 ± 0.30	17.10 ± 0.20
300 Zn^{2+}	36.73 ± 2.94	26.40 ± 0.17	25.17 ± 0.25	23.60 ± 0.26
600 Zn^{2+}	50.00 ± 0.78	43.37 ± 0.55	40.93 ± 0.35	38.13 ± 0.31
250 mg N kg^{-1} d.m. soil				
0	204.00 ± 2.00	142.33 ± 3.21	80.20 ± 1.82	27.77 ± 0.51
100 Ni^{2+}	221.00 ± 1.73	172.67 ± 2.52	93.67 ± 2.74	53.57 ± 0.45
300 Ni^{2+}	229.00 ± 1.73	182.00± 2.00	96.03 ± 2.11	65.83 ± 0.21
600 Ni^{2+}	212.33 ± 3.21	191.00 ± 2.65	104.67 ± 4.04	80.53 ± 0.55
100 Cu^{2+}	231.67 ± 4.04	178.67 ± 1.53	91.83 ± 2.66	47.30 ± 1.73
300 Cu^{2+}	239.67 ± 1.53	182.00 ±.2.65	91.80 ± 2.60	71.77 ± 0.25
600 Cu^{2+}	212.00 ± 2.65	195.00 ±.3.00	96.13 ± 2.74	81.77 ± 0.25
100 Zn^{2+}	236.67 ± 3.06	159.33 ± 2.08	92.13 ± 2.80	42.10 ± 0.30
300 Zn^{2+}	240.00 ± 1.73	185.67 ± 2.89	92.10 ± 0.53	77.03 ± 0.40
600 Zn^{2+}	234.67 ± 1.53	194.67 ± 2.08	103.33 ± 3.51	80.37 ± 0.32
$LSD_{0.01}$*	$a-0.71, b-0.6, c-0.50, d-0.71, a\cdot b-1.23, a\cdot c-1.01, b\cdot c-0.87, a\cdot d-1.42, b\cdot d$ $-1.23, c\cdot d-1.00, a\cdot b\cdot c-1.74, a\cdot b\cdot d-2.47, a\cdot c\cdot d-2.01, b\cdot c\cdot d-1.74,$ $a\cdot b\cdot c\cdot d-3.49$			

* $LSD_{0.01}$ for: a – heavy metal dose, b – heavy metal type, c – ammonium sulfate fertilization, d – soil incuba-
tion time.

Table 2

The effect of heavy metal contamination on the $N\text{-}NO_3^-$ content
of soil [mg N kg^{-1} d.m. soil]

Metal dose [mg kg^{-1} d.m. soil]	Soil incubation time in days			
	0	14	28	42
0 mg N kg^{-1} d.m. soil				
0	8.57 ± 0.03	10.80 ± 0.06	19.67 ± 0.40	24.67 ± 0.42
100 Ni^{2+}	6.07 ± 0.02	9.72 ± 0.04	17.83 ± 0.35	21.90 ± 0.20
300 Ni^{2+}	6.98 ± 0.12	9.35 ± 0.13	11.30 ± 0.17	15.13 ± 0.32
600 Ni^{2+}	7.55 ± 0.08	7.64 ± 0.03	9.44 ± 0.01	11.43 ± 0.45
100 Cu^{2+}	6.43 ± 0.03	10.47 ± 0.12	17.83 ± 0.21	21.83 ± 0.42
300 Cu^{2+}	8.19 ± 0.06	9.32 ± 0.38	13.53 ± 0.32	17.50 ± 0.17
600 Cu^{2+}	6.95 ± 0.02	8.21 ± 0.23	10.40 ± 0.17	13.33 ± 0.38
100 Zn^{2+}	7.05 ± 0.06	10.20 ± 0.17	18.40 ± 0.30	24.03 ± 0.29
300 Zn^{2+}	6.81 ± 0.05	9.22 ± 0.03	13.23 ± 0.29	18.43 ± 0.29
600 Zn^{2+}	7.07 ± 0.02	9.04 ± 0.02	10.23 ± 0.21	13.10 ± 0.36
250 mg N kg^{-1} d.m. soil				
0	7.14 ± 0.29	36.90 ± 2.43	132.33 ± 4.16	192.67 ± 2.08
100 Ni^{2+}	7.16 ± 0.06	26.30 ± 0.40	124.33 ± 4.04	164.67 ± 2.08
300 Ni^{2+}	5.91 ± 0.16	17.88 ± 0.30	53.43 ± 2.89	115.00 ± 2.65
600 Ni^{2+}	6.29 ± 0.17	15.97 ± 0.05	37.67 ± 0.57	54.60 ± 0.17
100 Cu^{2+}	5.96 ± 0.13	27.53 ± 0.23	128.33 ± 2.08	184.67 ± 2.52
300 Cu^{2+}	6.59 ± 0.20	18.89 ± 0.10	67.73 ± 0.06	152.33 ± 3.21
600 Cu^{2+}	8.27 ± 0.07	16.16 ± 0.34	36.53 ± 0.15	55.07 ± 0.35
100 Zn^{2+}	8.50 ± 0.31	30.77 ± 0.76	131.33 ± 4.16	191.00 ± 2.65
300 Zn^{2+}	8.43 ± 0.25	19.94 ± 0.09	76.47 ± 0.40	165.00 ± 3.61
600 Zn^{2+}	8.46 ± 0.24	16.28 ± 0.25	33.60 ± 0.52	58.50 ± 0.36
$LSD_{0.01}$*	$a - 0.57, b - 0.49, c - 0.40, d - 0.57, a \cdot b - 0.98, a \cdot c - 0.80, b \cdot c - 0.70, a \cdot d - 1.13, b \cdot d - 0.98, c \cdot d - 0.80, a \cdot b \cdot c - 1.39, a \cdot b \cdot d - 1.97, a \cdot c \cdot d - 1.60, b \cdot c \cdot d - 1.39, a \cdot b \cdot c \cdot d - 2.78$			

* $LSD_{0.01}$ for: a – heavy metal dose, b – heavy metal type, c – ammonium sulfate fertilization, d – soil incubation time.

Table 3

The effect of heavy metal contamination on nitrified nitrogen concentrations
in soil fertilized with ammonium sulfate [%]

Metal dose [mg kg^{-1} d.m. soil]	Soil incubation time in days		
	14	28	42
0	10.44 ± 1.00	45.07 ± 1.51	67.20 ± 0.76
100 Ni^{2+}	6.63 ± 0.16	42.60 ± 1.73	57.11 ± 0.76
300 Ni^{2+}	3.41 ± 0.12	16.85 ± 1.12	39.95 ± 1.19
600 Ni^{2+}	3.33 ± 0.01	11.29 ± 0.23	17.27 ± 0.24
100 Cu^{2+}	6.83 ± 0.12	44.20 ± 0.88	65.13 ± 0.91
300 Cu^{2+}	3.83 ± 0.12	21.68 ± 0.14	53.93 ± 1.31
600 Cu^{2+}	3.18 ± 0.23	10.45 ± 0.05	16.69 ± 0.23
100 Zn^{2+}	8.23 ± 0.27	45.17 ± 1.58	66.79 ± 1.17
300 Zn^{2+}	4.29 ± 0.05	25.29 ± 0.10	58.63 ± 1.53
600 Zn^{2+}	2.90 ± 0.09	9.35 ± 0.27	18.16 ± 0.28
LSD$_{0.01}$*	$a - 0.45, b - 0.39, c - 0.45, a \cdot b - 0.79, a \cdot c - 0.91, b \cdot c - 0.79, a \cdot b \cdot c - 1.57$		

* LSD$_{0.01}$ for: a – heavy metal dose, b – heavy metal type, c – soil incubation time.

Table 4

Inhibitory effect of heavy metals on soil nitrification [%]

Metal dose [mg kg^{-1} d.m. soil]	Soil incubation time in days		
	14	28	42
0 mg N kg^{-1} d.m. soil			
100 Ni^{2+}	10.00 ± 0.22	9.29 ± 3.13	11.21 ± 0.76
300 Ni^{2+}	12.89 ± 1.17	42.54 ± 0.49	38.62 ± 2.32
600 Ni^{2+}	29.28 ± 0.27	51.97 ± 1.01	53.65 ± 1.42
100 Cu^{2+}	3.11 ± 1.65	9.30 ± 2.25	11.45 ± 3.12
300 Cu^{2+}	13.68 ± 4.01	31.16 ± 2.43	29.03 ± 1.90
600 Cu^{2+}	24.00 ± 2.30	47.11 ± 1.31	45.93 ± 1.91
100 Zn^{2+}	5.59 ± 1.32	6.43 ± 1.57	2.55 ± 2.29
300 Zn^{2+}	14.68 ± 0.55	32.70 ± 1.89	25.27 ± 0.30
600 Zn^{2+}	16.35 ± 0.38	47.95 ± 2.14	46.89 ± 1.30

Table 4 contd.

Metal dose [mg kg^{-1} d.m. soil]	Soil incubation time in days		
	14	28	42
250 mg N kg^{-1} d.m. soil			
100 Ni^{2+}	28.53 ± 4.62	5.97 ± 4.73	14.53 ± 1.44
300 Ni^{2+}	51.42 ± 3.06	59.63 ± 1.62	40.31 ± 0.93
600 Ni^{2+}	56.59 ± 2.87	71.51 ± 1.16	71.66 ± 0.37
100 Cu^{2+}	25.16 ± 5.10	2.99 ± 1.88	4.14 ± 1.78
300 Cu^{2+}	48.67 ± 2.99	48.78 ± 1.62	20.92 ± 2.16
600 Cu^{2+}	56.09 ± 3.06	72.37 ± 0.91	71.42 ± 0.38
100 Zn^{2+}	16.30 ± 7.26	0.76 ± 0.02	0.87 ± 0.31
300 Zn^{2+}	45.83 ± 3.31	42.18 ± 1.57	14.35 ± 2.10
600 Zn^{2+}	55.74 ± 3.38	74.60 ± 0.59	69.64 ± 0.19
LSD$_{0.01}$*	$a - 0.97, b - 0.97, c - 0.79, d - 1.12, a \cdot b - 1.69, a \cdot c - 1.38, b \cdot c - 1.38, a \cdot d -$ 1.95, $b \cdot d - 1.95, c \cdot d - 1.59, a \cdot b \cdot c - 2.38, a \cdot b \cdot d - 3.37, a \cdot c \cdot d - 2.75, b \cdot c \cdot d -$ 2.75, $a \cdot b \cdot c \cdot d - 4.77$		

* LSD$_{0.01}$ for: a – heavy metal dose, b – heavy metal type, c – ammonium sulfate fertilization, d – soil incubation time.

As demonstrated by Zaborowska et al [23], heavy metals, in particular zinc, have an inhibiting effect on nitrification. In their study, zinc applied in the form of ZnSO$_4$ · 7H$_2$O at a dose of 5 to 2000 mg Zn^{2+} kg^{-1} had a significant negative effect on nitrification in both non-fertilized soil and soil fertilized with ammonium sulfate or urea. The process is adversely affected not only by individual heavy metals but also by their combinations, as demonstrated by Dai et al [24] and Vasquez-Murrieta et al [25]. According to Antil et al [1], soil contamination with nickel and cadmium, especially when applied at high doses of 2290 mg Ni^{2+} and 40 mg Cd^{2+} kg^{-1}, may lead to their accumulation in plants and may inhibit nitrification.

This study and the findings of other authors clearly indicate that elevated levels of heavy metals in soil have an adverse effect on nitrification. The higher the degree of soil contamination, the greater its inhibiting effect on the studied process. The above suggests that nitrification rate may be used as an indicator of the level of soil contamination with heavy metals.

Conclusions

1. Soil contamination with heavy metals (Ni^{2+}, Cu^{2+}, Zn^{2+}) significantly inhibited the nitrification process. In the course of the 42-day experiment, the tested metals slowed

down nitrification by 1 % to 15 % when applied at a dose of 100 mg kg^{-1} soil, and by 14 % to 40 % at a dose of 300 mg kg^{-1} soil. The highest contamination level of 600 mg Me kg^{-1} soil inhibited nitrification by 70 % to 72 %.

2. Nitrification was most adversely affected by nickel, it was less influenced by copper, while zinc had the least effect on the process.

3. A close correlation between the nitrification process and the degree and type of soil pollution with heavy metals renders nitrification rate a highly objective parameter in the evaluation of soil contamination.

References

[1] Antil R.S., Gupta A.P. and Narwal R.P.: Urban Water, 2001, **3**, 299–302.
[2] Omar S.A. and Ismail M.A.: Folia Microbiol. 1999, **44**(2), 205–212.
[3] Barabasz W., Albińska D., Jaśkowska M. and Lipiec J.: Polish J. Environ. Stud. 2002, **11**(3), 193–198.
[4] Barabasz W. : Post. Mikrob. 1992, **31**(1), 3–29.
[5] Brierley E.D.R. and Wood M.: Soil Biol. Biochem. 2001, **33**, 1403–1409.
[6] Burger M. and Jackson E.: Soil Biol. Biochem. 2003, **35**, 29–36.
[7] Maccarty G.W.: Biol. Fertil. Soils, 1999, **29**, 1–9.
[8] Mercik S., Korschens M., Bielawski W., Russel S. and Rumpel J.: Ann. W. Agr. U. SGGW Agr. 1995, **29**, 27–35.
[9] Dincer A.R. and Kargi F.: Enzym. Microbiol. Technol. 2000, **27**, 37–42.
[10] Kucharski J.: *Znaczenie procesu nitryfikacji*, [in:] Mikrobiologia na przełomie wieków. Siwicki A. (ed.). Wyd. UWM, Olsztyn 2000, 37–40.
[11] Simek M.: Rostl. Vyroba, 2000, **46**(9), 385–395.
[12] Deni J. and Penninckx M.J.: Appl. Environ. Microbiol. 1999, **65**(9), 4008–4013.
[13] Przybulewska K., Nowak A. and Stopa K.: Zesz. Probl. Post. Nauk. Roln. 2003, **492**, 287–293.
[14] Wyszkowska J. and Kucharski J.: Rocz. Glebozn. 2004, **55**(2), 517–525.
[15] Abramovitch R.A., Chang Qing L., Hicks E. and Sinard J.: Chemosphere 2003, **53**, 1077–1085.
[16] Wyszkowska J.: Biologiczne właściwości gleby zanieczyszczonej chromem sześciowartościowym, Rozprawy i monografie, Wyd. UWM, Olsztyn 2002, **65**, 1–134.
[17] Statsoft, Inc. Statistica (data analysis software system), version 6.0. www.statsoft.com. 2006.
[18] Wyszkowska J., Kucharski J. and Kucharski M.: Zesz. Probl. Post. Nauk Roln. 2006, **515**, 439–445.
[19] Sauvé S., Dumestre A., McBride M., Gillett J.W., Berthelin J. and Hendershot W.: Appl. Soil Ecol. 1999, **12**, 29–39.
[20] De Boer W. and Kowalchuk G.A.: Soil Biol. Biochem. 2001, **33**, 853–866.
[21] Kashem M.A. and Singh B.R.: Nutr. Cycl. Agroecosys. 2001, **61**, 247–255.
[22] Kyveryga P.M., Blackmer A.M., Ellsworth J.W. and Isla R.: Soil Sci. Soc. Amer. J. 2004, **68**(2), 545–551.
[23] Zaborowska M., Wyszkowska J. and Kucharski J.: EJPAU, 2007, **10**(4), #9.
[24] Dai J., Becquer T., Rouiller H. J., Reversat G., Bernhard-Reversat F. and Lavelle P.: Appl. Soil Ecol. 2004, **25**, 99–109.
[25] Vasquez-Murrieta M.S., Cruz-Mondragón C., Trujillo-Tapia N., Herrera-Arreola G., Govaerts B., Van Cleemput O. and Dendooven L.: Soil Biol. Biochem. 2006, **38**, 931–940.

PROCES NITRYFIKACJI
WSKAŹNIKIEM ZANIECZYSZCZENIA GLEB METALAMI CIĘŻKIMI

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Abstrakt: W doświadczeniu laboratoryjnym określono wpływ zanieczyszczenia gleby metalami ciężkimi na przebieg procesu nitryfikacji. W badaniach wykorzystano próbki gleby pobrane z poziomu ornopróch-

nicznego. W stanie naturalnym była to gleba brunatna właściwa o składzie granulometrycznym piasku gliniastego. Doświadczenie wykonano w trzech powtórzeniach. Próbki glebowe zanieczyszczono chlorkiem niklu, chlorkiem miedzi i chlorkiem cynku w następujących dawkach: 0, 100, 300, 600 mg Me kg^{-1} gleby. Azot wprowadzono w ilości: 0, 250 mg N kg^{-1} gleby w postaci siarczanu amonu. Następnie po dokładnym wymieszaniu, doprowadzono wilgotność gleby do 50 % kapilarnej pojemności wodnej. Tak przygotowaną glebę inkubowano w cieplarce w temperaturze 25°C przez 42 dni. W dniu założenia doświadczenia oraz w 14, 28 i 42 dniu w glebie oznaczono zawartość N-NH$_4^+$ i N-NO$_3^-$.

Stwierdzono, że zanieczyszczenie gleby metalami ciężkimi (Ni^{2+}, Cu^{2+}, Zn^{2+}) przyczyniło się do znacznego zmniejszenia intensywności nitryfikacji. Testowane metale w 42 dniu trwania doświadczenia hamowały nitryfikację w zakresie od 1 do 15 %, gdy były stosowane w dawce 100 mg kg^{-1} gleby i od 14 % do 40 %, gdy dodano je do gleby w ilości 300 mg kg^{-1} gleby. Zanieczyszczenie największe – 600 mg Me kg^{-1} gleby hamowało nitryfikację w zakresie od 70 do 72 %. Najbardziej niekorzystnie na proces nitryfikacji wpływał nikiel, nieco słabiej – miedź i najsłabiej – cynk. Ścisła zależność intensywności nitryfikacji od stopnia i rodzaju zanieczyszczenia gleby metalami ciężkimi czyni pomiar intensywności nitryfikacji obiektywnym parametrem oceny stanu zanieczyszczenia gleb metalami ciężkimi.

Słowa kluczowe: metale ciężkie, gleba, nitryfikacja, nikiel, miedź, cynk

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NITRIFICATION PROCESS IN SOIL CONTAMINATED WITH BENZENE

PROCES NITRYFIKACJI W GLEBIE ZANIECZYSZCZONEJ BENZENEM

Abstract: A laboratory experiment was conducted to determine the effect of light loam contamination with benzene doses of 0, 250, 500, 750 and 1000 $mm^3 \cdot kg^{-1}$ d.m. soil on the nitrification process. The $N\text{-}NH_4^+$ and $N\text{-}NO_3^-$ content of soil was measured at 7-day intervals over a period of 28 days. The soil nitrifying activity and nitrifying bacteria counts (MPN) were also determined.

The results of the study indicate that soil contamination with benzene in quantities exceeding 250 $mm^3 \cdot kg^{-1}$ d.m. soil inhibits the nitrification process. The highest level of benzene pollution (1000 $mm^3 \cdot kg^{-1}$) reduced the populations of phase II nitrifying bacteria 38-fold and lowered the soil nitrifying activity 3.6-fold. Benzene had a more toxic effect on phase II than phase I nitrifying of bacteria which could lead to the excessive accumulation of NO_2^- in soil contaminated with the studied hydrocarbon.

Keywords: benzene, nitrification, nitrifying bacteria, nitrifying activity

The nitrification process is one of the key stages in the nitrogen biogeochemical cycle [1]. It takes place with the involvement of both chemolithotrophic and chemoorganotrophic bacteria which are responsible for autotrophic and heterotrophic nitrification, respectively [2, 3]. The oxidation of $N\text{-}NH_4^+$ to $N\text{-}NO_3^-$ is more intense when it involves chemolithotrophic bacteria than a varied group of chemoorganotrophic microbes [3]. The growth of chemolithotrophs oxidizing reduced nitrogen compounds is limited by the soil pH [2]. Soil acidification significantly reduces those bacterial populations and changes the NH_4^+ to NO_3^- ratio in the soil at the expense of nitrate ions. Although they contribute less to the nitrification process, chemoorganotrophic nitrifiers are found in soils marked by a wider pH spectrum, and they are capable of oxidizing reduced nitrogen compounds even in highly acidic soils.

The nitrification process may be analyzed on various levels. The higher the nitrification intensity, the more fertile the soil, but the soil fertility and nitrifying activity

are largely determined by its physical and chemical properties rather than the nitrification process alone. Nitrification results in nitrogen loss due to N_2O production, NO_3^- leaching and denitrification which may take place in oxygen deficient soil niches [4, 5]. It may also contribute to higher nitrate accumulation in farming products [1].

Fertile soils with a neutral and lightly acidic pH are subject mostly to autotrophic nitrification. The process may be slowed down by various factors affecting not only the soil pH, but also its moisture content, temperature, content of organic matter, mineral and organic pollutants. Mineral pollutants are inclusive of heavy metals [6, 7], while organic contaminants consist of pesticides [8], oil-derivative substances [9] and hydrocarbons [10].

Oil-derivative substances are the main source of environmental pollution with benzene, toluene, ethylbenzene and xylene [11]. Benzene is absorbed by colloids in soil [12] and it is highly biodegradable [13–16]. Benzene may affect the microbiological and biochemical activity of soil both directly and indirectly through metabolites resulting from its transformation [14].

The objective of this study was to determine the effect of soil contamination with benzene on the nitrification process.

Materials and methods

A laboratory experiment was conducted in 6 replications. 100 g of air-dried soil screened through a 2 mm mesh sieve was placed in 150 cm^3 beakers. Under natural conditions, it was typical brown soil developed from light loam (sand – 49 %, silt and clay fraction – 37 %, pH_{KCl} – 6.5, C_{org} – 7.1 g kg^{-1}, total N – 0.58 g kg^{-1}; hydrolytic acidity – 1.28 cmol$^{(+)}$ kg^{-1}, total exchangeable alkaline cations – 13.26 cmol$^{(+)}$ kg^{-1} d.m. soil).

The variable experimental factors were:

1) level of benzene contamination: 0, 250, 500, 750 and 1000 mm^3 kg^{-1} d.m. soil;

2) ammonium sulfate dose in mg N kg^{-1} d.m. soil: 0 and 250;

3) soil incubation time in days: 0, 7, 14, 21 and 28.

Soil samples were contaminated with benzene (variable 1) and $(NH_4)_2SO_4$ (variable 2). All components were thoroughly mixed, and the moisture content of soil was brought to 60 % capillary water capacity with the use of distilled water. The beakers were incubated at a temperature of 25 ^{o}C (variable 3). The incubation process was interrupted on different days of the experiment (variable 3), and N-NH$_4^+$ and N-NO$_3^-$ levels were determined in the soil. The content of ammonia nitrogen was determined with Nessler's reagent, and the content of nitrate nitrogen – with phenoldisulfonic acid. Mineral nitrogen was extracted with a 1 % aqueous K_2SO_4 solution. The extractor to soil ratio was 5:1. The detailed procedure of extracting mineral nitrogen and determining N-NH$_4^+$ and N-NO$_3^-$ concentrations is presented in a previous study [10]. Soil samples were also analyzed to determine the most probable number (MPN) of phase I and II nitrifying bacteria by the serial dilution method [17], and nitrifying activity – by the Kandeler method [18].

The results were processed statistically with the use of Duncan's multiple range test and two-factorial and three-factorial analyses of variance. A statistical analysis was performed in the Statistica application [19].

Results and discussion

A negative correlation between $N-NO_3^-$ levels (Table 1) and soil contamination with benzene, and a positive correlation between $N-NH_4^+$ concentrations and the presence of this hydrocarbon in soil (Table 2) were observed in soil fertilized and not fertilized with ammonium sulfate. Benzene significantly modified the content of both nitrogen forms in soil fertilized and not fertilized with ammonium sulfate. The observed changes in the nitrogen transformation process were induced by benzene introduced to the soil in the amount of 500 mm^3 to 1000 mm^3 kg^{-1} d.m. soil. Benzene's harmful effects were intensified with an increase in soil contamination levels. When added in smaller quantities of 250 mm^3 kg^{-1}, benzene did not alter nitrate nitrogen and ammonia nitrogen levels.

Table 1

Benzene effect on the content of $N-NO_3^-$ in 1 kg d.m. soil [mg N kg^{-1}]

Benzene dose [mm^3 kg^{-1} d.m. soil]	Soil incubation time [days]				
	0	7	14	21	28
Without $(NH_4)_2SO_4$					
0	16.5 ± 0.7	34.4 ± 0.3	36.7 ± 0.3	39.9 ± 1.9	40.9 ± 0.7
250	16.5 ± 0.2	32.6 ± 1.2	37.0 ± 1.0	40.6 ± 0.8	39.2 ± 0.8
500	16.3 ± 0.1	29.8 ± 0.7	36.6 ± 1.6	39.5 ± 0.7	39.5 ± 2.1
750	16.2 ± 0.2	26.7 ± 0.5	33.8 ± 1.0	38.8 ± 0.7	39.5 ± 0.7
1000	16.3 ± 0.2	26.3 ± 0.3	32.7 ± 0.5	35.4 ± 0.7	37.8 ± 0.8
r	−0.707	−0.981	−0.902	−0.834	−0.838
With $(NH_4)_2SO_4$					
0	16.6 ± 0.2	46.8 ± 1.1	72.9 ± 2.5	178.1 ± 4.6	208.5 ± 1.5
250	16.6 ± 0.2	39.9 ± 0.4	68.8 ± 1.6	177.3 ± 3.5	207.0 ± 2.9
500	16.6 ± 0.3	32.3 ± 1.4	48.8 ± 2.4	100.5 ± 1.5	184.2 ± 4.6
750	16.6 ± 0.2	28.2 ± 0.8	36.4 ± 0.8	86.1 ± 2.5	96.7 ± 3.9
1000	16.4 ± 0.3	26.8 ± 1.4	34.7 ± 0.7	80.8 ± 2.9	83.8 ± 2.9
r	−0.728	−0.971	−0.965	−0.921	−0.933
$LSD_{0.01}$*	a − 0.8; b − 0.5; c − 0.8; a · b − 1.1; a · c − 1.7; b · c − 1.1; a · b · c − 2.4				

r – coefficient of correlation; * LSD for: a – benzene dose, b – ammonium sulfate fertilization, c – soil incubation time.

Table 2

Benzene effect on the content of $N-NH_4^+$ in 1 kg d.m. soil [mg N kg^{-1}]

Benzene dose [mm^3 kg^{-1} d.m. soil]	Soil incubation time [days]				
	0	7	14	21	28
Without (NH$_4$)$_2$SO$_4$					
0	5.0 ± 1.3	3.4 ± 0.5	3.6 ± 0.2	3.2 ± 0.3	5.7 ± 0.4
250	5.2 ± 0.3	3.2 ± 0.2	4.1 ± 0.3	3.1 ± 0.2	6.0 ± 0.5
500	5.5 ± 0.6	6.0 ± 0.5	7.2 ± 0.4	6.6 ± 0.4	6.2 ± 0.4
750	5.3 ± 0.6	7.4 ± 0.3	9.1 ± 0.8	11.1 ± 0.9	12.9 ± 0.6
1000	5.5 ± 0.3	12.6 ± 0.4	12.7 ± 0.6	14.6 ± 0.8	15.1 ± 0.7
r	0.849	0.930	0.978	0.964	0.910
With (NH$_4$)$_2$SO$_4$					
0	225.0 ± 9.4	84.4 ± 5.4	75.2 ± 4.5	60.4 ± 1.3	50.7 ± 3.4
250	223.4 ± 3.1	78.1 ± 2.9	78.5 ± 1.3	62.7 ± 1.3	54.2 ± 3.4
500	228.1 ± 6.1	89.5 ± 1.5	102.3 ± 6.5	88.4 ± 1.1	71.3 ± 1.1
750	226.6 ± 7.9	94.5 ± 1.5	118.1 ± 4.0	101.5 ± 2.3	100.9 ± 2.2
1000	221.9 ± 8.1	106.5 ± 5.0	118.8 ± 2.2	104.9 ± 1.9	102.0 ± 2.2
r	−0.200	0.889	0.957	0.960	0.957
LSD$_{0.01}$*	a − 1.7; b − 1.1; c − 1.7; a · b − 2.4; a · c − 3.8; b · c − 2.4; a · b · c − 5.4				

* Refer to the legend in Table 1.

Soil samples not contaminated with benzene were marked by the highest nitrifying activity at 2.39 % N d^{-1} (Fig. 1). The lowest level of nitrifying activity was determined in samples characterized by the highest benzene contamination (1000 mm^3 kg^{-1}). Benzene doses of 750 mm^3 kg^{-1} lowered nitrifying activity 2.9-fold, doses of 500
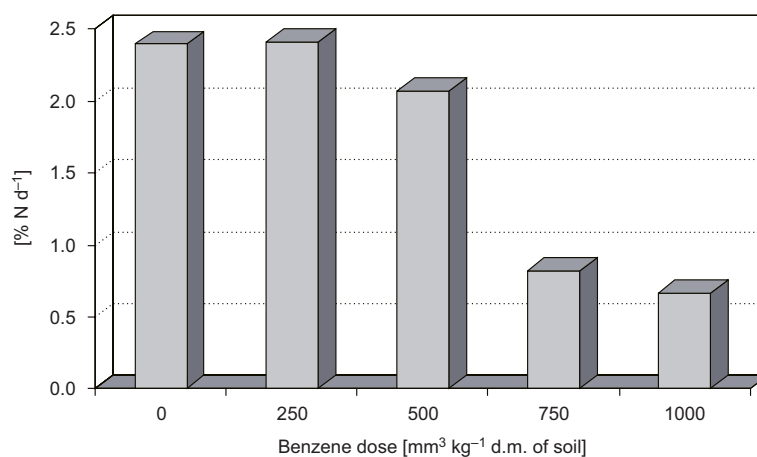
Fig. 1. Effect of benzene on the nitrification activity of soil as percentage of N d^{-1} nitrified

$mm^3 kg^{-1}$ – only 1.2-fold, while 250 mm^3 benzene per kg soil had no adverse effect on the nitrification process.

In this experiment, nitrification intensity varied over time. The highest quantities of nitrified nitrogen were observed on day 28, while the dynamics of the nitrification process was highest between the 14th and the 21st day of the experiment (Table 3). On day 14, soil samples not contaminated with benzene contained only 14.5 % nitrified nitrogen, and on day 21–55.3 %.

Table 3

Benzene effect on the quantity of nitrified nitrogen [%]

Benzene dose [$mm^3 kg^{-1}$ d.m. soil]	Soil incubation time [days]			
	7	14	21	28
0	4.95	14.47	55.29	67.04
250	2.92	12.71	54.71	67.12
500	0.99	4.90	24.40	57.86
750	0.60	1.05	18.90	22.88
1000	0.22	0.80	18.15	18.40
Average	1.94	6.78	34.29	46.66
r	−0.941	−0.956	−0.913	−0.928
LSD$_{0.01}$*	a − 0.7; b − 0.7; a · b − 1.6			

* LSD for: a – benzene dose, b – soil incubation time.

Benzene had an adverse effect on chemolithotrophic nitrifying bacteria. Benzene inhibitory effect on the nitrification process increased with a rise in its concentrations in soil. The studied pollutant had a long-term effect on both phase I (Fig. 2) and phase II (Fig. 3) nitrifying bacteria. On day 28, a benzene dose of 1000 $mm^3 kg^{-1}$ reduced *nitroso* group bacterial populations 3.5-fold in soil not fertilized with ammonium sulfate
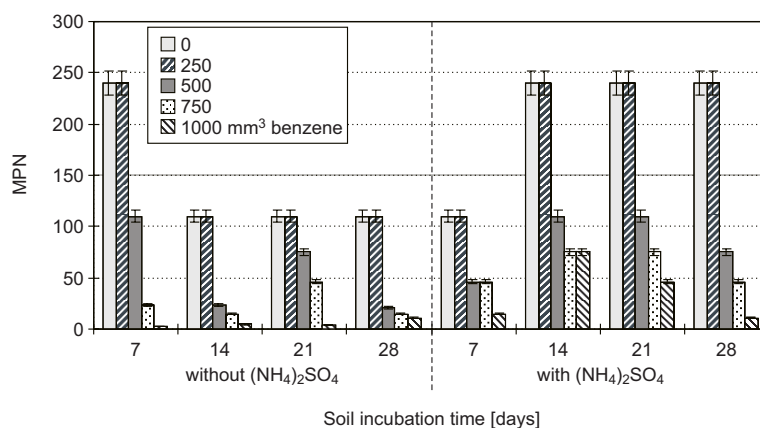
Fig. 2. Effect of benzene dose on the number of I phase nitrifying bacteria in 1 kg d.m. of soil (MPN 10^5)
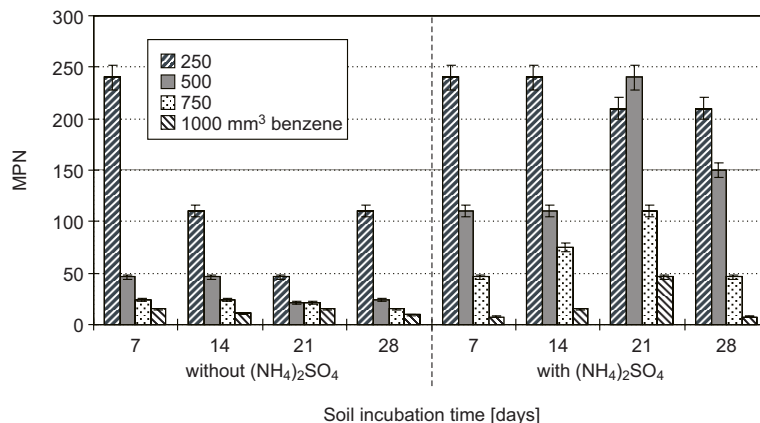
Fig. 3. Effect of benzene dose on the number of II phase nitrifying bacteria in 1 kg d.m. of soil (MPN 10^5)

and 21.8-fold in soil fertilized with ammonium sulfate, and led to an 11.8-fold and a 32-fold decrease in *nitro* group bacterial counts, respectively. Benzene more toxic effect on phase II than phase I nitrifying bacteria is particularly dangerous as it exposes soil microorganisms not only to the harmful effect of benzene but also to the toxic influence of N-NO$_2^-$ which may be accumulated in larger quantities under such conditions. Benzene has a completely different impact on bacteria than commercial nitrification inhibitors [1] which have a selective, toxic effect on phase I nitrifying bacteria and, consequently, they do not lead to the excessive accumulation of NO$_2^-$ in the soil.

The results of this study indicate that benzene contamination upsets the soil metabolic balance and has an adverse effect on nitrogen transformation. Benzene harmful impact on the nitrification process was observed throughout the entire period of the experiment, but it was alleviated towards the end of the study as benzene is biodegradable under both aerobic and anaerobic conditions [13–16]. In an aerobic environment, benzene is transformed by oxygenases into phenol or catechol, while in an anaerobic environment it is reduced and hydroxylated to phenol carboxylated to benzoate or methylated to toluene [14].

Benzene toxic effect on nitrifying bacteria and soil nitrifying activity was similar to that exerted by fluorene [10], anthracene, phenanthrene [20], benzopyrene and chrysene [21]. Similarly to benzene, fluorene inhibitory effect on the nitrification process was also reduced over time.

Conclusions

1. Soil contamination with benzene in quantities exceeding 250 mm^3 kg^{-1} d.m. soil may inhibit the nitrification process.

2. The highest benzene concentrations (1000 mm^3 kg^{-1}) in soil reduced the populations of phase II nitrifying bacteria 38-fold and lowered the soil nitrifying activity 3.6-fold.

3. Benzene has a more toxic effect on phase II than phase I nitrifying bacteria. The above contributes to the harmful impact of this hydrocarbon on soil microorganisms – by creating an environment conducive to the accumulation of NO_2^- ions, benzene has a destructive influence on many bacteria.

References

[1] Fillery J.R.P.: Plant Soil 2007, **294**, 1–7.
[2] De Boer and Kowalchuk G.A.: Soil Biol. Biochem. 2001, **33**, 853–866.
[3] Islam A., Chen D., and White R.E.: Soil Biol. Biochem. 2007, **39**, 972–975.
[4] Mathieu O., Henault C., Leveque J., Baujard E., Milloux M.J. and Andreux F.: Environ. Pollut. 2006, **144**, 933–940.
[5] Meyer R.L., Allen D.E. and Schmidt S.: Marine Chem. 2008, **110**, 68–76.
[6] Sauve S., Dumestre A., McBride M., Gillett J.W., Berthelin J. and Hendershot W.: Appl. Soil Ecol. 1999, **12**, 29–39.
[7] Wyszkowska J., Kucharski M. and Kucharski J.: Ekol. Techn. 2008, **16**, 195–200.
[8] Kara E.E., Arli M. and Uygur V.: Biol. Fertil. Soils 2004, **39**, 474–478.
[9] Kucharski J., Jastrzębska E. and Wyszkowska J.: Acta Agrar.. Silv., Ser. Agrar. 2004, **42**, 249–255.
[10] Kucharski J., Wyszkowska J. and Borowik A.: Roczn. Glebozn. 2008, **59**, 147–153.
[11] Ezquerro O., Ortiz G., Pons B. and Tena M.T.: J. Chromatogr. 2004, **1035**, 17–22.
[12] Kim S.B., Ha H.C., Choi N.C. and Kim D.J.: Hydrol. Proces. 2006, **20**, 4307–4316.
[13] Kim J.M., Le N.T., Chung B.S., Park J.H., Bae J.W., Madsen E.L. and Jeon C.O.: Appl. Environ. Microbiol. 2008, **74**, 7313–7320.
[14] Tan N.N.C.G., Van Doesburg W., Langenhoff A.A.M. and Stams A.J. M.: Biodegradation 2006, **10**, 11–17.
[15] Genovese M., Denaro R., Cappello S., Marco D.G., Spada G.L., Giuliano L., Genovese L. and Yakimow M.M.: J. Appl. Mircobiol. 2008, **105**, 1694–1702.
[16] Franzmann P.D., Zappia L.R., Power T.R., Davis G.B. and Patterson B.M.: FEMS Microbiol. Ecol. 1999, **30**, 67–76.
[17] PN-77 C-04615/20. Water and sewage. Microbiological tests. Determination of autotrophic nitrifying bacteria in liquid medium cultures (in Polish).
[18] Kandeler E.: *Nitrification during long-term incubation*, [in:] Schinner F., Ohlinger R., Kandeler E. and Margesin R. (eds), Methods in soil biology, Springer-Verlag, Berlin–Heidelberg, Germany 1996, 149–151.
[19] StatSoft, Inc.: STATISTICA (data analysis software system), 2006, version 7.1. www.statsoft.com.
[20] Barajas-Aceves M., Vera-Aguilar E. and Bernal M.P.: Biosour. Technol. 2002, **85**, 217–223.
[21] Cervelli S., Di Giovanni F., Perna C. and Perret D.: Water, Air, Soil Pollut. 2000, **124**, 125–139.

PROCES NITRYFIKACJI W GLEBIE ZANIECZYSZCZONEJ BENZENEM

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Abstrakt: W doświadczeniu laboratoryjnym badano wpływ zanieczyszczenia gliny lekkiej benzenem w dawkach: 0, 250, 500, 750 i 1000 mm^3 · kg^{-1} s.m. gleby na przebieg procesu nitryfikacji. Przez 28 dni w odstępach 7-dniowych oznaczano zawartość N-NH$_4^+$ i N-NO$_3^-$ w glebie. Określano także aktywność nitryfikacyjną gleby oraz miano (NPL) bakterii nitryfikacyjnych.

Stwierdzono, że zanieczyszczenie gleby benzenem w ilościach większych od 250 mm^3 · kg^{-1} s.m. gleby powoduje zakłócenia w przebiegu procesu nitryfikacji. Największe zanieczyszczenie gleby benzenem (1000 mm^3 · kg^{-1}) 38-krotnie zmniejszało liczebność bakterii II fazy nitryfikacji i 3,6-krotnie obniżało aktywność nitryfikacyjną gleby. Benzen okazał się bardziej toksyczny dla bakterii II fazy nitryfikacji niż dla bakterii I fazy, co w przypadku zanieczyszczenia nim gleby może doprowadzić do nadmiernej kumulacji NO$_2^-$.

Słowa kluczowe: benzen, nitryfikacja, bakterie nitryfikacyjne, aktywność nitryfikacyjna

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MINERALIZATION OF ORGANIC NITROGEN COMPOUNDS IN ALLUVIAL AND DELUVIAL SOILS OF MORAINIC, RIVERINE AND DELTA LANDSCAPES

MINERALIZACJA ORGANICZNYCH ZWIĄZKÓW AZOTU W GLEBACH NAPŁYWOWYCH OBSZARÓW MŁODOGLACJALNYCH W KRAJOBRAZIE MORENOWYM DOLIN RZECZNYCH I DELTOWYM

Abstract: The process of mineralization of organic nitrogen compounds in alluvial and deluvial soils of morainic, riverine and delta landscapes was studied. The research was carried out in autumn 2008, after growing season. Inorganic nitrogen compounds were determined by adding 1 % K_2SO_4 after incubation of soil samples. Furthermore, the redox potential (Eh) and the oxygen diffusion rate (ODR) were measured and rH factor was calculated. The results show that the most beneficial soil-site conditions for the mineralization of organic nitrogen compounds are in deluvial soils in the landscape of lakeland hills. In these soils the amount of nitrogen compounds converted to inorganic forms was the highest and the content of $N-NO_3$ was low and medium according to the established standards. The value of Eh potential amounted to 390 mV and the oxygen diffusion rate to 74.2 $\mu g \, m^{-2} \, s^{-1}$. The $N-NO_3:N-NH_4$ ratio exceeded 1.0. In surface horizons of alluvial soils of riverine and delta landscapes, despite higher quantities of organic matter and total nitrogen than in deluvial soils, the amounts of inorganic nitrogen compounds were similar. In subsurface horizons of alluvial soils, small amounts of inorganic nitrogen compounds were released and the $N-NO_3:N-NH_4$ ratio was below one. Different site conditions, in which process of mineralization of organic nitrogen compounds took place, led to statistically significant differences between deluvial and alluvial soils, taking into consideration the content of $N-NO_3$ and the sum of $N-NO_3$ and $N-NH_4$.

Keywords: alluvial soils, deluvial soils, nitrates, ammonium, morainic landscape, riverine landscape, delta landscape

The land relief of young glacial region of northern Poland was shaped during the Vistula glaciation. The soil cover was formed in postglacial period and was protected by natural forest vegetation. The development of agriculture caused changes in land use and intensification of anthropogenic denudation processes [1, 2]. Deluvial and alluvial

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soils were formed by the slope and riverine holocene deposits. These soils are situated in local depressions and in river valleys and therefore play an important role in the circulation and transformation of biogens. In catena sequence, deluvial soils occur at the foot of the slope between eroded soils on the slope and soils in depression. These soils play a role as biogeochemical barriers and are important in environmental protection. It should be stressed that deluvial and alluvial deposits often cover organic soils occurring in depressions and diminish the rate of organic matter mineralization [3, 4].

Research on mineralization of nitrogen compounds in peat-muck soils is widespread in the literature [5–9]. However studies concerning transformations of nitrogen compounds in mineral and organic-mineral soils are rare [10, 11]. In the process of mineralization of organic matter, which rate depends on the range of site factors, large quantities of nitrates ($N-NO_3$) and ammonium ($N-NH_4$) may be released [5]. The nitrate-nitrogen that is not uptaken by plants, may infiltrate and contaminate ground-water after growing season as well as when the amount of $N-NO_3$ in the soil exceeds plant needs [8, 11, 12].

Taking into consideration an important role of alluvial and deluvial soils in the process of transformation of nitrogen compounds and the range of site factors affecting this process, the research should be carried out with regard to various soil-site conditions [7, 9, 10, 13]. The aim of the paper was to study the process of mineralization of organic nitrogen compounds in alluvial and deluvial soils of morainic, riverine and delta landscapes of north-eastern Poland.

Materials and methods

The research was carried out in alluvial and deluvial soils of young glacial landscapes of north-eastern Poland using catena approach. The soils of the following landscapes: morainic hills and plains, lakeland hills, riverine and delta were chosen [14, 15]. In the landscape of morainic hills and plains, comprising Sepopol Plain and small area of Mazurian Lakeland, Troksy site is located. In the landscape of lakeland hills, comprising major part of Mazurian Lakeland, Lutry, Nawiady and Linowo sites are situated. In delta landscape, at Vistula and Pasleka estuary, Jeglownik and Braniewo sites are located. In riverine landscape, at Olsztyn Lakeland and Sepopol Plain, Rownina Gorna and Smolajny sites were chosen.

The results of the analysis of mineralization of organic nitrogen compounds in studied soils, regarding site conditions, are shown in chosen, representative pedons (Table 1, 2). Whereas in Table 3 and 4, the content of inorganic nitrogen compounds as well as mean values are presented for each horizon of studied soils.

The process of mineralization of nitrogen compounds was examined in autumn 2008 (at the turn of November and December), after growing season. In collected soil samples the following properties were analyzed: texture of mineral formations by hydrometer method of Casagrande modified by Proszyński, soil reaction in water and potassium chloride, potentiometrically, moisture content during sampling after drying to constant weight at 105 ^{o}C, soil specific density of mineral formations by pycnometric

method, soil specific density of organic formations by calculation according to the formula suggested by Okruszko [16]:

$$SD = 0.011 \times A + 1.451$$

SD – specific density; A – ash content, after dry ashing of soil samples at a temperature of 550 $^{\circ}$C.

Bulk density and total porosity were determined in a 100 cm^3 undisturbed core sample. Humus content was measured by the Tiurin method and total nitrogen by the Kjeldahl method. For the analysis of inorganic nitrogen compounds (N-NO$_3$ and N-NH$_4$), undisturbed soil samples in 100 cm^3 cores were used. Nitrogen compounds were determined in an extract of 1 % K$_2$SO$_4$ after 14-day incubation of soil samples at a temerature of 28 $^{\circ}$C. For N-NO$_3$ determination, phenol disulphonic acid was used and for N-NH$_4$, Nessler's reagent was applied [5]. Furthermore, the redox potential (Eh) and the oxygen diffusion rate (ODR) were measured and rH factor was calculated on the base of redox potential Eh and soil reaction according to the formula:

$$rH = (Eh \; x \; 29^{-1}) + 2pH.$$

Statistical analyses were conducted using Statistica 8.0. The significance tests and correlation analyses were applied [17].

Results

Landscape of morainic hills and plains

In the landscape of morainic hills and plains, land denivelation and the erosion risk are low. At Troksy site, humous deluvial soils, shallow and of medium depth, which evolved from eroded black earths occur. They are used as arable fields. The soils were developed from heavy loam and among all studied soils contained the highest amounts of clay ($\varnothing < 0.002$ mm), ranging between 28 % and 32 %. The amount of organic matter varied between 75.5 g · kg^{-1} and 99.0 g · kg^{-1} (Table 1). The groundwater level was high, at a depth of 0.68 m. The content of air in Ap horizon was low and amounted to 7.3 %, value of Eh potential did not exceed 300 mV (280 mV) and the oxygen diffusion rate (ODR) was below 70 μg · m^{-2} · s^{-1} amounting to 51.2 μg · m^{-2} · s^{-1} (Table 2). The values of the analyzed factors suggest bad air conditions in the soils (predominance of reduction processes). Despite high content of organic matter, the amounts of nitrogen compounds released in deluvial deposits were small and amounted to 9.35–9.08 mg · kg^{-1}. In deluvial soils, in autumn 2004, the amount of released ammonium was higher [10]. More ammonium was released in peat lying underneath (on average 22.75 mg · kg^{-1}).

The N-NO$_3$:N-NH$_4$ ratio is an indicator of the conditions of organic matter mineralisation. It can be concluded that in studied soils beneficial conditions for nitrification were in Ap horizon, where the ratio was equal to 2.41. In subsurface horizons this ratio was below 1.0.

Landscape of lakeland hills

In the landscape of lakeland hills, soil cover is diversified. Deluvial soils of various depth, which developed on strongly decomposed alder peats predominate. For the study, Lutry and Nawiady sites, used as extensive pastures and Linowo site used as arable land were chosen. A horizons of deluvial soils had loam and sandy loam texture. They contained small amounts of clay, from 6 % to 15 % (Table 1).

Table 1

Properties and soil-site conditions of the studied soils

Horizon	Depth	Soil texture PTG 2008	Clay fraction of $\varnothing < 0.002$ mm	Organic matter	Moisture	Air porosity	Ground level water
	cm		%	$g \cdot kg^{-1}$	% vol.		m
Landscape of morainic hills and plains							
Troksy – Humous deluvial soil, shallow*							
Ap*	10–15	heavy loam	28	99.0	38.4	7.3	0.68
A2	30–35	heavy loam	32	75.5	41.0	4.6	
OtniszR3	50–55	reed peat	—	764.0	80.7	3.1	
OtniszR3	70–75	reed peat	—	873.0	83.8	0	
Landscape of lakeland hills							
Lutry – Proper deluvial soil, deep							
Ah	10–15	light loam	9	27.6	26.7	20.1	1.25
A2	30–35	heavy loam	15	9.3	26.5	16.9	
A3	70–75	heavy loam	10	8.3	30.8	13.1	
OtniolR3	110–115	alder wood peat	—	524.0	74.1	10.7	
Nawiady – Humous deluvial soil, shallow							
Ah	10–15	sandy loam	6	55.3	25.5	23.4	0.64
A2	30–35	loam	9	42.2	28.4	17.9	
OtniolR3	50–55	alder wood peat	—	208.0	67.3	5.9	
OtniolR3	70–75	alder wood peat	—	487.0	82.0	0.5	
Riverine landscape							
Rownina Gorna – Humous deluvial soil, deep							
Ap	10–15	loam	14	51.4	33.1	14.3	< 1.50
A2	30–35	loam	20	10.9	33.9	8.9	
A3	55–60	loam	21	13.8	39.3	6.4	
Rownina Gorna – Humous alluvial soil, deep							
Aa	10–15	silty clay loam	29	76.4	51.3	8.3	0.56
A2	30–35	silty clay loam	38	27.2	52.0	4.3	
A3	50–55	silty clay	49	48.4	62.1	2.2	
A4	90–95	silty clay	45	16.0	62.8	0	

Table 1 contd.

Horizon	Depth	Soil texture PTG 2008	Clay fraction of $\varnothing < 0.002$ mm	Organic matter	Moisture	Air porosity	Ground level water
	cm		%	$g \cdot kg^{-1}$	% vol.		m
Delta landscape							
Jeglownik – Humous alluvial soil, shallow							
Ap	10–15	light loam	8	57.4	40.6	12.3	0.70
A2	30–35	silt loam	11	86.4	48.1	8.1	
OtniszR2	50–55	reed peat	—	79.6	80.6	7.4	

* Systematics of Polish soils [19].

As compared with deluvial soils in the landscape of morainic hills and plains, the content of organic matter (8.3–55.3 %) and moisture (26.5–30.8 %) was lower and the amount of air (16.9–23.4 %) was higher. Despite lower amounts of organic matter and total nitrogen in surface horizon (Ah), more inorganic nitrogen compounds were released (10.86–13.89 mg $\cdot$ kg^{-1}) as compared with the soils of morainic hills and plains. In the process of mineralisation, more nitrates were released. This is regarded as beneficial for nitrification. The value of redox potential was high and amounted to 390 mV, and the oxygen diffusion rate to 74.2 μg m^{-2} s^{-1}. The N-NO$_3$:N-NH$_4$ ratio was greater than 1.0. The amount of N-NO$_3$ (expressed in the volume of d.m. – mg $\cdot$ dm^{-3}) was low and medium according to the ranges regarding their supply with nitrogen compounds [5].

Riverine landscape

In riverine landscape, the research was carried out in two catenas: in Guber river valley at Rownina Gorna site and in Lyna river valley at Smolajny site. On the slopes of Guber river valley, humous deluvial soils, deep, used as arable land occurred, whereas in the valley itself, alluvial soils, also deep, used as permanent grasslands were located. It should be stressed that in the place where the valley and slope meet, alluvial and deluvial processes overlap. Deluvial soils had loam texture and contained 14–21 % of clay in humus horizon. The groundwater level was low, at a depth of less than 1.5 m. The amount of air in Ap horizon amounted to 14.3 %. Alluvial soils situated in extensive river valley were formed from silty-clayey loam and clay and contained more clay fraction (29–49 %) than deluvial soils. The content of organic matter and moisture was also higher. The amount of air in surface horizon amounted to merely 8.3 % and was the lowest among studied soils. Despite the fact that surface horizons of alluvial soils contained one and a half as much organic matter as deluvial soils, the amounts of inorganic nitrogen compounds were similar in both soils (Table 2). In subsurface horizons of alluvial soils ammonification processes prevailed and the nitrate: ammonium ratio did not exceed one. Low values of Eh potential (40–160 mV), ODR (16.6–32.0

$\mu g \cdot m^{-2} \cdot s^{-1}$) and rH factor (13.8–18.7) prove bad air conditions in these soils and suggest predominance of reduction processes.

Table 2

Content of inorganic nitrogen compounds and air properties of the studied soils

Horizon	Depth	N-total	N-NO$_3$	N-NH$_4$	N-NO$_3$ + N-NH$_4$	$\dfrac{\text{N-NO}_3}{\text{N-NH}_4}$	Eh	ODR	rH
	cm	g · kg^{-1}	mg · kg^{-1} d.m. soil				mV	µg · m^{-2} · s^{-1}	
Landscape of morainic hills and plains									
Troksy – Humous deluvial soil, shallow									
Ap	10–15	5.67	6.42	2.66	9.08	2.41	280	51.2	22.9
A2	30–35	3.25	2.52	2.83	5.35	0.89	170	44.8	18.9
OtniszR3	50–55	26.20	8.89	21.34	30.23	0.42	140	38.4	15.6
OtniszR3	70–75	16.97	4.74	10.52	15.26	0.45	55	14.0	12.7
Landscape of lakeland hills									
Lutry – Proper deluvial soil, deep									
Ah	10–15	1.58	6.14	4.72	10.86	1.30	390	74.2	23.0
A2	30–35	0.58	4.02	2.84	6.86	1.42	320	65.2	21.0
A3	70–75	0.47	1.20	1.04	2.24	1.15	235	48.6	19.7
OtniolR3	110–115	19.54	6.82	21.76	28.58	0.31	150	35.8	17.4
Nawiady – Humous deluvial soil, shallow									
Ah	10–15	3.10	11.65	2.24	13.89	5.20	370	61.4	26.8
A2	30–35	2.67	7.64	4.96	12.60	1.54	300	46.0	24.5
OtniolR3	50–55	9.47	0.57	49.21	49.78	0.01	185	23.0	20.6
OtniolR3	65–70	16.23	0.27	8.45	8.72	0.03	110	15.3	17.4
Riverine landscape									
Rownina Gorna – Humous deluvial soil, deep									
Ap	10–15	3.50	6.52	2.31	8.53	2.82	345	57.6	24.7
A2	30–35	0.84	1.75	0.68	2.43	2.57	315	46.1	23.7
A3	55–60	1.25	1.21	0.74	1.95	1.63	265	42.2	21.7
Rownina Gorna – Humous alluvial soil, deep									
Aa	10–15	6.17	5.58	3.13	8.71	1.78	310	44.8	24.1
A2	30–35	2.05	2.71	2.94	5.65	0.92	160	32.0	18.7
A3	50–55	3.12	1.12	1.65	2.77	0.68	85	25.6	15.5
A4	90–95	2.00	0.62	1.56	2.18	0.40	40	16.6	13.8
Delta landscape									
Jeglownik – Humous alluvial soil, shallow									
Ap	10–15	3.30	3.73	1.62	5.35	2.30	325	49.9	24.8
A2	30–35	4.80	1.94	2.01	4.02	0.97	205	38.4	19.9
OtniszR2	50–55	23.61	2.44	8.72	11.16	0.28	110	28.1	15.4

Delta landscape

In this landscape, Jeglownik site in Vistula delta and Braniewo site in Pasleka delta were chosen. At Jeglownik, shallow humous alluvial soils were developed from sandy loam and silt loam and were overlying medium decomposed (30–60 % of decomposition) reed peat. The soils occur on plain at about sea level. The groundwater level was at a depth of 0.7 m and the content of air in Ap horizon amounted to 12.3 %. In humus horizon the soils contained $57.4–86.4$ g $\cdot$ kg^{-1} of organic matter. In such conditions, the processes of organic matter mineralization are not intense. The content of inorganic nitrogen released in the studied soils amounted to 5.35 mg $\cdot$ kg^{-1}. The N-NO$_3$:N-NH$_4$ ratio exceeded 1.0 only in Ap surface horizon. According to the ranges regarding their supply with nitrogen, the analyzed soils contain little amounts of nitrates. In subsurface horizon, the Eh potential was below 300 mV and the ODR factor amounted to 38.4 µg $\cdot$ m^{-2} $\cdot$ s^{-1}, which indicates good conditions for nitrification.

Mineralization of nitrogen compounds in alluvial and deluvial soils

Different origin and site conditions, in which alluvial and deluvial soils developed, are reflected by the process of mineralization of organic nitrogen compounds (Table 3 and 4). In deluvial soils, which are typical for morainic landscape, despite lower amounts of total nitrogen, after growing season twice more inorganic nitrogen compounds was released than in alluvial soils. The amount of N-NO$_3$ according to established standards was medium and in alluvial soils it was small. Deluvial soils, as compared with alluvial, have better water-air conditions for the process of nitrification. Mean value of Eh potential in deluvial soils amounted to 386 mV and the oxygen diffusion rate amounted to 69.2 µg $\cdot$ m^{-2} $\cdot$ s^{-1}, whereas in alluvial soils these values were as follow: Eh – 311 mV, ODR – 47.0 µg $\cdot$ m^{-2} $\cdot$ s^{-1}.

Table 3

Content of inorganic nitrogen compounds and air properties of deluvial soils

Horizon Depth	Value	N-total	N-NO$_3$	N-NH$_4$	N-NO$_3$ + N-NH$_4$	$\dfrac{\text{N-NO}_3}{\text{N-NH}_4}$	Eh	ODR	rH
cm		g $\cdot$ kg^{-1}	mg $\cdot$ kg^{-1} d.m. soil				mV	µg $\cdot$ m$^{-2} \cdot$ s^{-1}	
Ap	x	3.22	9.59	4.86	14.45	3.73	386	69.2	25.1
10–15	S	1.34	4.38	6.37	7.18	3.09	74.07	12.93	2.41
n = 10	CV	41.6	45.7	131.0	49.7	82.8	19.2	18.7	9.6
A2	x	2.25	5.56	3.88	9,44	1.70	307	55.2	22.6
30–35	S	1.11	3.32	2.92	5.41	0.77	76.01	17.94	2.72
n = 10	CV	49.3	59.7	75.3	57.3	45.3	24.8	32.5	12.0
A3	x	2.71	4.04	5.05	9.09	1.28	292	51.9	22.2
70–75	S	2.73	2.84	6.71	9.24	0.54	39.94	7.90	1.70
n = 5	CV	100.7	70.3	132.8	101.7	42.2	13.7	15.2	7.7
Otni	x	18.38	4.19	24.73	28.92	0.21	146	28.9	17.4
< 50	S	6.94	3.39	14.32	14.10	0.17	47.56	12.06	3.27
n = 8	CV	37.8	80.9	57.9	48.7	81.0	32.6	41.7	18.8

x – mean, S – standart deviation; CV – coefficient of variation; n – number of samply.

In alluvial soils, the rate of mineralization of organic nitrogen compounds decreased with depth and the N-NH$_4$ form prevailed (Table 4).

Content of inorganic nitrogen compounds and air properties of alluvial soils

Horizon Depth	Value	N-total	N-NO$_3$	N-NH$_4$	N-NO$_3$ + N-NH$_4$	$\overline{\frac{N-NO_3}{N-NH_4}}$	Eh	ODR	rH
cm		g · kg^{-1}	mg · kg^{-1} d.m. soil				mV	µg · m^{-2} · s^{-1}	
Ap	x	3.89	4.57	2.43	7.00	1.92	311	47.0	22.4
10–15	S	1.67	1.53	0.96	2.47	0.26	15.48	2.62	2.38
n = 4	CV	42.9	33.5	39.5	35.3	13.5	5.0	5.6	10.6
A2	x	2.71	3.26	4.41	7.67	0.86	236	45.4	19.7
30–35	S	1.87	2.62	4.58	7.17	0.15	101.02	22.78	3.41
n = 4	CV	69.0	80.4	103.8	93.5	17.4	42.8	50.2	17.3
A3	x	2.09	0.82	1.62	2.44	0.53	89	21.6	14.8
50–55	S	0.62	0.29	0.66	0.91	0.13	35.60	7.32	1.60
n = 3	CV	29.7	35.4	40.7	37.3	24.5	40.0	33.9	10.8
Otni	x	20.17	1.65	7.60	9,25	0.38	27	17.4	11.7
< 50	S	3.30	1.03	4.70	4.16	0.41	80.21	9.86	3.36
n = 3	CV	16.4	62.4	61.8	45.0	107.9	461.0	56.7	8.7

In organic horizons (Otni), particularly in deluvial soils, substantially more nitrogen compounds were released than in overlying silt deposits. During the mineralization, five times more N-NH$_4$ than N-NO$_3$ was released in organic horizons of both deluvial and alluvial soils. Correlation coefficients calculated for the relationship between inorganic nitrogen compounds and clay or moisture content, took on minus values (Table 5).

Pearson's correlation coefficients between clay fraction, organic matter, moisture and air content and the amount of N-NO$_3$, N-NH$_4$

Form of N	Clay fraction	Org. matter	N-total	Moisture	Air porosity	Eh	ODR	rH
Deluvial soil, n = 25								
N-NO$_3$	−0.582*	0.505*	0.322	−0.294	0.701*	0.752*	0.622*	0.724*
N-NH$_4$	−0.393	0.208	0.360	0.348	0.028	0.289	0.360	0.106
N-NO$_3$ + NH$_4$	−0.630*	0.450*	0.449*	0.074	0.439*	0.655*	0.629*	0.507*
Alluvial soil, n = 13								
N-NO$_3$	−0.712*	0.434	0.626*	−0.264	0.801*	0.871*	0.891*	0.861*
N-NH$_4$	−0.499	0.134	0.275	−0.292	0.464	0.571*	0.811*	0.536
N-NO$_3$ + NH$_4$	−0.642*	0.294	0.470	−0.299	0.664*	0.761*	0.911*	0.736*

* Correlations significant at p ≤ 0.05.

Correlation between N-NO$_3$ and clay proved to be statistically significant in deluvial soils (r = –0.582*) as well as in alluvial soils (r = –0.712*). In the studied soils, the amount of nitrates was significantly positively correlated with the following parameters: volume of air, Eh, ODR and rH factors. In deluvial soils the amount of ammonium nitrogen was positively but not significantly correlated with the mentioned parameters. In alluvial soils the correlation proved to be significant only between N-NH4 and Eh, ODR.

On the basis of statistical analyses, it should be concluded that regarding redox potential, oxygen diffusion rate and rH factor (Table 6), the differences between deluvial and alluvial soils are statistically significant (p = 0.01). Diverse site conditions, in which mineralization took place, is demonstrated by statistically significant differences in N-NO$_3$ content (p = 0.01) and the sum of N-NH$_4$ and N-NO$_3$ (p = 0.05). However these differences are not significant in relation to N-NH$_4$.

Table 6

The significance of the difference between the means

Specification	Deluvial soils n = 25	Alluvial soils n = 13
Clay (fraction of $\varnothing$ < 0.002 mm) [%]	11.5	14.2
N-total [g · kg^{-1}]	2.73	2.83
Organic matter	49.39	42.5
N-NO$_3$ [mg · kg^{-1} d.m. of soil]	6.87**	2.72**
N-NH$_4$	4.51	2.73
N-NO$_3$ + N-NH$_4$	11.36*	5.45*
Eh [mV]	335**	202**
ODR [µg · m^{-2} · s^{-1}]	60.16**	36.8**
rH	23.5**	18.6**

* Differences significant at p ≤ 0.05; ** differences significant at p ≤ 0.01.

Conclusions

1. Alluvial and deluvial soils situated in morainic, riverine and delta landscapes, varied in texture, content of organic matter and site conditions.

2. The results indicate that the amount and forms of nitrogen that are released in the process of mineralization of organic matter depend on site conditions.

3. The highest amounts of nitrate and ammonium nitrogen were released in deluvial soils in the landscape of lakeland hills. These soils have the most beneficial soil-site conditions for nitrification and contain little and medium amounts of N-NO$_3$.

4. In subsurface horizons of alluvial soils occurring in delta and riverine landscapes and of deluvial soils in the landscape of morainic hills and plains, the conditions for nitrification were not beneficial. The value of Eh potential did not exceed 300 mV and more N-NH$_4$ than N-NO$_3$ was released in the process of mineralization.

5. During mineralization of organic nitrogen compounds, twice more nitrates and ammonium were released in deluvial soils than in alluvial soils.

Acknowledgement

References

[1] Sienkiewicz M.: Rozwój denudacji antropogenicznej w środkowej części Polski Północnej. UM, Toruń 1998, 103.
[2] Starkel L.: Przegl. Geograf. 1988, **60**(3), 251–265.
[3] Bieniek B.: Właściwości i rozwój gleb napływowych Pojezierza Mazurskiego. Acta Acad. Agricult. Tech. Olst., Agricultura, Suppl. B, 1997, **64**, 80.
[4] Orzechowski M., Smólczyński S. and Sowiński P.: Roczn. Glebozn. 2004, **55**(2), 311–320.
[5] Gotkiewicz J.: Zróżnicowanie intensywności mineralizacja azotu w glebach organicznych związane z odrębnością warunków siedliskowych. Rozpr. habilit. IMUZ, Falenty 1983, 111.
[5] Gotkiewicz J.: Bibl. Wiad. IMUZ 1987, **68**, 43–55.
[6] Gotkiewicz J.: Zesz. Probl. Post. Nauk Roln. 1996, **440,** 121–129.
[7] Pawluczuk J.: Ann. UMCS, Sec. E, 2004, **59**(2), 559–567.
[8] Maciak F.: Zesz. Probl. Post. Nauk Roln. 1977, **186**, 119–142.
[9] Smólczyński S.: Zesz. Probl. Post. Nauk Roln. 2006, **513**, 413–421.
[9] Turbiak J. and Miatkowski Z.: Zesz. Probl. Post. Nauk Roln. 2006, **513**, 507–513.
[10] Orzechowski M.: Zesz. Probl. Post. Nauk Roln. 2006, **513**, 1285–292.
[11] Sapek B.: Zesz. Probl. Post. Nauk Roln. 1996, **440**, 331–341.
[12] Gotkiewicz J. and Gotkiewicz M.: Bibl. Wiad. IMUZ 1987, **77**, 59–76.
[13] Pawluczuk J.: Roczn. Glebozn. 2006, **59**(1), 183–190.
[14] Kondracki J.: Geografia fizyczna Polski. PWN, Warszawa 1988, 463.
[15] Gotkiewicz J. and Smołucha J.: Zesz. Probl. Post. Nauk Roln. 1996, **331**, 119–136.
[16] Okruszko H.: Wiad. IMUZ 1971, **10**(1), 47–54.
[17] StatSoft, Inc.: 2007, STATISTICA, version 8.
[18] Smólczyński S. and Orzechowski M.: Water-Environ.-Rural Area 2009, **9**(1), 141–150.
[19] Systematyka gleb Polski. Roczn. Glebozn. 1989, **40**(3/4), 150.

MINERALIZACJA ORGANICZNYCH ZWIĄZKÓW AZOTU W GLEBACH NAPŁYWOWYCH OBSZARÓW MŁODOGLACJALNYCH W KRAJOBRAZIE MORENOWYM DOLIN RZECZNYCH I DELTOWYM

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Abstrakt: W glebach deluwialnych i aluwialnych w krajobrazie morenowym, dolin rzecznych i deltowym badano przebieg procesu mineralizacji organicznych związków azotu. Badania prowadzono jesienią 2008 r., po zakończeniu wegetacji. Azot mineralny oznaczono po inkubacji w wyciągu glebowym 1 % K_2SO_4. Ponadto wykonano pomiar potencjału redoks (Eh), natężenia dyfuzji tlenu (ODR) i obliczono wskaźnik rH.

Wyniki badań wskazują, że najkorzystniejsze warunki siedliskowo-glebowe do przebiegu procesu mineralizacji organicznych związków azotu występowały w glebach deluwialnych w krajobrazie pagórkowatym pojeziernym. W glebach tych uwalniało się najwięcej azotu mineralnego, według przyjętych norm zawartość azotu $N-NO_3$ była mała i średnia. Wartość potencjału Eh dochodziła do 390 mV, a natężenia dyfuzji tlenu do 74.2 $\mu g \cdot m^{-2} \cdot s^{-1}$. Stosunek azotu $N-NO_3 : N-NH_4$ kształtował się powyżej jedności. W poziomach powierzchniowych gleb aluwialnych w krajobrazie dolin rzecznych i deltowym pomimo większej zawartość

materii organicznej i N-ogólnego niż glebach deluwialnych, ilości uwalnianych mineralnych form azotu były zbliżone. W poziomach podpowierzchniowych gleb aluwialnych uwalniały się bardzo małe ilości azotu mineralnego, a stosunek azotu azotanowego do amonowego nie przekraczał jedności. Zróżnicowane warunki siedliskowe, w których przebiegały procesy mineralizacji związków azotu, spowodowały, że między glebach deluwialnych i aluwialnych wstępują statystycznie istotne różnice w zawartość azotu $N\text{-}NO_3$ oraz sumy $N\text{-}NO_3 + N\text{-}NH_4$.

Słowa kluczowe: gleby aluwialne, gleby deluwialne, azot azotanowy, azot amonowy, krajobraz morenowy, dolin rzecznych, deltowy

Apolonia OSTROWSKA[1] and Grażyna PORĘBSKA[1]

MINERAL COMPOSITION OF PLANTS AS AN INDICATOR OF THEIR QUALITY IN NITROGEN STRESS CONDITION

SKŁAD MINERALNY ROŚLIN JAKO WSKAŹNIK ICH JAKOŚCI W WARUNKACH NADMIARU AZOTU W ŚRODOWISKU

Abstract: The aim of this paper is to determine: relationships between the size of yield and the use of nitrogen necessary to its production for the assessment of N excess in the environment, and whether and to what extent the mineral composition of yield may be used as an indicator of N excess and the quality of yields. No correlation was found between the rye grain and potato tubers yield sizes and the content of N, P, K, Ca and Mg in a mass unit. N excess in the rye growth environment elevated N accumulation in comparable grain yields and leads to a disorder of between element relationships. N share in the sum of accumulated elements was found to increase to above 75 %, and, in some drastic cases, to even more than 80 %. At the same time, shares of the remaining elements were found to decline, in particular those of Ca and Mg. A similar effect of soil N excess was found in potatoes. Plant mineral composition taking into account the between element relationships may be used as an index of N excess in the environment and thus as an index of plant quality with respect to qualitative-quantitative stream of mineral elements entering the trophic chain.

Keywords: rye, potatoes, yield, nitrogen, mineral composition

The effect of N excess on the forest environment has been dealt with by numerous authors. The studies have focused, among other things, on establishing the so-called critical N values for a given state of the environment [1–4], N metabolism in plants [5–10], disorders of mineral composition in the tree foliage [2, 3, 11] as well as nitrate leaching to surface and ground waters [12–15]. The effect of N excess on soils and crops has been examined mainly from the view point of nitrate leaching to surface and ground waters [16–18], although some studies dealt with the evaluation of N excess and its effects within a definite natural space, eg farm holding, region [19].

Estimation of the effect of N or any other single element on soil and plant properties, on the basis of either its uptake by plants, its metabolism or accumulation and transformation in the soil, constitutes only a part in the evaluation of element flow

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disturbances in the environment [10, 20, 21]. Disorders of relations between elements resulting from the input of specific elements (deposition, waste, fertilizers) at the level of primary production project onto successive links of the trophic chain including humans. However, this important question has not so far been given enough attention in the literature. The authors have been dealing with the subject for many years.

The aim of this paper is to determine:

– relationships between the size of yield and the use of N necessary to its production for the assessment of N excess in the environment,

– whether and to what extent the mineral composition of yield may be used as an indicator of N excess and the quality of yields.

Materials and methods

Yields of rye and potatoes were analyzed as well as their chemical composition. To this end comprehensive data were acquired from the Institute of Crops, Fertilization and Soil Study. The data were already earlier described in the papers concerning chemical composition of plants [20], element flow between soil and plant [22, 23], and possibilities for estimating mineral composition of primary agricultural products with regard to the relationships between elements [21]. In this paper the effect of N excess was examined.

Chemical composition was examined of more than 200 rye samples (grain and straw) along with the same number of potato samples collected in the years 1976–1981 at model farm holdings situated in various regions of Poland. The plants were cultivated under similar agrotechnical and fertilization conditions. In the paper, solely rye grain and potato tubers were analyzed since the chemical composition of seeds (rye) is widely deemed to be most stable. Simultaneously the relationships were examined between the size of crop and the amount of N used for its production as nitrogen in agricultural production is regarded as one of the basic yield producing factors.

The interpretation of plant mineral composition was made by the author's own ANE method (*Accumulation of Nutrient Elements*). The above method is based on the analysis of elements contained in plants as both the Σ (sum) of all elements in a mass unit and the share of each element in this sum [24].

Coefficients of correlation between the crop size and the content of N, P, K, Ca and Mg in a mass unit of rye were calculated for all the samples analyzed and for five collective groups of samples representing crops only slightly differing in size. In the case of potatoes the correlation coefficients were calculated only for the collective groups of crops of approximately the same size.

Results

No correlation was found when comparing yield size and chemical composition in a mass unit of grain yield (Table 1).

Table 1

Chemical composition in rye grain in mmolc/kg in relation to crop size

Yield [Mg/ha]	N	P	K	Ca	Mg	Yield [Mg/ha]	N	P	K	Ca	Mg
	[mmol$_c$/kg]						[mmol$_c$/kg]				
1.6	966.5	108.4	135.5	33.4	96.2	2.8	889.5	95.0	144.0	39.2	108.2
1.8	1316.3	128.2	154.1	33.0	100.5	2.8	1529.6	126.2	124.3	36.5	109.0
1.8	1043.0	124.8	108.0	32.2	94.0	2.8	1343.5	116.1	152.0	20.5	77.0
2.0	913.0	121.1	115.1	36.6	66.8	2.8	1300.0	125.1	128.4	20.0	95.1
2.0	1078.2	109.4	131.3	20.4	119.6	2.8	1511.2	118.0	97.7	22.2	95.9
2.0	674.7	64.1	60.1	12.0	523.7	2.8	1300.0	112.0	133.7	25.0	100.3
2.2	1229.3	113.2	93.0	30.0	106.9	2.9	1062.3	135.8	143.2	34.3	116.4
2.2	1151.4	55.3	120.5	55.3	35.5	2.9	1436.0	108.7	143.5	9.8	94.7
2.3	1329.3	116.3	181.6	33.5	104.0	2.9	1035.0	116.0	95.2	45.5	88.3
2.3	1572.0	56.7	107.3	10.4	108.8	2.9	1207.0	115.5	114.0	7.6	76.0
2.4	1257.3	106.5	109.8	40.4	100.1	2.9	1093.0	72.4	108.7	19.5	63.0
2.4	885.5	93.9	156.8	17.3	88.9	2.9	1137.0	116.0	162.3	55.0	70.2
2.4	1278.7	106.0	120.7	17.9	107.6	2.9	1045.1	123.2	141.5	21.0	70.0
2.4	1165.8	115.7	141.9	26.2	92.5	2.9	1291.0	122.3	158.7	14.9	49.6
2.5	1150.0	102.7	107.2	65.5	64.0	2.9	1014.0	124.8	104.5	24.4	89.6
2.5	1159.0	101.8	108.0	64.0	88.2	3.0	1014.0	109.4	105.2	30.0	108.0
2.5	1242.5	105.9	99.6	18.7	90.3	3.0	1300.7	132.1	145.8	29.2	108.1
2.5	1024.0	99.8	55.0	17.9	83.2	3.0	975.0	128.3	109.8	34.4	75.4
2.5	325.0	135.5	13.0	24.7	108.4	3.0	895.0	106.2	115.1	20.4	142.0
2.5	950.0	106.4	92.3	25.6	107.7	3.0	1263.6	57.7	85.8	20.3	132.6
2.5	995.8	106.0	130.2	40.2	70.0	3.0	1290.6	128.2	108.0	27.0	133.0
2.6	1278.7	138.6	112.5	138.6	86.0	3.0	912.1	84.6	121.4	23.3	79.7
2.6	1171.0	57.4	117.7	54.5	34.4	3.0	903.2	114.0	129.0	33.0	86.0
2.6	1460.0	152.8	253.3	38.2	102.6	3.0	1064.0	85.8	133.7	19.7	104.1
2.6	1180.4	93.1	114.5	32.1	103.8	3.0	994.0	97.3	135.1	18.9	104.0
2.6	1156.4	106.8	85.1	24.5	88.0	3.0	843.2	110.4	125.6	9.3	74.4
2.6	1100.0	112.7	150.8	39.6	117.3	3.0	1114.0	110.1	125.8	7.1	72.9
2.7	1015.2	132.0	145.2	40.0	149.7	3.0	1114.0	121.5	80.0	7.2	101.5
2.7	1035.3	113.6	168.2	31.6	89.2	3.0	1171.3	119.2	123.8	31.0	94.4
2.7	1204.5	99.8	170.5	32.2	99.8	3.1	1286.0	100.0	155.8	55.2	75.4
2.7	995.0	104.6	93.0	10.3	89.1	3.1	1724.0	175.5	116.3	45.3	166.0
2.7	964.0	64.4	140.5	14.2	103.1	3.1	1067.0	119.4	130.7	20.0	82.4
2.7	1186.0	135.0	154.6	40.2	99.6	3.1	1151.0	129.7	79.0	25.3	98.0
2.7	813.8	106.8	133.8	20.2	49.5	3.1	1236.0	129.3	71.7	29.6	92.0
2.7	1113.8	119.2	146.9	30.5	43.6	3.2	1106.0	116.6	139.0	40.4	91.1
2.8	1356.0	140.1	123.3	35.2	105.7	3.2	1400.0	93.0	83.0	30.4	83.0
2.8	963.5	105.9	156.8	26.3	84.4	3.2	1465.0	15.1	15.1	7.5	13.5
2.8	965.0	105.9	143.9	49.7	44.5	3.2	1394.0	134.6	118.6	19.5	92.1
2.8	865.4	102.7	102.7	29.5	89.7	3.2	1271.0	125.0	93.0	30.5	83.3
2.8	931.0	120.0	146.3	59.9	74.5	3.2	1265.0	132.0	143.0	35.4	108.6
2.8	1258.5	135.4	117.4	13.1	107.6	3.2	1121.0	119.0	126.4	25.3	93.7
2.8	1169.7	62.7	122.5	21.9	83.2	3.2	1329.0	136.6	150.5	30.0	117.3

Yield [Mg/ha]	N	P	K	Ca	Mg	Yield [Mg/ha]	N	P	K	Ca	Mg
	[mmol_c/kg]						[mmol_c/kg]				
2.8	1076.2	130.6	107.4	39.2	98.7	3.2	1253.0	103.0	108.4	9.4	66.7
3.2	943.0	121.1	127.5	10.3	83.7	3.8	1132.0	93.3	93.3	24.4	91.8
3.4	1050.0	103.8	135.5	40.4	108.4	3.8	1072.0	96.8	132.0	17.6	133.4
3.4	829.0	103.8	107.5	92.7	86.5	3.8	1170.0	133.4	136.5	32.2	59.8
3.4	1043.0	93.8	125.6	45.5	82.8	4.0	923.0	83.0	70.0	40.0	68.5
3.4	2422.0	136.0	106.4	32.5	140.0	4.0	879.0	120.0	117.4	35.5	67.3
3.5	1715.0	100.4	119.2	50.2	102.5	4.3	885.0	123.4	143.8	22.0	54.8
3.5	1186.0	103.5	122.4	56.6	94.1	4.3	970.0	134.4	145.1	25.5	68.5
3.5	1014.0	77.1	123.5	45.2	66.4	5.0	1321.0	132.4	154.5	90.2	140.0
3.5	1128.0	128.5	127.4	22.2	44.3						

This lack of correlation was corroborated by low correlation coefficients regardless whether the comparisons were made using all the samples under analysis or using five collective groups of yield samples differing in size (Table 2). However, when the grain + straw yield size was compared with the element content in the whole biomass, the values of correlation coefficients for N, P and K were, respectively, 0.604; 0.759 and 0.710, while for Ca and Mg, respectively, 0.395 and 0.278.

Table 2

Correlation coefficient between yield size of grain and element content in a mass unit

Yield [Mg/ha]	Number of samples	Correlation coefficient				
		N	P	K	Ca	Mg
1.6–2.5	19	0.114	–0.290	–0.298	0.054	–0.132
2.6–2.9	37	0.012	0.095	–0.157	–0.344	–0.121
3.0–3.4	33	0.330	0.007	–0.025	0.469	–0.086
3.5–5.0	12	–0.177	0.500	0.404	0.407	0.327
1.5–5.0	101	0.023	0.092	0.053	0.092	0.021

Afterwards, the mineral composition of rye grain was compared taking into account yields selected for extreme differences in N content per a mass unit while maintaining the same yield size (Table 1, 3). The above comparison was based on the value of N accumulation in grain and its effect on the accumulation of the remaining elements, in other words, on the effect of N on the mineral composition of grain. The latter turned to be highly differentiated regardless the size of yield, what was mainly related to excessive accumulation of N. The differentiation of sums of the elements accumulated (N, P, K, Ca and Mg) at the same yield size was observed. At the same time, in many cases, the sums of elements in a mass unit were similar at varying sizes of grain yield. Likewise, shares of individual elements in the element sum fluctuated independently from the size of yield. In the element sum, N was found to take from ca. 68 % to more than 85 %, while the remaining elements (P, K, Ca and Mg) took from ca 15 to ca 32 %. With the increase in the share of N, the shares of Ca and Mg were most frequently

observed to decline, by even several fold in the case of Ca. In the extreme cases, when the share of N exceeded 80 %, the remaining elements decreased their proportions, and, inversely, the decline in the N share to ca 70 % and below was accompanied by an increase in shares of K in particular, but also of those of Ca and Mg (Table 3).

Table 3

Mineral composition of rye grain in relation to N accumulation in crops

Yield [Mg/ha]	N [kg in yield]	Σ NPKCaMg [mmol$_c$/kg]	N	P	K	Ca	Mg
			[% share in Σ]				
< 2	22	1340	72.1	8.0	10.1	2.6	7.2
	33	1732	76.0	7.4	8.9	1.9	5.8
2.0	26	1253	73.0	9.7	9.2	2.9	5.2
	30	1459	74.0	7.5	9.0	1.4	8.2
2.2	35	1418	81.0	3.9	8.6	3.9	2.6
	38	1572	78.2	7.2	5.9	1.9	6.8
2.3	43	1765	75.3	6.6	10.2	1.9	6.0
	51	1855	85.0	3.0	5.8	0.6	5.6
2.4	30	1242	71.0	7.8	12.6	1.4	7.2
	42	1614	77.9	6.6	6.8	2.5	6.2
2.5	33	1282	74.1	8.3	7.2	2.0	8.4
	44	1557	79.8	6.8	6.4	1.2	5.8
2.6	41	1520	72.4	7.4	9.9	2.6	7.8
	53	2007	72.7	7.6	12.6	1.9	5.2
2.7	38	1482	68.5	8.9	9.8	2.7	10.1
	45	1607	75.0	6.2	10.6	2.0	6.2
2.8	34	1190	72.7	8.6	8.6	2.6	7.5
	60	1926	79.4	6.5	6.5	1.9	5.7
2.9	42	1380	75.0	8.4	6.9	3.3	6.4
	58	1793	80.0	6.1	8.0	0.6	5.3
3.0	35	1163	72.5	9.5	10.8	0.8	6.4
	55	1716	75.8	7.7	8.5	1.7	6.3
3.1	46	1416	75.3	8.4	9.2	1.4	5.6
	75	2227	77.4	7.9	5.3	2.0	7.4
3.2	42	1286	73.3	9.4	9.9	0.8	6.6
	66	1746	84.0	4.9	6.6	1.0	3.3
3.4	39	1219	68.1	8.5	8.8	7.6	7.0
	115	2837	85.4	4.8	3.8	1.1	4.9
3.5	55	1450	77.8	8.8	8.8	1.5	3.1
	84	2087	82.2	4.8	5.7	2.4	4.9
3.8	58	1452	73.8	6.8	9.0	1.2	9.2
	62	1532	76.4	8.7	8.9	2.1	3.9
4.0	49	1219	72.1	9.8	9.6	2.9	5.6
	52	1184	78.0	7.0	5.9	3.3	5.8
5.0	83	1838	72.0	7.2	8.4	4.9	7.5
		Comparative standard of rye grain mineral composition					
		1600	74,0	7.3	8.7	2.6	6.4

So-called comparative standard was elaborated by Ostrowska (unpublished data) for the assessment of mineral composition of rye: the element sum Σ attained 1600 mmol$_c$/kg, wherein N constituted 74 %, P – 7.3 %, K – 8.7 %, Ca – 2.6 %, Mg – 6.4 %, while the combined share of Na, Mn, Cu, Fe and Zn – ca 1 %.

Significant differences could be observed when comparing the data analyzed with the values defined as standard, as concerns both the value of element sum Σ and its ion composition and it was mainly the amount of N accumulated which was held responsible for these differences.

Table 4

Yields and mineral composition of potatoes from farm holdings

Yield [Mg/ha]	Number of samples	Parameter	Σ [mmol$_c$/kg]	N	P	K	Ca	Mg	Na
				[% share in Σ]					
12.0–19.8	69	mean	1876.1	54.1	4.7	33.3	2.3	5.2	0.4
		s.d.	371.4	6.7	1.8	6.0	2.6	4.5	0.4
		v%	20	12	38	18	110	87	104
20.0–25.3	94	mean	2008.0	57.0	4.4	31.0	2.6	4.7	0.3
		s.d.	402.8	6.5	1.3	5.0	3.8	1.3	0.4
		v%	20	11	30	16	147	28	104
26.0–29.5	61	mean	1897.5	57.9	4.4	30.9	1.8	4.7	0.3
		s.d.	321.0	6.6	1.2	5.8	1.1	1.2	0.2
		v%	17	11	27	19	58	26	72
30.0–35.0	71	mean	1886.0	57.1	4.5	30.9	2.3	4.8	0.4
		s.d.	355.6	8.1	1.4	6.5	1.8	1.3	0.5
		v%	19	14	31	21	78	27	134
36.0–46.0	5	mean	1717.2	54.5	4.5	34.8	1.5	4.4	0.4
		s.d.	382.6	2.1	0.5	2.9	0.7	1.3	0.1
		v%	22	4	11	8	44	29	27
12.0–46.0	300	mean	1922.4	56.5	4.5	31.6	2.3	4.8	0.4
		s.d.	371.1	7.0	1.4	5.8	2.7	2.4	0.4
		v%	19	12	32	18	116	51	107

s.d. – standard deviation, v – variability coefficient.

A similar method was used for analyzing the chemical composition of potatoes (Tables 4–6). It was shown that both the element sum and its ion composition are similar regardless that respective yields varied in size with two-four fold differentiation of yield size. These values were probably conditioned by the type of potato fertilization applied in the farm holdings where mainly manure was used. Comparison of the latter results with those obtained in crops cultivated under conditions of differentiated mineral fertilization revealed significant differences in the value of element sum and the proportions of respective elements in the sum depending upon the type of fertilization applied (Table 5).

Table 5

Mineral composition of potatoes depending on fertilization type
(based on data Kuszelewski & Łabętowicz)

Fertilization	Σ [mmol$_c$/kg]	N	P	K	Ca	Mg
		[% share in Σ]				
0	1695	57.3	4.6	31.5	1.6	5.0
N	2167	70.0	3.3	24.5	0.7	1.5
PK	1680	41.3	3.4	51.0	1.5	2.8
Manure	1736	53.6	4.6	34.0	2.5	5.3

Excessive N accumulation caused by the mineral nitrogen fertilization in potatoes, as in rye, was responsible for ca 20 % rise in the value of element sum as compared with the values obtained in potatoes from dung fertilized fields. The share of N in this sum increased from ca 54 % to 70 %, what was accompanied by about three fold decrease in the shares of Ca and Mg as well as ca 30 % decrease in the share of K. It is worth emphasizing that, at the deficit of N (fertilization with P, K), the share of N decreased to ca 41 %, while an increase was observed in the share of K in the first place. This means that an increase in the amounts of N or K in the environment influences the accumulation of the remaining elements by plants what manifests itself in the ion composition of element sum (Table 5). The coefficients of correlation between the element content in a potato mass unit and the crop size were insignificant, except for the highest crops (above 35 Mg/ha) for which they are contained with the limits 0.4–0.7. It should be added that when considering crops which exceeded 35 Mg/ha the calculations were made for five replications only, while in the remaining groups of crops there were several tens of replications (Table 6).

Table 6

Correlation coefficients between potato yield size and element content in a mass unit

Element	Yield [Mg/ha]					
	12.0–46.0 n = 300	12.0–19.9 n = 69	20.0–25.9 n = 94	26.0–29.9 n = 61	30.0–35.0 n = 71	> 35.0 n = 5
N	0.052	0.032	0.006	0.188	0.045	0.588
P	0.033	0.324	0.164	0.055	0.066	0.656
K	0.112	0.219	0.089	0.165	0.065	0.442
Ca	0.041	0.258	0.071	0.089	0.073	0.703
Mg	0.082	0.041	0.174	0.135	0.009	0.710
Na	0.006	0.047	0.058	0.065	0.012	0.257
Σ	0.031	0.096	0.071	0.073	0.029	0.592

n – number of samples.

Discussion

The content of an element or elements in a plant or in its parts (leaves, stems) is regarded as an index or even as a limit of plant supply with a given element [20, 25].

The relationships between element content in a mass unit of plants and size of crop provide, in turn, a basis for the assessment of plant demand for nutrients which ensure the production of maximum crop. The above relationships have been differently established, among others using a DRIS method [20, 26–30]. For the assessment of the element contents in plants the comparative values have been elaborated which exists in the literature as, among others, standards, limit numbers, criteria and indices [27, 31–33]. These problems have been discussed in a monograph interpreting the chemical composition of plants [20].

The content of elements in crops has been linked to their size [27], to what one can agree under condition that element accumulation is examined in the whole biomass produced within a given area. In a mass unit, the content of element (elements) must not be, and, mostly is not linked to the size of crop, however, not uncommonly it has lower values for higher crops, what was also observed in our studies. Whereas no relationship was found between the size of crop (rye or potatoes) and the content of elements in a mass unit. It is because the crop maximization depends on both nutritional- and extra-nutritional factors, and the more the latter are approximating the optimum, the higher dilution of element content may occur in a mass unit.

The mineral composition may be identified with the chemical composition only in respect of the initial content of elements in a plant, significant differences have been noted when it comes to the interpretation of this content. When examining the values of element sum in mass unit and the values of shares of individual elements in their sum it became apparent that rye grain may display a large variety of its mineral composition even at the same size of crops. A higher accumulation of N is manifested by a higher share of N in the element sum. An increase in N share above 75 % is accompanied by a decrease in shares of mostly Ca and Mg, whereas when the share of N is higher than 80 %, than the remaining elements decrease their shares as well. Particular attention was paid to the share of Ca in Σ, which was found to decrease from the value of ca 2–3 %, according to the comparative standard, to the values lower than 1 %. This decrease in Ca accumulation in plants along with the increase in N in the growth environment was also reported in other papers [34, 35].

The differentiation of mineral composition in rye can hardly be discussed from the viewpoint of its nutritional value, despite that this issue should be considered given the presence of rye and other grain in the diet.

The interest in the excess of N in the agricultural environment arose mostly due to its effect on soil properties [36–38], and in particular on the contamination of ground and surface waters. The evaluation of N excess is made, among others, basing on the N balance in the environment, in the system: input – accumulation – output. However, according to Vikkari [39] this method is only an appraisal in view of many factors which have either immediate or intermediate effects on N cycles.

In general, the N excess is most frequently measured on the basis of pollution load in waters [19], inter alia when the soil is saturated with N [40, 41]. The excess of N in the environment was also measured by the degree of N binding in a plant [2, 6, 7]. It was observed that the more N was accumulated in plants the higher was its amount remaining in the mineral easily hydrolyzing form. Thus, as the measure of N excess the

ratio of N total to N mineral may be used, which under conditions of nitrogen stress may approximate the value of 1 [9, 10]. The excess of N has also been measured by determining the level of the so-called critical load for N deposition above which negative effects are manifested in the forest environment [42], and by the ratio of C:N, which shows N binding in the soil organic matter [15, 41, 43].

N content and its transformation in plant and soil have been studied by many authors. However, there is lack of papers concerning the mineral composition of plants taking into account the disorders of between elements relationships resulting from excess or deficit of individual elements. From our studies the conclusion can be drawn that the sum of elements accumulated in a mass unit constitutes an index of plant nutrient supply. The share of elements in their sum constitutes, in turn, an index of either excess or deficit of respective elements, in particular of N in the environment. The mineral composition of plants in general may be regarded as an index of plant quality with respect to the amount of elements entering the trophic chain and the between element relationships.

Conclusions

1. Disorders in the mineral composition of plants, and especially those in the relationships between elements in their sum accumulated in a mass unit are an index of excess/deficit of an element (elements) in the environment.

2. The mineral composition of rye and potatoes differs with respect to both the element sum and the share of elements in their sum independently from the yield size, but it depends on the amount of N accumulated.

3. The excess of N in the environment brings about its excessive accumulation in the crop; crops of the same size may differ as much as twice with respect to N accumulation.

4. No correlation was found between the crop size and the content of N, P, K, Ca and Mg in a mass unit in both rye grain and potato tubers, however, there was a correlation between the crop size and accumulation of N, P and K in these crops.

References

[1] Augustin S., Bolte A., Holzhausen M. and Wolff B.: Eur. J. Forest Res. 2005, **124**, 289–300.
[2] Elvir J.A., Wiersma G.B., Day M.E., Greenwood M.S. and Fernandez I.J.: Forest Ecol. Manage. 2006, **221**, 207–214.
[3] Ostrowska A., Porębska G., Sienkiewicz J., Borzyszkowski J. and Król H.: Soil and plant properties in environmental monitoring. IOŚ Warszawa 2006, 1–159 (in Polish).
[4] Sirulnik A.G., Allen E.B., Meixner T. and Allen M.F.: Soil Biol. Biochem. 2007, **29**, 24–32.
[5] Collier M.D., Fotelli M.N., Nahm M., Kopriva S., Rennenberg H., Hanke D.E. and Geßler A.: Plant, Cell, Environ. 2003, **26**, 1549–1560.
[6] Fotelli M.N., Nahm M., Heidenfelder A., Papen H., Rennenberg H. and Geßler A.: New Phytologist 2002, **154**, 85–97.
[7] Nahm M., Holst T., Matzarakis A., Mayer H., Rennenberg H. and Geßler A.: Eur. J. Forest Res. 2006, **125**, 1–14.
[8] Rothstein D.E. and Cregg B.M.: Forest Ecol. Manage. 2005, **219**, 69–80.
[9] Ostrowska A.: Roczn. Glebozn. 1974, **XXV**, suppl. 133–142.

[10] Ostrowska A. and Porębska G.: Arch. Environ. Protect. 2008, **34**(3), 193–200.

[11] Hendriks C.M.A., de Vries W. and van den Burg J.: Effects of acid deposition on 150 forest stands in the Netherlands. Relationships between forest vitality characteristics and the chemical composition of foliage, humus layer, mineral soil and soil solution. Raport 69.2. DLO Winand Staring Centre, Wageningen 1994.

[12] Herrmann M., Pust J. and Pott R.: Plant Soil 2005, **273**, 129–137.

[13] Van der Salm C., de Vries W., Reinds G.J. and Diese N.B.: Forest Ecol. Manage. 2007, **238**, 81–91.

[14] Rothe A., Huber Ch., Kreutzer K. and Weis W.: Plant Soil 2002, **240**, 33–45.

[15] Dise N.B., Matzner E. and Forsius M.: Environ. Pollut. 1998, **102**, 453–456.

[16] Sapek A.: *Groundwater from meadow soils as a link of nitrogen and phosphorus cycle in the environment*, [in:] Element cycling in the Environment. Monography t. III, IOŚ Warszawa 2005, 190–193 (in Polish).

[17] Munoz-Carpena R., Ritter A., Bosch D.D. Schaffer B. and Potter T.L.: Agric. Water Manage. 2008, **95**, 633–644.

[18] Entry J.A. and Sojka R.E.: J. Environ. Manage. 2008, **87**, 364–372.

[19] Sapek B.: *Estimation of environmental risk in the light of soil and water monitoring within farm*, [in:] Element cycling in the Environment. Monography, t. I, IOŚ Warszawa 2001, 295–304 (in Polish).

[20] Ostrowska A. and Porębska G.: Chemical composition of plants its interpretation and application in the environmental protection. Monography. IOŚ Warszawa 2002 (in Polish).

[21] Ostrowska A.: Polish J. Environ. Stud. 1999, **8**, supl. II, 51–56.

[22] Ostrowska A.: Post. Nauk Roln. 2005, **4**, 119–131 (in Polish).

[23] Ostrowska A.: *Element cycling in the environment, distortions and environmental risk involved*, [in:] Element cycling in the Environment, II International Scientific-Technical Conference, Warsaw 27–29 October 1997, IOŚ Warszawa 1997, 105–116.

[24] Ostrowska A.: Application of ANE value and of shares of individual elements in this value for determining the difference between various plant species. Genetic aspects of plant mineral nutrition. Martinus Nijhoff Public. **27**, 1987.

[25] Bell P.F., Vaughn A. and Bourgeois W.J.: J. Plant Nutr. 1997, **20**(6), 733–743.

[26] Kenworthy A.L.: Soil Sci. Soc. Amer. Spec. Pub. 1967, vol. 2.

[27] Mercik S., Sommer K. and Rossing K.: Roczn. Nauk Roln. 1993, Ser. A, **110**(1–2), 33–57 (in Polish).

[28] Sumner M.E.: Soil Sci. Amer. J. 1981, **45**, 87–90.

[29] Walworth J.L. and Sumner M.E.: Adv. Plant Nutr. 1986, **3**, 193–241.

[30] Walworth J.L. and Sumner M.E.: Adv. Soil Sci. 1987, **6**, 149–188.

[31] Parent L.E., Poirier M. and Asselin M.: J. Plant Nutr. 1995, **18**(5), 1013–1025.

[32] Montanez L. and Sanz M.: J. Plant Nutr. 1994, **17**(10), 1647–1657.

[33] Ingestad T.: Physiol. Plant. 1979, **45**, 373–380.

[34] Ostrowska A.: Effect of nutrition conditions on ionic proportions in plants on the examine of common pine (*Pinus silvestris* L). Inst. Warzywn., Skierniewice 1985 (in Polish).

[35] Perakis S.S., Maguire D.A., Bullen T.D., Cromack K., Waring R.H. and Boyle J.R.: Ecosystems 2006, **9**, 63–74.

[36] Ostrowska A. and Porębska G.: Polish J. Soil Sci. 2001, **XXXIV**/1, 35–42.

[37] Qian Ch. and Cai Z.: Plant Soil 2007, **300**, 197–205.

[38] Prietzel J., Stetter U., Klemmt H.J. and Rehfuess K.E.: Plant Soil 2006, **289**, 153–170.

[39] Yli-Viikari A., Hietala-Koivu R., Huusela-Veistola E., Hyvonen T., Perala P. and Turtola E.: Ecol. Indicators 2007, **7**, 150–163.

[40] Aber J.D. and Magill A.H.: Forest Ecol. Manage. 2004, **196**, 1–5.

[41] Rowe E.C., Evans C.D., Emmett B.A., Reynolds B., Helliwell R.C., Coull M.C. and Curtis C.J.: Water, Air, Soil Pollut. 2006, **177**, 335–347.

[42] Groffman P.M., Baron J.S., Blett T., Gold A.J., Goodman I., Gunderson L.H., Levinson B.M., Palmer M.A., Paerl H.W., Peterson G.D., LeRoy Poff N., Rejeski D.W., Reynolds J.F., Turner M.G., Weathers K.C. and Wiens J.: Ecosystems 2006, **9**, 1–13.

[43] Evans Ch.D., Reynolds B., Jenkins A., Helliwell R.C., Curtis Ch.J., Goodale Ch.L., Ferrier R.C., Emmett B.A., Pilkington M.G., Caporn S.J.M., Carroll J.A., Norris D., Davies J. and Coull M.C.: Ecosystems 2006, **9**(3), 453–462.

SKŁAD MINERALNY ROŚLIN JAKO WSKAŹNIK ICH JAKOŚCI W WARUNKACH NADMIARU AZOTU W ŚRODOWISKU

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Abstrakt: Celem pracy było ustalenie związków między ilością plonów i zużyciem azotu na ich wyprodukowanie z punktu widzenia oceny nadmiaru azotu w środowisku oraz ustalenie, czy i na ile skład mineralny plonów może być wskaźnikiem jego nadmiaru. Nie stwierdzono korelacji między plonem ziarna ani ziemniaków a zawartością N, P, K, Ca i Mg w jednostce masy. Nadmiar azotu w środowisku wzrostu żyta powoduje jego większą akumulację w plonach ziarna tej samej ilości oraz zaburzenie relacji między składnikami. Udział azotu w sumie akumulowanych składników wzrasta powyżej 75 %, a w drastycznych przypadkach powyżej 80 %, zaś udziały pozostałych składników są redukowane, zwłaszcza udział Ca i Mg. Podobny efekt nadmiaru azotu występuje także w ziemniakach. Skład mineralny roślin pod względem relacji między składnikami może być wskaźnikiem nadmiaru azotu w środowisku, a tym samym ich jakości pod względem ilościowo-jakościowego strumienia składników mineralnych wchodzących do łańcucha troficznego.

Słowa kluczowe: żyto, ziemniaki, ilość plonu, azot, skład mineralny

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EFFECT OF INTERCROPS
ON THE CONTENT OF MINERAL NITROGEN IN SOIL
IN AUTUMN AND SPRING

WPŁYW MIĘDZYPLONÓW NA ZAWARTOŚĆ AZOTU MINERALNEGO
W GLEBIE JESIENIĄ I WIOSNĄ

Abstract: The aim of the present research was to determine the influence of undersown crops and stubble crops on the content of mineral forms of nitrogen in soil profile in autumn and spring.

Field experiments were carried out at the Experimental Farm in Zawady, owned by the University of Podlasie in Siedlce. The following combinations of intercrops were taken into account: control object (without intercrop), undersown crops – biomass plowed down in autumn (white clover, Italian ryegrass), stubble crop – biomass plowed down in autumn (oil radish), stubble crop – biomass left in the form of mulch (oil radish) till spring. The content of nitrate and ammonia ions were determined twice, *ie* in autumn and spring, in two layers of soil (0–30 and 31–60 cm). The results pointed out that, putting the intercrops into the cultivation limited the content of mineral nitrogen in soil in autumn, and increased in spring. The highest concentration of nitrate and ammonia ions was noted in soil in spring, when white clover was plowed down. When the surface of soil was mulched with stubble crop from white mustard in the time of winter, it decreased the content of mineral nitrogen in spring.

Keywords: undersown crop, stubble crop, mulch, mineral nitrogen, soil

In today's agriculture more and more attention is paid to protect the soil environment. A special role is attributed to the intercrops, which may be regarded as "accumulators" of unused nutrients in forecrop to plants subsequently incoming in the crop rotation. Its leaching into groundwater of the areas covered with flora or litter is several times smaller than the soil remaining in the black fallow [1–5]. Stubble crops prolongs the duration of cover crops, and undersown crops moreover increases the compactness of cornfield. On this basis, it appears that the contamination of agricultural activity of watercourse and water tanks from farms growing the intercrops is smaller than from farms growing plants only in the main yield [2, 5]. It is recommended to

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leave the stubble crops for a period of winter in the form of mulch [3, 6, 7]. This solution should reduce the leaching of nitrates from the soil during the autumn–winter period. Still there is a little on the subject of the experimental data. So there emerges a need to conduct a study to determine the effect of undersown crops and stubble crops on the content of mineral forms of nitrogen in the soil profile in spring and autumn.

Material and methods

Field experiments were carried out in 2000–2003 at the Experimental Farm in Zawady, owned by the University of Podlasie in Siedlce. The researches were carried out on a soil which was rated to autogenic soil, russet soil order, fawn soil type made from hard sandy loam. This experiment was established on a very good cereal complex soil, belonging to the quality class IVa. The arable layer of soil characterized with pH 6.4–6.6, Hh 0.916–0.921 cmol(+) $\cdot$ kg^{-1}, S 10.87–10.92 cmol(+) $\cdot$ kg^{-1}, T 11.79–11.84 cmol(+) $\cdot$ kg^{-1}, V 92.20–92.23 %, and the content of N_{tot} 0.684–0.695 g $\cdot$ kg^{-1}, in it N-NH$_4$ 4.39–4.47 mg $\cdot$ kg^{-1} and N-NO$_3$ 7.18–7.26 mg $\cdot$ kg^{-1}, assimilable forms: P 50.2–50.8 mg $\cdot$ kg^{-1}, K 112.5–113.7 mg $\cdot$ kg^{-1} and Mg 53.5–54.2 mg $\cdot$ kg^{-1}. The experiment was a three-replicate split blocks design. The size of plot at the beginning was 20 m^2, and during the harvest it was 15 m^2. The following combinations of intercrops were taken into account: control object (without intercrop cultivation), undersown crops – biomass plowed down in autumn (white clover 18 kg ha^{-1}, Italian ryegrass 30 kg ha^{-1}), stubble crop – biomass plowed down in autumn (oil radish 30 kg ha^{-1}), stubble crop – biomass left in the form of mulch till spring (oil radish 30 kg ha^{-1}). Undersown crops were sown into spring barley cultivated for grain, and stubble crops were sown after its harvest. In early spring mineral fertilizers were used: 60 kg N, 39.6 kg P and 99.6 kg K per 1 ha. Spring barley was sown in the first decade of April. Undersown crops were sown into spring barley by the seeder across the rows in a day of sowing of protective plant. The harvest of spring barley was made in the third decade of July. After the harvest of spring barley on each plot which was assigned to undersown crops cultivation the mineral fertilization was used: 60 kg N $\cdot$ ha^{-1}, 13.2 kg P $\cdot$ ha^{-1} and 49.8 kg K $\cdot$ ha^{-1}. Oil radish which was cultivated in stubble catch crop was sown in the first decade of August. In autumn, in third decade of October, from each plot of undersown crop mean samples of fresh mass and after harvest remnants were collected with its root mass from 30 cm of soil layer to establish the yield of dry mass. Intercrops which were grown produced per 1 ha the following quantities of dry mass: white clover 5.2 Mg ha^{-1}, Italian ryegrass 6.3 Mg ha^{-1} and oil radish 4.4 Mg ha^{-1}. On the control object from the harvesting of spring barley to the late autumn black fallow was maintained. Soil attempts, from each plot were collected twice, ie in autumn (the third decade of October) and in spring (the first decade of April), from two layers of soil (0–30 and 31–60 cm) to denote the contents of ammonium and nitrate ions by calorimeter method [8]. Soil sample were collected by using of soil gimlet. After soil sample collection (about 200 g) it was placed in a plastic bag. These samples were kept in the refrigerated storage until the analysis. Received results of researches were drawn up statistically. Average for significant sources of variation were compared with the Tukey test.

The experimental years was characterised with changeable weather conditions. About the success of undersown crops decides the amount of rainfalls and temperature during the months of the growing season (Table 1). The most favourable was year 2000. A little bit worse weather conditions were noted in 2002, and the worse in 2001. Taking into account the amount of rainfalls and temperatures, with the lack of rainfalls in autumn–spring season it could be claimed that in every year of researches the lower amount of rainfalls was noted. The warmest, with the lowest amount of rainfalls was autumn–spring season in 2000/2001, and the coldest with higher amount of rainfalls was 2002/2003 season.

Table 1

The weather conditions in the period of conducting investigations
according to the Meteorological Station in Zawady

Months	Temperature [°C]					Rainfall [mm]				
	2000	2001	2002	2003	Average from 1951–1990	2000	2001	2002	2003	Average sum from 1951–1990
I	–1.1	–1.1	–0.4	–3.7	–3.1	5.8	19.9	8.7	7.7	24.5
II	2.2	–1.9	3.2	–56	–3.2	24.5	9.4	37.5	4.7	23.3
III	3.7	1.5	4.0	1.4	1.0	19.2	3.6	15.8	7.0	27.0
IV	12.9	8.7	90	7.1	7.2	47.5	69.8	12.9	13.6	29.4
V	16.4	15.5	17.0	15.6	13.2	24.6	28.0	51.3	37.2	54.3
VI	19.5	17.1	17.2	18.4	16.2	17.0	36.0	61.1	26.6	69.3
VII	19.0	23.8	21.0	20.0	17.6	155.9	55.4	99.6	26.1	70.6
VII	19.1	20.6	20.2	18.5	16.9	43.6	24.0	66.5	4.7	59.8
IX	11.8	12.1	12.9	13.5	12.7	61.1	108.0	18.7	24.3	48.2
X	11.7	10.6	6.9	5.4	8.0	3.2	28.0	48.9	38.0	32.0
XI	6.7	2.3	3.8	4.7	2.6	32.6	28.0	16.1	14.7	39.2
XII	1.3	–6.6	–7.7	0.5	0.4	22.0	13.4	0.7	17.0	37.3

Results and discussion

Statistic analysis indicates the important influence of intercrops on the content of mineral nitrogen which was determined in soil profile in autumn (Table 2). The highest content of mineral nitrogen in soil was determined on control object, without intercrops cultivation. It is consistent with the results of research of Fotyma [9] and Nowakowski and Krüger [4], who found that in autumn at the end of the growing season of plants as a result of reduced nitrogen taking up and mineralization of organic nitrogen may increase the content of this component in the soil again. In own researches introduction the intercrops to the cultivation, especially non-papilionaceous plants (Italian ryegrass and oil radish) significantly decreased the content of mineral nitrogen in the soil. Also after white clover the content of mineral nitrogen in soil was significantly lower than in control object, but higher than noted after intercrops cultivation from non-papiliona-ceous plants. Losses of mineral nitrogen in the soil found in late autumn following

intercrops cultivation was clear, though far less than obtained in the other studies [1, 6, 7, 10]. It should be stressed that in conditions of intensive agriculture the quota of this component remaining in the soil after the cultivation of cereals is large, hence the greater impact of intercrop. Moreover in favourable habitat conditions (better soils, longer growing season) biomass produced by intercrop is greater, and consequently also higher intake of nitrogen.

Table 2

The effect of intercrops on the content of mineral forms of nitrogen in the soil determined in the autumn [mg · kg^{-1} d.m. of soil] (average from 2000–2002)

Intercrop	N-NH$_4^+$		N-NO$_3^-$		Total	
	The layer of soil [cm]					
	0–30	31–60	0–30	31–60	0–30	31–60
Control object	4.83	2.36	7.23	4.83	12.06	7.19
White clover	2.12	1.37	4.81	2.34	6.93	3.71
Italian ryegrass	1.27	1.08	3.45	1.79	4.72	2.87
Oil radish	1.38	1.12	3.58	1.83	4.96	2.95
Oil radish – mulch	1.32	1.11	3.57	1.81	4.89	2.92
Average	2.18	1.41	4.53	2.52	6.71	3.93
LSD$_{0.05}$	0.23	0.18	0.46	0.32	1.14	0.86

Analyzing this experiment data the content of mineral nitrogen in two layers of soil clearly demonstrated a higher concentration of this component in the upper soil layer than in bedrock. It is confirmed by Kuś and Jonczyk researches [3]. Own researches and Mazur et al [11] and Trawczynski [12] researches showed a higher content of nitrogen than ammonium ion in two layers of soil. The concentration of mineral nitrogen determined in the soil profile in spring was significantly modified by the factor of experiment (Table 3).

Table 3

The effect of intercrops on the content of mineral forms of nitrogen in the soil determined in the spring [mg · kg^{-1} d.m. of soil] (average from 2001–2003)

Intercrop	N-NH$_4^+$		N-NO$_3^-$		Total	
	The layer of soil [cm]					
	0–30	31–60	0–30	31–60	0–30	31–60
Control object	5.34	3.74	8.82	6.85	14.36	10.54
White clover	7.16	2.76	19.26	5.74	26.42	8.50
Italian ryegrass	5.81	2.12	13.84	3.80	19.65	5.92
Oil radish	6.47	2.38	14.12	3.97	20.86	6.35
Oil radish – mulch	5.63	1.86	10.75	2.69	16.38	4.55
Average	5.72	2.57	13.16	5.01	18.93	7.57
LSD$_{0.05}$	0.67	0.34	1.32	0.60	1.26	0.89

Introduction of intercrops into the cultivation significantly increased the content of mineral nitrogen in the soil, especially after white clover plowing down. This positive impact which aim is to stimulate the processes of mineralization of organic nitrogen in the soil, referred to as "priming effect" [7, 9, 12]. Significantly lower content of mineral nitrogen in the soil was recorded after plowing down of the non-papilionaceous plants, and the lowest after oil radish left in the form of mulch till spring. Kuś and Jończyk [3] and Nowakowski and Krüger [4] claimed that intercrop biomass left till spring on the surface of the field is degraded slower than on objects with ploughing. It has shown that the use of such a solution poses less risk of potential loss of nitrogen from the soil during the autumn–winter period. Analyzing the content of mineral forms of nitrogen in the soil, in spring and autumn higher concentration of nitrate ions was noted than ammonium ions. It is similar to Möler and Stiner [7] and Mazur et al [11] researches. It should be noted, that problems with limiting the losses of nitrogen in the soil, including the cultivation of intercrops, gain a particular relevance in recent period.

Conclusion

1. Intercrops introduction into the cultivation significantly reduced the content of mineral nitrogen in the soil in autumn, and increased in spring. The highest concentration of nitrate and ammonium ions was noted in soil in spring, after white clover plowing.

2. Mulching the surface of the soil in the period of winter by stubble crop from oil radish significantly decreased the content of mineral nitrogen in the soil in spring. In autumn and spring, on every object the highest concentration of nitrate ions was noted than ammonium ions.

3. The top layer of soil characterized with higher mineral nitrogen content than the lower layer.

References

[1] Buchner W. and Apel B.: Top Agrar. 1989, **6**, 52–56.
[2] Duer I.: Fragm. Agronom. 1996, **1**(49), 29–43.
[3] Kuś J. and Jończyk K.: Roczn. Nauk Roln., 1999, Ser. A, **114**(3–4), 83–95.
[4] Nowakowski M. and Krüger K.W.: Biul. Inst. Hodow. Aklim. Rośl. 1997, **202**, 105–115.
[5] Songin W.: Post. Nauk Roln. 1998, **2**, 43–51.
[6] Jackson L.E., Wyland L.J. and Stivers L.J.: J. Agric. Sci. 1993, **121**, 55–62.
[7] Möler K. and Stinner W.: Eur. J. Agronom. 2009, **30**, 1–16.
[8] Ostrowska A., Gawliński S. and Szczubiałka Z.: Metody analizy i oceny właściwości gleb i roślin. Inst. Ochr. Środ., Warszawa **rok???**, 331 pp. (in Polish).
[9] Fotyma E.: Zesz. Probl. Post. Nauk Roln. 1996, **440**, 89–100.
[10] Hansen B., Kristensen E.S., Grant R., Hogh-Jensen H., Simmelsgaard S.E. and Olsen J.E.: Eur. J. Agronom. 2000, **13**, 65–82.
[11] Mazur T., Wojtas A., Sądej W. and Mazur Z.: Zesz. Probl. Post. Nauk Roln. 1996, **440**, 257–261.
[12] Trawczyński C.: Biul. Inst. Hodow. Aklim. Rośl. 2001, **217**, 177–185.

WPŁYW MIĘDZYPLONÓW NA ZAWARTOŚĆ AZOTU MINERALNEGO W GLEBIE JESIENIĄ I WIOSNĄ

Katedra Szczegółowej Uprawy Roślin
Akademia Podlaska w Siedlcach

Abstrakt: Celem przeprowadzonych badań było określenie wpływu wsiewek międzyplonowych i międzyplonów ścierniskowych na zawartość mineralnych form azotu oznaczonego w profilu glebowym jesienią i wiosną.

Badania polowe przeprowadzono w RSD w Zawadach należącej do Akademii Podlaskiej w Siedlcach. W doświadczeniu badano następujące kombinacje międzyplonów: obiekt kontrolny (bez międzyplonu), wsiewka międzyplonowa – biomasa przyorana jesienią (koniczyna biała, życica wielokwiatowa), międzyplon ścierniskowy – biomasa przyorana jesienią (rzodkiew oleista), międzyplon ścierniskowy – biomasa pozostawiona do wiosny w formie mulczu (rzodkiew oleista). Zawartość jonów amonowych i azotanowych oznaczono dwukrotnie, tj. jesienią i wiosną, w dwóch warstwach gleby (0–30 i 31–60 cm). Otrzymane wyniki pozwalają stwierdzić, iż wprowadzenie do uprawy międzyplonów zmniejszało zawartość azotu mineralnego w glebie jesienią, a zwiększało wiosną. Największe stężenie jonów amonowych i azotanowych odnotowano w glebie wiosną, po przyoraniu koniczyny białej. Mulczowanie powierzchni gleby w okresie zimy międzyplonem ścierniskowym z rzodkwi oleistej zmniejszało zawartość azotu mineralnego wiosną.

Słowa kluczowe: wsiewka międzyplonowa, międzyplon ścierniskowy, mulcz, azot mineralny, gleba

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LEACHING OF NITROGEN FORMS
FROM SOIL FERTILIZED WITH SEWAGE SLUDGE

WYMYWANIE FORM AZOTU
Z GLEBY NAWOŻONEJ OSADAMI ŚCIEKOWYMI

Abstract: The aim of the study has been to evaluate the extent of loss of various nitrogen forms leached from soil fertilized with sewage sludge, farmyard manure and NPK. Sewage sludge and FYM were applied as a single dose of 10 Mg $\cdot$ ha^{-1} or two doses, each of 5 Mg $\cdot$ ha^{-1}. It has been demonstrated that all the objects fertilized with sewage sludge of sewage based composts experienced more severe leaching of total nitrogen and nitrogen forms compared with the control. More total nitrogen was leached from soil to which sewage sludge was introduced as a dose divided into two applications (2×5 Mg $\cdot$ ha^{-1}) than from soil which received a single rate of this fertilizer (10 Mg $\cdot$ ha^{-1}). Nitrate(V) nitrogen dominated among the mineral forms of nitrogen in soil filtrate. Higher loss of this nitrogen form occurred in treatments receiving compost made from sewage sludge with straw (10 Mg $\cdot$ ha^{-1}) or dried and granulated sewage sludge than when composted sewage sludge or traditional fertilization were applied. Water was more polluted with N-NH$_4^+$ when sewage sludge compost was used, but when it was made with straw, N-NO$_2^-$ was the predominant water pollutant.

Keywords: nitrogen leaching, sewage sludge, compost, soil

Soil fertilization with rates of nutrients higher than demanded by crops may cause changes in the ionic equilibrium of soil solution and contribute to migration of nutrients to surface and groundwater. Thus, it is necessary to determine the level of loss of nutrients in order to guarantee suitable crop nutrition while protecting natural environment from pollution. Being a source of nutrients and organic matter, sludge from wastewater treatment plants can be used to fertilize soil, once it meets the norms established to monitor the content of heavy metals and pathogenic microorganisms.

Amounts of nitrogen washed from soil depend on several factors, including types and rates of fertilizers. Many authors claim that there is positive correlation between the rate

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of fertilizers and the leaching of nutrients from soil [1]. Many authors indicate that there is a relationship between rates of fertilizers and amounts of nutrients leached from soil [2–6]. The concentration of nitrogen in soil leachate is also conditioned by the type of soil. Mineral forms of this element are highly mobile, particularly when their uptake by plants is limited or when high rates of fertilizers are introduced to light soils [7]. Migrating downwards the soil profile, nutrients and rainfall can reach groundwater and, eventually, surface water. One way to monitor quality of this water is via lysimetric tests [8].

The aim of the present study has been to determine the loss of total nitrogen and nitrogen forms from soil fertilized with sewage sludge versus analogous loss when natural and mineral fertilizers are used.

Material and methods

In order to evaluate the effect of sewage sludge on potential leaching of nutrients from soil, a model lysimetric experiment has been performed under controlled laboratory conditions. The experiment was established as strict field trials, during which composted sewage sludge, sewage sludge with straw as well as dried and granulated sludge were examined. The effect produced by sewage sludge was compared with the one obtained when conventional fertilization, consisting of FYM or NPK, was used. Sewage sludge and FYM were applied as a single rate of $10 \text{ Mg} \cdot \text{ha}^{-1}$ in the first year of the experiment, or an identical dose divided into two treatments, each of $5 \text{ Mg} \cdot \text{ha}^{-1}$, introduced to soil in the first and third year of the trials. The soil used in this lysimetric experiment was sampled from three soil horizons: 0–30 cm, 31–60 cm and 61–90 cm. While filling lysimeters with soil material, the original position of soil genetic layers was maintained so as to create conditions as close as possible to the ones in the field. In total, each cylinder was filled with 7.5 kg soil, ie 2.5 kg from each soil horizon.

For washing the soil, redistilled water was used in the amount corresponding to the average annual rainfall in the province of Warmia and Mazury (605 mm).

The following determinations were made in the soil filtrate: total nitrogen by Kjedahl's method, ammonia nitrogen by colorimetry with Nessler's reagent, nitrate(V) nitrogen using an ion-selective electrode, nitrate(III) nitrogen by colorimetry with sulphanilic acid and 1-naphthylamine. Organic nitrogen was calculated as a difference between total and mineral nitrogen.

Results and discussion

In most of the treatments fertilized with sewage sludge or sludge composts, the amounts of total nitrogen and nitrogen forms leached from soil were lower than in the control objects or the treatments involving mineral fertilization (Tables 1–6). The amounts of leached forms of nitrogen in fertilized objects were varied and depended on the type of a fertilizer and its application method. More total nitrogen was leached from the soil to which fertilizers were introduced in doses divided into two applications $(2 \times 5 \text{ Mg} \cdot \text{ha}^{-1})$ compared with the one which received the same rate of fertilizers

given as a single dose (10 Mg · ha^{-1}). The highest quantity of total nitrogen leached from soil, on average 16.64 mg per lysimeter (11.46 kg N · ha^{-1}), was noticed in soil filtrates obtained from treatments fertilized with sewage compost (Table 1). Soil fertilized with sludge compost mixed with straw (both as a double dose 2 × 5 Mg · ha^{-1} or a single dose 10 Mg · ha^{-1}) was determined to lose as much total nitrogen as soil nourished with dried and granulated sludge.

Table 1

Total nitrogen leaching

Dose	Control	NPK	FYM	Dried and granulated sewage sludge	Composted sewage sludge	Composted sewage sludge + straw
[mg per lysimeter]						
10 Mg · ha^{-1}	16.63	18.48	14.78	12.32	16.02	13.55
2 × 5 Mg · ha^{-1}			16.02	14.78	17.25	14.78
Average			15.40	13.55	16.64	14.16
[kg · ha^{-1}]						
10 Mg · ha^{-1}	11.45	12.73	10.18	8.48	11.03	9.33
2 × 5 Mg · ha^{-1}			11.03	10.18	11.88	10.18
Average			10.61	9.33	11.46	9.76

Experiments reported by other researchers prove that fertilization contributes to more profound leaching of nitrogen from soil, and mixed organic and mineral fertilization causes higher nitrogen loss than organic fertilization alone [9]. It has also been shown that higher nitrogen loss can occur when sludge composts [1] or soil liming [3] are applied. Some authors relate nitrogen loss with soil conditions, suggesting that more nitrogen is lost in sandy and loamy soils compared with loess soil [10]. The amount of leached nitrogen can be as high as 140 kg N · ha^{-1}, which is observable particularly in fallow sandy soils [11, 12].

In our experiment, most organic nitrogen was leached from unfertilized soil (Table 2). The leaching of organic nitrogen from fertilized treatments was nearly 32 % lower than from the control object. Among the fertilized objects, similarly to total nitrogen, most organic nitrogen was found in the soil filtrate from soil enriched with mineral fertilizers. More organic nitrogen was lost in the object fertilized with sewage sludge compost, under either of the fertilization methods, than in the objects where dried and granulated sludge or sludge compost with straw were applied.

In a study by Mazur and Sadej [9] on the effect of natural and mineral fertilizers on amounts of leached organic nitrogen, it was found out that more of this nitrogen form was lost following a long-term application of mineral rather than organic fertilizers. These authors found similar quantities of organic nitrogen in all objects treated with natural fertilizers, irrespective of the type and rate of a fertilizer.

Table 2

Organic nitrogen leaching

Dose	Control	NPK	FYM	Dried and granulated sewage sludge	Composted sewage sludge	Composted sewage sludge + straw
[mg per lysimeter]						
10 Mg · ha^{-1}			7.83	6.25	10.38	5.98
2 × 5 Mg · ha^{-1}	13.11	12.23	10.65	8.80	9.42	8.45
Average			9.24	7.53	9.90	7.22
[kg · ha^{-1}]						
10 Mg · ha^{-1}			5.39	4.30	7.15	4.12
2 × 5 Mg · ha^{-1}	9.03	8.42	7.33	6.06	6.49	5.82
Average			6.36	5.18	6.82	4.97

The amount of leached mineral nitrogen ranged from 3.52 to 7.83 mg per lysimeter. Independently from the type or dose of the applied fertilizer, in all the fertilized objects the amount of leached mineral nitrogen was higher than in the control. Higher average loss of mineral nitrogen occurred in the objects fertilized with sludge compost than with dried and granulated sludge (Table 3).

Table 3

Mineral nitrogen leaching

Dose	Control	NPK	FYM	Dried and granulated sewage sludge	Composted sewage sludge	Composted sewage sludge + straw
[mg per lysimeter]						
10 Mg · ha^{-1}			6.95	6.07	5.64	7.57
2 × 5 Mg · ha^{-1}	3.52	6.25	5.37	5.98	7.83	6.33
Average			6.16	6.03	6.74	6.95
[kg · ha^{-1}]						
10 Mg · ha^{-1}			4.79	4.18	3.88	5.21
2 × 5 Mg · ha^{-1}	2.42	4.34	3.70	4.12	5.39	4.36
Average			4.25	4.15	4.64	4.79

The objects which were treated with a split dose of sewage sludge on two dates were found to have more mineral nitrogen leached than the objects where the same amount of sludge was applied in a single dose. A reverse dependence occurred in the case of composted sewage sludge and straw or dried sewage sludge. The amount of mineral nitrogen leached from soil fertilized with NPK was nearly 1.8-fold higher versus the control.

The content of ammonia nitrogen in filtrates was varied. The amount of this form of nitrogen varied over a wide range, from 0.17 to 2.46 mg per lysimeter (Table 4).

Table 4

N-NH$_4^+$ leaching

Dose	Control	NPK	FYM	Dried and granulated sewage sludge	Composted sewage sludge	Composted sewage sludge + straw
[mg per lysimeter]						
10 Mg · ha^{-1}			1.49	1.23	1.23	1.06
2 × 5 Mg · ha^{-1}	0.88	2.20	1.06	0.17	2.46	1.14
Average			1.28	0.70	1.85	1.10
[kg · ha^{-1}]						
10 Mg · ha^{-1}			1.03	0.85	0.85	0.73
2 × 5 Mg · ha^{-1}	0.60	1.52	0.73	0.12	1.69	0.79
Average			0.88	0.49	1.27	0.76

Among the soil enriching substances, higher N-NH$_4^+$ leaching was caused by composted sewage sludge than by dried and granulated sludge or composted sludge and straw. The smallest amount of ammonia nitrogen was leached from the soil to which dried and granulated sludge was introduced in the treatment consisting of 2 × 5 Mg · ha^{-1}. Single application of the same sludge caused a seven-fold higher leaching of ammonia nitrogen compared with the object where the same quantity of the fertilizer was introduced in a double application. Fertilization with the conventional organic fertilizer, such as farmyard manure, caused increased leaching of ammonia nitrogen, with higher quantities of this nitrogen form found out in the object fertilized once than in the one which received a dose divided into two parts.

The extent of ammonia nitrogen leaching can also be influenced by the pH of the substratum. When the pH is lower, the amount of this nitrogen form leached from soil can rise considerably [13]. High ammonia nitrogen loss has also been observed when liquid natural fertilizers such as liquid manure or mixed mineral and organic fertilization were applied [9].

Among the mineral forms of nitrogen in filtered water, nitrate(V) nitrogen dominated. The amount of nitrate(V) nitrogen leached from soil was several times higher compared with ammonia nitrogen (Table 5). Among the objects treated with sewage sludge, the highest leaching of nitrate(V) nitrogen appeared in the combination treated with dried and granulated sewage sludge introduced twice, 5 Mg · ha^{-1} each time. Similar amounts of nitrate(V) nitrogen were leached from soil enriched with composted sewage sludge and straw added as a single dose. These results are in accord with the ones obtained by Czyzyk and Kozdras [3]. As for the other objects, independently from the type of fertilizer or fertilization method, the amounts of nitrate(V) nitrogen ions were approximately the same. The extent of this form of nitrogen lost from soil was more profoundly affected by sludge than by mineral fertilization or farmyard manure. Introduction of nitrogen via mineral fertilizers added to soil proved to produce better effects compared with the other fertilizers, as the loss of N-NO$_3^-$ was the lowest under this fertilization treatment. Similar results were reported by Cwojdzinski and

Majcherczak [14], who determined that more nitrate(V) nitrogen was released from soil when mixed mineral and organic fertilization was applied than after exclusive mineral treatment.

Table 5

N-NO$_3^-$ leaching

Dose	Control	NPK	FYM	Dried and granulated sewage sludge	Composted sewage sludge	Composted sewage sludge + straw
[mg per lysimeter]						
10 Mg · ha^{-1}			4.14	4.05	4.31	5.19
2 × 5 Mg · ha^{-1}	2.55	3.87	4.05	5.37	4.14	4.31
Average			4.10	4.71	4.23	4.75
[kg · ha^{-1}]						
10 Mg · ha^{-1}			2.85	2.08	2.97	3.57
2 × 5 Mg · ha^{-1}	1.76	2.67	2.79	3.70	2.85	2.97
Average			2.82	2.89	2.91	3.27

Amounts of nitrates leached from soil also depend on the type of crops grown on it. As Smoron et al [15] report, the smallest concentrations of this form of nitrogen have been recorded in leachate from soils under permanent grassland. Additionally, the extent of nitrate(V) nitrogen loss was also affected by the duration of the vegetative growth of plants. More of this nitrogen form was lost from soils under crops characterised by a short growing period. In a study conducted by Pondel [16], the concentration of nitrate(V) nitrogen in lysimetric, drainage and groundwater as well as in watercourses from agricultural basins or downhill effluents varied over a wide range, from 1 to over 40 kg N · ha^{-1} annually.

Table 6

N-NO$_2^-$ leaching

Dose	Control	NPK	FYM	Dried and granulated sewage sludge	Composted sewage sludge	Composted sewage sludge + straw
[mg per lysimeter]						
10 Mg · ha^{-1}			1.32	0.79	0.09	1.32
2 × 5 Mg · ha^{-1}	0.09	0.18	0.26	0.44	1.23	0.88
Average			0.79	0.62	0.66	1.10
[kg · ha^{-1}]						
10 Mg · ha^{-1}			0.91	0.54	0.06	0.91
2 × 5 Mg · ha^{-1}	0.06	0.12	0.18	0.30	0.85	0.60
Average			0.55	0.42	0.46	0.76

The smallest amount of nitrate(III) nitrogen was found in filtrate obtained from the soil fertilized with composted sewage sludge applied as a single dose of 10 Mg · ha^{-1} (Table 6). The leaching of N-NO$_2^-$ in that case was over 13-fold lower than in the object receiving the same fertilizer applied as a split dose of 5 Mg · ha^{-1} applied on two dates. More extensive leaching of this nitrogen form occurred in the soil fertilized with sewage sludge than in the one treated with FYM or NPK. Mineral fertilization caused a two-fold increase in the content of nitrate(III) nitrogen relative the control.

Conclusions

1. Fertilization of soils with sewage sludge or composted sewage does not lead to elevated leaching of total nitrogen or nitrogen forms compared with conventional fertilization. More total nitrogen is leached from soil which is enriched with dried sewage sludge or with composted sludge and straw applied in a single dose (10 Mg · ha^{-1}) relative to soil where such fertilizers are applied as two doses (2 × 5 Mg · ha^{-1}). When compost is made from sewage sludge alone, it is more beneficial to apply it as a single rather than a split dose.

2. The amount of mineral nitrogen leached from soil fertilized with sewage sludge is small, ranging from 3.88 to 5.39 kg · ha^{-1}. Higher average losses of mineral nitrogen are observed under the influence of composted sludge is applied than when dried and granulated sewage is used.

3. Among the mineral forms of nitrogen, nitrate(V) nitrogen is leached most extensively. The amount of this form of nitrogen washed away from fertilized soils is on average 70 % higher compared with the control. The most severe leaching of this nitrogen form occurred when dried and granulated sludge was introduced to soil as 2 × 5 Mg · ha^{-1} rates or when composted sewage sludge and straw were used.

4. The amount of ammonia nitrogen leached from soils enriched with sewage sludge or sludge composts was nearly 2-fold lower compared with this nitrogen form leached from soil fertilized with dried and granulated sludge, applied as 2 × 5 Mg · ha^{-1}. Single application of 10 Mg · ha^{-1} of dried sludge causes a 7-fold increase in the leaching of ammonia nitrogen.

5. Among the mineral forms of nitrogen, nitrate(III) nitrogen was leached the least extensively. Using processed sludge fertilizers in a single dose of 10 Mg · ha^{-1}, we could observe that the leaching of this nitrogen form was much lower than when the same amount of sludge fertilizer was spilt into two equal doses applied on two different dates.

References

[1] Gondek K. and Kopeć M.: Acta Agrophys. 2008, **12**(1), 79–89.
[2] Koblak-Kalińska E.: II Konf. Nauk.-Techn., Puławy–Lublin–Jeziórko 1997, 10–22.
[3] Czyżyk F. and Kozdraś M.: Zesz. Probl. Post. Nauk Roln. 2003, **494**, 85–92.
[4] Ruszkowska M., Rębowska Z., Sykut S. and Kusio M.: Pamięt. Puław. 1988, **91**, 216–233.
[5] Ruszkowska M., Sykut S. and Kusio M.: Zesz. Nauk AR w Krakowie, Sesja Nauk 278, 1993, **37**, 153–167.

[6] Mazur T.: Materiały Sympozjum nt. Przyrodnicze i antropogeniczne przyczyny oraz skutki zakwaszenia gleb. Wyd. AR, Lublin 1993, 19–26.

[7] Pondel H., Ruszkowska M., Sykut S. and Terelak H.: Roczn. Glebozn. 1991, **XLII**(3/4), 97–107.

[8] Sykut S. and Ruszkowska M.: Zesz. Probl. Post. Nauk Roln. 1996, **440**, 375–379.

[9] Mazur T. and Sądej W.: Folia Univ. Agric. Stetin, AR-T Olsztyn 1999, 257–261.

[10] Sykut S.: Pamięt. Puław. 1993, **103**, 11–33.

[11] Mroczkowski W., Sykut S. and Ruszkowska M.: Pamięt. Puław. 1997, **111**, 89–102.

[12] Terelak H., Terelak-Motowicka T., Sadurski W. and Tujaka A.: Stan i antropogeniczne zmiany jakości wód w Polsce. Wyd. Uniwersytetu Łódzkiego, Łódź 2000, 269–277.

[13] Spychaj-Fabisiak E. and Murawska B.: Zesz. Probl. Post. Nauk Roln. 1994, **414**, 21–28.

[14] Cwojdziński W. and Majcherczak E.: Zesz. Probl. Post. Nauk Roln. 1993, **411**, 107–112.

[15] Smoroń S., Kopeć S. and Misztal A.: Zesz. Probl. Post. Nauk Roln. 1996, **440**, 367–374.

[16] Pondel H.: Some aspects of chemical contamination of soil. MAB Scope. Wyd. PAN, Warszawa 1989, 11–39.

WYMYWANIE FORM AZOTU Z GLEBY NAWOŻONEJ OSADAMI ŚCIEKOWYMI

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Abstrakt: Celem badań było określenie ilości strat różnych form azotu na drodze wymycia z gleby nawożonej osadami ściekowymi, obornikiem i NPK. Osady ściekowe i obornik zastosowano jednorazowo w dawce 10 Mg · ha^{-1} oraz dwukrotnie po 5 Mg · ha^{-1} w pierwszym i w trzecim roku doświadczenia. Wykazano, że we wszystkich obiektach, na których stosowano dodatki użyźniające w postaci osadów ściekowych lub kompostów z nich wytworzonych wymycie azotu ogółem i jego form było większe w porównaniu z obiektem kontrolnym. Większe ilości azotu ogółem wymyto z gleby, do której wprowadzano osady ściekowe w dawce podzielonej na dwie części (2 × 5 Mg · ha^{-1}) w porównaniu do gleby, gdzie zastosowano je w dawce jednorazowej (10 Mg · ha^{-1}). Spośród mineralnych form azotu w wodach przesiąkowych dominował azot azotanowy(V). Większe straty tej formy azotu notowano w obiektach nawożonych kompostem z osadu ściekowego z dodatkiem słomy (10 Mg · ha^{-1}) oraz wysuszonym i zgranulowanym osadem ściekowym (2 × 5 Mg · ha^{-1}) w porównaniu z kompostowanym osadem ściekowym oraz nawożeniem tradycyjnym. Do zanieczyszczenia wody N-NH$_4^+$ w największym stopniu przyczynił się kompost z samych osadów ściekowych, natomiast N-NO$_2^-$ kompost ten z dodatkiem słomy.

Słowa kluczowe: wymywanie azotu, osady ściekowe, kompost, gleba

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MINERALIZATION OF NITROGEN COMPOUNDS IN UPPER-SILTED ORGANIC SOILS OF NORTH-EASTERN POLAND

MINERALIZACJA ZWIĄZKÓW AZOTU W ODGÓRNIE NAMULONYCH GLEBACH ORGANICZNYCH POLSKI PÓŁNOCNO-WSCHODNIEJ

Abstract: The paper deals with the changes in the content of nitrate and ammonium nitrogen after incubation of undisturbed soil samples, the redox potential (Eh), and oxygen diffusion rate (ODR) in mucky and peat-muck soils, strongly and slightly silted, occurring in two young glacial landscapes (morainic and of ice-dammed lakes). The highest amounts of inorganic nitrogen were released in slightly silted peat-muck soils, and the least in mucky soils. In the soils of the landscape of ice-dammed lakes, the redox potential, the oxygen diffusion rate and amounts of inorganic nitrogen were lower than in the soils of morainic landscape. The amount of nitrate nitrogen ($N-NO_3$) in soil surface layers oscillated between 4.65 mg $\cdot$ dm^{-3} and 15.08 mg $\cdot$ dm^{-3} in the landscape of ice-dammed lakes and between 6.49 mg $\cdot$ dm^{-3} and 18.23 mg $\cdot$ dm^{-3} in morainic landscape. These values suggest that the analysed soils contain very little and medium amounts of nitrates. Deluvial deposits which accumulated on the surface of organic soils were diminishing the rate of organic matter mineralization in subsurface peat formations.

Keywords: $N-NO_3$, $N-NH_4$, mucky soils, strongly and slightly silted peat-muck soils, morainic landscape, landscape of ice-dammed lakes

There is clear distinction between organic soils formed in numerous, irregularly situated depressions of young glacial landscape of north-eastern Poland and such soils in other regions of Poland. The relief induces slope denudation processes which contribute to accumulation of deluvial deposits on the soil surface, of various thickness and texture as well as to silting of soils surface layers occurring farther from the slope. Consequently, specific soil sequence of mucky and silted peat-muck soils is found [1]. As these soils are formed close to the slopes, they play an important role in nutrients cycles in young glacial landscape [2, 3]. Moreover, as they contain substantial amounts

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of organic matter, they can release great amounts of inorganic nitrogen compounds (N-NO_3 and N-NH_4) [4]. The nitrates that are not uptaken by plants are washed out from the soil profile and contribute to contamination of groundwater and surface waters [5].

Mineralization of organic nitrogen compounds depends on various site factors (soil moisture, temperature, type of soil formation, degree of transformation by soil-forming processes and land use) [6] and occurs with seasonal variation, also in winter [7–9]. The intensity of release of mineral nitrogen compounds in organic soils which are modified by deluvial process has not been thoroughly analyzed [9].

The aim of the study was to measure the amounts of inorganic nitrogen released in a toposequence of upper-silted mucky soils and peat-muck soils with different degree of silting. The deluvial silts of the soils studied, have different texture and are situated in two different young glacial landscapes: morainic and of ice-dammed lakes.

Materials and methods

For this study, three land depressions in two landscapes were selected. First one is located in the landscape of ice-dammed lakes in Sepopol Plain (Reszel site) and two other in morainic landscape in Olsztyn Lakeland (Lutry site) and in Mragowo Lakeland (Prusinowo site). Along the transect, from the slope to the peatland, the following soil sequence was found: mucky soils, strongly and slightly silted peat-muck soils. In mucky soils, the surface horizon has thickness of 30 cm and consists of organic-mineral deluvium. It contains 10–20 % of organic matter (mean content of organic matter is given in Tables 4–6). In peat-muck soils, the thickness of muck layers is of 25–33 cm, and the muck-forming process is medium advanced.

At Reszel site, on the slopes surrounding the peatland, black earths that were formed from clay occur. In a depression, four soil profiles were studied. Two of them were classified as mucky soils. Deluvial deposit was underlain by the muck layer of the thickness of 15–20 cm. Medium decomposed reed peat lay underneath. Peat-muck soils were also developed from reed peat. Black earths, mucky soils and strongly silted peat-muck soils are drained and used as arable fields. Slightly silted peat-muck soils are not cultivated.

The soils on the slopes at Lutry site were formed from sandy loam. Mucky soils and strongly silted peat-muck soils (two soil profiles) were formed on strongly decomposed alder peats of small thickness, overlying clayey gyttia at a depth of 85 cm. Slightly silted peat-muck soils were formed on sedge peats that overlie alder peats at a depth of 52 cm. The subsoil at a depth of 80 cm consists of organic gyttia lying on calcareous gyttia deposits. The soils at Lutry site are used as pastures.

Mucky soils and peat muck soils at Prusinowo site were formed on strongly decomposed alder peats underlain by medium decomposed reed peats at a depth of 60–140 cm. Calcareous gyttia lies beneath. The soils are used as grasslands.

The research was carried out in summer and winter 2007 and in spring, summer and autumn 2008. Mineral nitrogen compounds were analyzed in a 100 cm^3 undisturbed core samples (in four replicates) taken from surface horizons (5–10 cm and 15–20 cm)

and from peat formations underneath. Inorganic nitrogen compounds were determined in a soil extract of 1 % K_2SO_4 after 14-day incubation at a temperature of 28 ^{o}C [6, 11]. During incubation, actual soil moisture content was maintained (soil moisture content at sampling time). For $N-NO_3$ determination, phenoldisulphonic acid was used and for $N-NH_4$, Nessler's reagent was applied.

Furthermore, basic soil physical properties (loss-on-ignition, bulk density, specific density, moisture at sampling time, total porosity) were determined. The oxygen diffusion rate (ODR) and the redox potential (Eh) were measured in field conditions. The rH factor was calculated on the base of Eh and pH according to the formula: $rH = Eh \cdot 29^{-1}+2pH$.

Statistical analyses were conducted with Statitsica 8.0.

Results and discussion

The amount of released nitrate and ammonium nitrogen as well as the values of the parameters determining water-air properties of soils (groundwater level, moisture content, air content, ODR, Eh) showed seasonal variations (Tables 1–3). The results for surface layers (5–10 cm) of some chosen soil profiles (mucky soils, strongly and slightly silted peat-muck soils), demonstrating the highest dynamics of moisture and air conditions, were presented.

The lowest groundwater level was reported for the soils at Lutry site in summer 2008 (0.90–1.15 m below ground level) and in autumn 2008 (0.85–1.05 m below ground level) (Table 1). In summer 2007 and spring 2008, the groundwater level was high and oscillated between 0.25 and 0.378 m below ground level. In the soils at Prusinowo site, this level was the lowest in summer 2008 (0.72–0.90 m below ground level) (Table 2) whereas in other seasons it oscillated between 0.35 and 0.60 m below ground level. In the soils at Reszel site, in autumn 2008, the groundwater dropped to 0.90 m below ground level (Table 3) and in other seasons it was between 0.35 and 0.65 m below ground level. At the studied sites, irrespective of the season, the highest groundwater level was observed in slightly silted peat-muck soils.

The drying of surface horizons was accompanied by the decrease of groundwater level. In summer 2008, the amount of air (39.4 % vol.) in strongly silted muck horizons at Lutry site was equal to half of total porosity (Table 1). In the periods when soils were drying, an increase of ODR factor was observed. In each season, the redox potential (Eh) also showed variations. However the Eh values were not related to the moisture or air content in the soil, but resulted from various resistance of the studied formation to oxidation and reduction processes.

The amounts of inorganic nitrogen that were released in the soils, beside seasonal variations, depended on the soil type and site (Tables 1–3). In Tables 1–3, the content of nitrogen compounds is expressed in $mg \cdot dm^{-3}$ of soil dry matter in order to compare the studied soils to abundance classes suggested by Gotkiewicz [6].

The highest amounts of mineral nitrogen ($N-NO_3$ and $N-NH_4$) were released during summer and autumn 2008. The relationship between $N-NO_3$ and $N-NH_4$ was typical. In spring and winter the $N-NO_3$: $N-NH_4$ ratio exceeded 1.0, which indicates good

Table 1

Content of mineral nitrogen and water-air properties in soil surface horizons (5–10 cm) of morainic landscape (Lutry site)

Soil horizon	Specification		Sampling time				
			23.08.07	20.12.07	24.04.2008	22.07.08	03.10.08
AO	NO_3	$[mg \cdot dm^{-3}]$	11.32	7.15	10.13	6.49	7.62
	NH_4	$[mg \cdot dm^{-3}]$	5.27	5.90	9.94	8.12	5.84
	$NO_3 + NH_4$	$[mg \cdot dm^{-3}]$	16.59	13.05	20.07	14.61	13.46
	Ratio $NO_3 : NH_4$		2.15	1.21	1.02	0.80	1.30
	Moisture	[% vol.]	59.2	59.3	62.7	42.7	54.6
	Air content	[% vol.]	14.1	14.3	10.6	30.6	18.7
	Eh	[mV]	300	330	280	310	280
	ODR	$[\mu g \cdot m^{-2} \cdot s^{-1}]$	47.3	51.2	46.0	53.7	52.4
	GWL	[m]	0.28	0.93	0.38	1.15	1.05
Mtsz	NO_3	$[mg \cdot dm^{-3}]$	13.41	8.78	13.24	7.56	10.28
	NH_4	$[mg \cdot dm^{-3}]$	6.97	5.66	11.20	15.40	11.16
	$NO_3 + NH_4$	$[mg \cdot dm^{-3}]$	20.38	14.44	24.40	22.96	21.44
	Ratio $NO_3 : NH_4$		1.92	1.55	1.18	0.49	0.92
	Moisture	[% vol.]	65.1	61.6	65.5	39.6	58.8
	Air content	[% vol.]	13.9	17.4	13.5	39.4	20.2
	Eh	[mV]	265	285	270	300	280
	ODR	$[\mu g \cdot m^{-2} \cdot s^{-1}]$	37.1	44.8	38.4	47.3	46.0
	GWL	[m]	0.30	0.84	0.35	1.10	0.95
Mtz	NO_3	$[mg \cdot dm^{-3}]$	14.18	9.38	12.10	18.23	17.36
	NH_4	$[mg \cdot dm^{-3}]$	6.74	7.33	8.77	20.55	16.60
	$NO_3 + NH_4$	$[mg \cdot dm^{-3}]$	20.92	16.71	20.87	39.48	33.96
	Ratio $NO_3 : NH_4$		2.10	1.28	1.38	0.92	1.05
	Moisture	[% vol.]	66.7	71.2	75.7	53.5	67.2
	Air content	[% vol.]	14.1	9.6	5.1	27.3	13.6
	Eh	[mV]	280	265	235	320	320
	ODR	$[\mu g \cdot m^{-2} \cdot s^{-1}]$	40.9	48.6	34.5	43.5	43.5
	GWL	[m]	0.25	0.62	0.35	0.90	0.85

Explanation: AO – humus horizon of mucky soils, Mtsz – strongly silted muck, Mtz – slightly silted muck, GWL – groundwater level.

Table 2

Content of mineral nitrogen and water-air properties in soil surface horizons (5–10 cm)
of morainic landscape (Prusinowo site)

Soil horizon	Specification		Sampling time				
			23.08.07	21.12.07	25.04.08	21.07.08	04.10.08
AO	NO_3	$[mg \cdot dm^{-3}]$	8.15	8.54	8.50	9.35	10.98
	NH_4	$[mg \cdot dm^{-3}]$	5.29	4.64	4.29	8.03	7.60
	$NO_3 + NH_4$	$[mg \cdot dm^{-3}]$	13.44	13.18	12.79	17.38	18.58
	Ratio $NO_3 : NH_4$		1.54	1.84	1.98	1.16	1.44
	Moisture	[% vol.]	52.1	43.4	41.3	38.6	40.9
	Air content	[% vol.]	7.8	16.5	18.6	21.3	19.0
	Eh	[mV]	310	300	245	305	305
	ODR	$[\mu g \cdot m^{-2} \cdot s^{-1}]$	48.6	55.0	42.2	57.6	43.5
	GWL	[m]	0.47	0.55	0.65	0.72	0.55
Mtsz	NO_3	$[mg \cdot dm^{-3}]$	11.17	8.16	8.52	9,47	9.80
	NH_4	$[mg \cdot dm^{-3}]$	7.92	6.20	5.73	10.33	8.50
	$NO_3 + NH_4$	$[mg \cdot dm^{-3}]$	19.09	14.36	14.25	19.80	18.30
	Ratio $NO_3 : NH_4$		1.64	1.32	1.14	0.92	1.15
	Moisture	[% vol.]	59.6	60.8	59.4	51.6	63.2
	Air content	[% vol.]	8.1	6.9	8.3	16.1	4,5
	Eh	[mV]	315	280	280	325	255
	ODR	$[\mu g \cdot m^{-2} \cdot s^{-1}]$	57.8	44.8	39.6	66.0	38.7
	GWL	[m]	0.42	0.51	0.45	0.90	0.48
Mtz	NO_3	$[mg \cdot dm^{-3}]$	13.98	8.96	8.75	13.13	8.90
	NH_4	$[mg \cdot dm^{-3}]$	8.19	7.12	6.10	17.02	10.89
	$NO_3 + NH_4$	$[mg \cdot dm^{-3}]$	22.17	16.08	14.85	30.15	19.79
	Ratio $NO_3 : NH_4$		1.71	1.26	1.43	0.76	0.82
	Moisture	[% vol.]	68.1	72.5	63.3	64.2	72.7
	Air content	[% vol.]	7.9	3.5	12.4	11.8	3.3
	Eh	[mV]	240	315	260	285	270
	ODR	$[\mu g \cdot m^{-2} \cdot s^{-1}]$	43.5	33.5	35.6	44.8	34.5
	GWL	[m]	0.40	0.47	0.35	0.85	0.42

Explanation: as in Table 1.

Table 3

Content of mineral nitrogen and water-air properties in soil surface horizons (5–10 cm)
of ice-dammed lakes landscape (Reszel site)

Soil horizon	Specification		Sampling time				
			23.08.07	20.12.07	25.04.2008	22.07.08	03.10.08
AO	NO_3	[mg · dm^{-3}]	7.03	4.94	4.65	5.13	11.42
	NH_4	[mg · dm^{-3}]	7.12	5.77	5.19	4.83	6.14
	$NO_3 + NH_4$	[mg · dm^{-3}]	14.15	10.71	9.84	9.96	17.56
	Ratio $NO_3 : NH_4$		0.99	0.86	0.90	1.06	1.86
	Moisture	[% vol.]	45.1	50.4	49.6	46.8	34.8
	Air content	[% vol.]	9.8	4.5	5.3	8.1	20.1
	Eh	[mV]	265	235	205	230	245
	ODR	[µg · m^{-2} · s^{-1}]	40.9	35.8	39.6	51.2	53.3
	GWL	[m]	0.55	0.45	0.46	0.55	0.82
Mtsz	NO_3	[mg · dm^{-3}]	12.88	6.11	7.72	6.07	9.66
	NH_4	[mg · dm^{-3}]	7.65	5.69	5.66	14.32	4.40
	$NO_3 + NH_4$	[mg · dm^{-3}]	20.53	11.80	13.38	20.39	14.06
	Ratio $NO_3 : NH_4$		1.68	1.07	1.36	0.42	2.19
	Moisture	[% vol.]	58.6	62.4	61.1	60.3	50.9
	Air content	[% vol.]	13.4	9.6	10.9	11.7	21.1
	Eh	[mV]	260	210	170	260	235
	ODR	[µg · m^{-2} · s^{-1}]	38.4	33.3	40.9	52.4	55.8
	GWL	[m]	0.5	0.42	0.43	0.65	0.85
Mtz	NO_3	[mg · dm^{-3}]	15.08	7.42	9.56	7.19	7.47
	NH_4	[mg · dm^{-3}]	7.61	6.91	7.08	11.94	10.27
	$NO_3 + NH_4$	[mg · dm^{-3}]	22.69	14.33	16.64	19.13	17.74
	Ratio $NO_3 : NH_4$		1.98	1.07	1.35	0.60	0.73
	Moisture	[% vol.]	56.5	67.1	65.3	63.6	65.9
	Air content	[% vol.]	16.9	6.3	8.1	9.8	7.5
	Eh	[mV]	255	230	180	240	140
	ODR	[µg · m^{-2} · s^{-1}]	40.7	37.1	38.4	39.6	33.0
	GWL	[m]	0.45	0.38	0.40	0.40	0.39

Explanation: as in Table 1.

conditions for nitrification but during post-growing season it may cause enhanced infiltration of nitrates from the soil profile to groundwater. In summer the value of the investigated ratio was often below 1.0 due to low moisture content and high temperatures, which indicates the diminishing of the rate of nitrification.

In the landscape of ice-dammed lakes, the amount of nitrates (N-NO$_3$) in soil surface layers oscillated between 4.65 mg · dm^{-3} in mucky soils in spring and 15.08 mg · dm^{-3} in slightly silted peat-muck soils in summer 2007 (Table 3). The sum of nitrate and ammonium nitrogen compounds averaged from 6.49 to 22.69 mg · dm^{-3}. In morainic landscape, the amount of N-NO$_3$ released in the soils varied from 6.49 mg · dm^{-3} in mucky soils to 18.23 mg · dm^{-3} in slightly silted peat-muck soils. The sum of N-NO$_3$ and N-NH$_4$ varied from 12.79 mg · dm^{-3} and 39.48 mg · dm^{-3} (Tables 1, 2). The obtained values of nitrogen content were compared with the ranges regarding their supply with nitrogen compounds [6] and it was estimated that the analyzed soils contain from very little to medium amounts of nitrates (N-NO$_3$). It should be noted that mineralization of nitrogen compounds takes place also during post-growing season. In the soils of morainic landscape the content of nitrates at this period, oscillated between 7.15 mg · dm^{-3} and 9.38 mg · dm^{-3}. In the landscape of ice-dammed lakes it amounted to 4.94–7.40 mg · dm^{-3}.

In order to stress the differences in the amounts of inorganic nitrogen compounds released from the studied soil types, mean values of the analyzed parameters (for each season) were calculated for surface horizons (0–30 cm) and for underlying peat formations. The results are presented in Tables 4, 5 and 6.

In the studied toposequence of mucky and silted peat-muck soils, the farther from the slope the more increased moisture content and lower air content, as well as ODR and Eh factors (Tables 4–6). Similar relationships were observed for the content of the studied parameters in the soil profile. In both landscape of ice-dammed lakes (Reszel site) (Table 6) and morainic landscape (Lutry and Prusinowo sites) (Tables 4, 5) the same soil types demonstrated lower content of redox potential and ODR factor.

Mean values of analyzed nitrogen compounds as well as their sum, expressed in mg · dm^{-3}, increased, in the surface horizons, along with organic matter content. The highest values were reported for slightly silted peat-muck soils (Tables 4–6). More distinctive differences between the studied soils are observed when the content of inorganic nitrogen compounds is expressed per unit of soil dry matter. In morainic landscape, the amount of mineral nitrogen compounds in humus horizons of mucky soils (Tables 4, 5) was three times as less and in the landscape of ice-dammed lakes, twice as less as in slightly silted muck formations (Table 6). In morainic landscape, the differences in the content of inorganic nitrogen were statistically significant between surface soil formations (AO, Mtsz, Mtz) (Tables 4, 5). In the landscape of ice-dammed lakes, the amounts of nitrogen compounds released in slightly and strongly silted mucks did not show significant differences, as they contain similar quantities of organic matter (Table 6).

In hydrogenic soils, the majority of nitrogen compounds is organic and the processes of mineralization and immobilization are related to the transformation of carbon compounds. Therefore, the content of nitrogen compounds was additionally expressed per unit of organic matter. It appears that more nitrate and ammonium nitrogen (N-NO$_3$

Table 4

Mean content of mineral nitrogen and water – air properties of the soils in morainic landscape (Lutry site)

Soil horizon	OM	N-NO₃	N-NH₄	NO₃ + NH₄	N-NO₃	N-NH₄	NO₃ + NH₄	N-NO₃	N-NH₄	NO₃ + NH₄	W	P	Eh	ODR	rH
	g · kg⁻¹	mg · dm⁻³			mg · kg⁻¹			mg · kg⁻¹ of OM			% vol.		mV	µg · m⁻² · s⁻¹	[-]
*Mucky soil with mineral-organic layer in the top horizon															
1 AO	156.0	8.54	7.01	15.55	13.43	11.03	24.46	86.09	70.69	156.79	55.7	17.6	280.0	47.3	21.5
OtniolR₃	716.0	4.36	7.22	11.57	12.63	20.93	33.56	17.63	29.24	46.87	68.28	12.1	217.0	34.3	20.8
OtniolR₃	758.0	1.61	7.00	8.61	6.76	29.40	36.16	8.91	38.79	47.70	81.4	4.7	142.0	24.8	17.1
*Peat-muck soil, strongly silted															
2 Mtsz	379.5	8.11	9.80	17.91	17.24	20.65	37.89	46.40	55.30	101.70	60.18	16.9	246.0	37.5	21.4
OtniolR₃	675.0	4.23	9.54	13.77	13.27	29.81	43.08	19.62	44.13	63.75	77.8	5.5	160.0	21.0	18.9
*Peat-muck soil, slightly silted															
3 Mtz	658.5	12.99	11.98	24.97	38.16	35.25	73.41	57.73	53.63	111.36	69.3	12.0	238.5	35.7	19.5
OtnituR₂	782.0	3.53	7.80	11.33	23.21	51.33	74.54	29.68	65.64	95.32	89.0	1.9	133.0	19.0	16.0
OtniolR₃	875.0	1.17	7.40	8.57	6.91	43.52	50.43	7.89	49.73	57.63	88.8	0.4	86.0	10.5	14.3
Statistically significant differences		2 < 3		1 < 3, 2 < 3	1 < 3, 2 < 3	1 < 2 < 3	1 < 2 < 3	1 > 2, 3		1 > 2, 3				1 > 2, 3	

Explanation: OM – organic matter, W – moisture, P – air content, AO – humus horizon of mucky soils, Mtsz – strongly silted muck, Mtz – slightly silted muck, Otnitu – sedge peat, Otniol – alder wood peat, R₂ – medium decomposed peat, R₃ – strongly decomposed peat.
* According to Polish Soils Classification System [18].

Table 5

Mean content of mineral nitrogen and water – air properties of the soil in morainic landscape (Prusinowo site)

Soil horizon	OM	N-NO₃	N-NH₄	NO₃+NH₄	N-NO₃	N-NH₄	NO₃+NH₄	N-NO₃	N-NH₄	NO₃+NH₄	W	P	Eh	ODR	rH
	$g \cdot kg^{-1}$	$mg \cdot dm^{-3}$			$mg \cdot kg^{-1}$			$mg \cdot kg^{-1}$ of OM			% vol.		mV	$\mu g \cdot m^{-2} \cdot s^{-1}$	[-]
*Mucky soil with mineral-organic layer in the top horizon															
1 AO	156.0	8.94	6.23	15.17	8.56	7.79	16.35	55.56	50.70	106.27	46.0	13.1	265.5	46.2	21.4
OtniolR₃	754.0	2.66	8.23	10.89	10.35	33.31	43.66	13.88	44.79	56.68	83.8	3.6	186.0	32.2	18.2
OtniszR₂	828.0	0.78	9.14	9.93	3.59	42.54	46.13	4.33	51.44	55.78	88.0	0.0	97.0	19.7	15.1
*Peat-muck soil, strongly silted															
2 Mtsz	325.0	9.05	8.47	17.52	13.61	12.83	26.44	4196	39.6	81.60	63.5	6.1	273.5	42.7	22.5
OtniolR₃	718.0	6.27	10.06	16.33	22.20	36.29	58.49	30.39	49.66	80.05	76.7	3.8	155.0	26.3	18.0
OtniszR₂	825.0	1.09	9.48	10.7	13.47	48.79	62.26	16.17	59.13	75.30	87.4	0.5	76.8	18.3	14.4
*Peat-muck soil, slightly silted															
3 Mtz	620.0	9.59	10.98	20.57	24.87	28.98	53.85	40.22	46.28	86.51	72.7	6.4	261.0	35.8	21.7
OtniolR₃	816.0	2.14	10.34	12.48	16.32	48.19	64.51	20.00	59.05	79.05	84.6	1.9	186.0	32.2	18.2
OtniszR₂	838.0	0.81	9.62	9.84	13.59	50.36	63.95	16.21	60.90	76.31	87.9	0.62	78.0	16.9	15.3
Statistically significant differences			1 < 2, 3	1 < 2, 3	1 < 2 < < 3	1 < 2 < < 3	1 < 2 < < 3	1 > 2, 3		1 > 2, 3	1 > 2, 3				

Explanation: OM – organic matter, W – moisture, P – air content, AO – humus horizon of mucky soils, Mtsz – strongly silted muck, Mtz – slightly silted muck, Otniol – alder wood peat, Otnisz – reed peat, R₂ – medium decomposed peat, R₃ –strongly decomposed peat.
* According to Polish Soils Classification System [18].

Tabela 6

Mean content of mineral nitrogen and water – air properties of the soil in ice-dammed lakes landscape (Reszel site)

Soil horizon	OM	N-NO₃	N-NH₄	NO₃+NH₄	N-NO₃	N-NH₄	NO₃+NH₄	N-NO₃	N-NH₄	NO₃+NH₄	W	P	Eh	ODR	rH
	$g \cdot kg^{-1}$	$mg \cdot dm^{-3}$			$mg \cdot kg^{-1}$			$mg \cdot kg^{-1}$ of OM			% vol.		mV	$\mu g \cdot m^{-2} \cdot s^{-1}$	[-]
*Mucky soil with mineral-organic layer in the top horizon															
1 AO	194.0	6.87	5.84	12.71	8.72	7.33	16.06	44.75	37.65	82.41	55.0	9.8	213.7	36.3	20.9
Mt	34.1	5.31	7.09	12.40	8.88	11.40	20.28	25.81	30.33	56.14	62.9	5.6	167.0	27.8	18.5
OtniszR₂	84.5	2.29	6.45	8.74	13.04	36.51	49.55	24.93	56.55	81.48	85.7	3.4	100.0	18.9	14.5
*Peat-muck soil, strongly silted															
2 Mtsz	479.0	7.19	7.84	15.03	13.65	14.91	28.56	28.52	31.09	59.61	61.5	11.7	204.0	35.7	20.7
OtniszR₂	861.0	3.58	8.13	11.71	21.46	48.68	70.16	24.92	56.56	81.48	84.3	6.3	120.0	18.9	15.3
*Peat-muck soil, slightly silted															
3 Mtz	515.0	8.09	9.46	17.55	15.96	18.11	34.07	33.82	37.01	70.83	67.8	7.5	169.0	29.0	19.9
OtniszR₂	764.0	2.14	14.58	16.72	15.48	105.62	121.10	20.26	138.25	158.51	89.7	2.0	21.0	12.3	13.7
Statistically significant differences			1 < 2, 3	1 < 3	1 < 2, 3	1 < 2, 3	1 < 2, 3	1 > 2		1 > 2	1 < 3 2 / < 3	2 < 3 2 / > 3	1 > 3	1 > 3	

Explanation: OM – organic matter, W – moisture, P – air content, AO – humus horizon of mucky soils, Mtsz – strongly silted muck, Mtz – slightly silted muck, Otnisz – reed peat, R₂ – medium decomposed peat.
* According to Polish Soils Classification System [18].

and N-NH$_4$) is released in organic-mineral formations of mucky soils (AO) than in mucks (Mtsz, Mtz), and the differences between them turned to be statistically significant. The results indicate high intensity of organic matter mineralization in organic-mineral (AO) formations despite the fact they contain several times less organic matter than mucks. Similar results were reported by Lachacz [12], who applied the same incubation method, and found that muck-like formations demonstrate greater intensity of mineralization than mucks which contain substantially more organic matter. In studied AO formations of mucky soils, the sum of inorganic nitrogen compounds, expressed in mg · kg^{-1} of organic matter, was from twice to four times lower as compared with muck-like formations [12]. However it should be stated that muck-like formations lack clayey fraction and have specific humus compounds.

It should also be noted that the amount of inorganic nitrogen compounds [mg · kg^{-1} of organic matter] released in the soils of ice-dammed lakes is considerably lower than in the soils of morainic landscape (Tables 4–6). The differences between mucky soils and strongly silted peat-muck soils of both landscapes were statistically significant. It indicates differences in the quality of soil organic matter subjected to the process of mineralization, which was also found by Lachacz [12]. It can be assumed that fine-grained texture of deluvial deposits can have an influence on the mineralization of organic matter, despite adverse soil water and air conditions (lower values of ODR and Eh) in the landscape of ice-dammed lakes. Great amounts of colloidal clay fraction, allow formation of humus and clay minerals bondings. These bonds are strong and resistant to mineralization [13]. The diminishing rate of organic matter mineralization by adding clay minerals was reported by Liwski and Maciak [14] in laboratory conditions. In morainic landscape, deluvial deposits accumulated at the foot of the slope demonstrate variation of texture and often lack clay fraction [15].

It should also be stressed that lower amounts of inorganic nitrogen compounds were released in peat formation underlying deluvial deposits of mucky soils than in peat-muck soils (Tables 4–6). It proves the statement [16, 17] that deluvial deposits protect peat formations lying beneath against processes of mineralization. It is particularly important in case of alder peats, which are most susceptible to trans-formations.

Conclusions

1. The amounts of nitrate(V) and ammonium nitrogen in upper-silted mucky soils as well as in slightly and strongly silted peat-muck soils, showed seasonal variations and dependence on the soil type and landscape position.

2. The content of nitrates in the studied soils was from very little to medium. The highest quantities of inorganic nitrogen were released in slightly silted peat-muck soils and the least in mucky soils.

3. In the landscape of ice-dammed lakes, soil water-air conditions were adverse and the amount of inorganic nitrogen was lower than in the soils of morainic landscape. Slow rate of organic matter mineralization can result from formation of organic-mineral bonds.

4. Deluvial deposits lying on the surface of organic soils diminished the rate of organic matter mineralization in peat formations beneath.

Acknowledgement

References

[1] Piaścik H., Sowiński P., Orzechowski M. and Smólczyński S.: Zesz. Probl. Post. Nauk Roln. 2001, **476**, 491–496.

[2] Gotkiewicz J., Hutorowicz H., Lossow K., Mosiej J., Pawłat H., Szymczak T. and Traczyk T.: *Czynniki kształtujące obieg wody i biogenów w krajobrazie młodoglacjalnym*, [in:] Obieg wody i bariery biogeochemiczne w krajobrazie rolniczym. UAM, Poznań 1990, 188.

[3] Gotkiewicz J., Piaścik H. and Sapek A.: Zesz. Probl. Post. Nauk Roln. 1992, **401**, 311–320.

[4] Gotkiewicz J. and Gotkiewicz M.: Bibl. Wiad. IMUZ, 1991, **77**, 59–77.

[5] Sapek B.: Zesz. Probl. Post. Nauk Roln. 1996, **440**, 331–341.

[6] Gotkiewicz J.: Zróżnicowanie intensywności mineralizacji azotu w glebach organicznych związane z odrębnością warunków siedliskowych. Rozpr. habilit. IMUZ, Falenty 1983, 111.

[7] Pawluczuk J.: Ann. UMCS, Sec. E, 2004, **59**(2), 559–567.

[8] Smólczyński S.: Zesz. Probl. Post. Nauk Roln. 2006, **513**, 413–421.

[9] Smólczyński S. and Orzechowski M.: Water – Environment-Rural Areas 2009, **9**(1) (25), 121–150.

[10] Piaścik H. and Gotkiewicz J.: Zesz. Probl. Post. Nauk Roln. 2001, **478**, 511–518.

[11] Gotkiewicz, J.: Rocz. Nauk. Roln., Ser. F 1974, **78**(4), 25–34.

[12] Łachacz A.: Geneza i właściwości płytkich gleb organogenicznych na sandrze mazursko-kurpiowskim. Rozprawy i monografie **49**, UWM, Olsztyn 2001, 119.

[13] Walczyna J.: Roczn. Glebozn. 1974, **25**(2), 179–200.

[14] Liwski S. and Maciak F.: Zesz. Probl. Post. Nauk Roln. 1973, **146**, 187–208.

[15] Bieniek B.: *Właściwości i rozwój gleb napływowych Pojezierza Mazurskiego*. Acta Acad. Agricult. Tech. Olst., Agricultura, Suppl. B, 1997, **64,** 80.

[16] Gotkiewicz J., Okruszko H. and Smołucha J.: Zesz. Probl. Post. Nauk Roln. 1996, **431**, 181–201.

[17] Orzechowski M. and Smólczyński S.: Zesz. Probl. Post. Nauk Roln. 2002, **487**, 205–212.

[18] Systematyka gleb Polski. Roczn. Glebozn. 1989, **40**(3/4), 150.

MINERALIZACJA ZWIĄZKÓW AZOTU W ODGÓRNIE NAMULONYCH GLEBACH ORGANICZNYCH POLSKI PÓŁNOCNO-WSCHODNIEJ

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Abstrakt: W glebach namurszowych oraz silnie i słabo zamulonych glebach torfowo-murszowych położonych w dwóch strefach krajobrazu młodoglacjalnym (morenowej i zastoiskowej) oznaczono: zawartość azotu azotanowego i amonowego po inkubacji próbek o zachowanej strukturze, potencjał oksydoredukcyjny (Eh) oraz natężenie dyfuzji tlenu (ODR).

Największe ilości azotu mineralnego w uwalniały się w słabo zamulonych glebach torfowo-murszowych, a najmniejsze w glebach namurszowych. W glebach krajobrazu zastoiskowego wartości potencjału redoks (Eh), natężenia dyfuzji tlenu (ODR) oraz ilości azotu mineralnego były mniejsze niż w glebach krajobrazu morenowego. Zawartość azotu azotanowego (N-NO$_3$) w warstwach wierzchnich gleb w krajobrazie zastoiskowym wahała się od 4,65 w mg · dm^{-3} do 15,08 mg · dm^{-3}, a w krajobrazie morenowym od 6,49 mg · dm^{-3} do 18,23 w mg · dm^{-3} i mieściła się w zakresie zasobności od bardzo małej do średniej. Namuły deluwialne zalegające na powierzchni gleb organicznych ograniczały proces mineralizacji materii organicznej głębiej zalegających utworów torfowych.

Słowa kluczowe: azot azotanowy(V), azot amonowy, gleby namurszowe, torfowo-murszowe silnie i słabo zamulone, krajobraz morenowy, krajobraz zastoiskowy

Cezary TRAWCZYŃSKI[1]

INFLUENCE OF DRIP IRRIGATION AND FERTIGATION ON THE YIELD OF POTATO TUBERS AND CONTENT OF NITROGEN MINERAL IN THE SOIL

WPŁYW NAWADNIANIA KROPLOWEGO I FERTYGACJI NA PLON BULW ZIEMNIAKA I ZAWARTOŚĆ AZOTU MINERALNEGO W GLEBIE

Abstract: The field experiment was conducted in the years 2006–2008 at Plant Breeding and Acclimatization Institute, Division Jadwisin on the light and acid soil. The aim of the research was to compare tubers yield and content of mineral nitrogen in the soil after harvest of potato by different doses in solid (100 i 150 kg N $\cdot$ ha^{-1}) and liquid nitrogen form – fertigation (mean of 43.0 kg N $\cdot$ ha^{-1}) to the soil applied. The control was object non-fertilized and non-irrigated. The objects were divided on: irrigated and non-irrigated. Drip irrigation method in this experiment was applied. The nitrogen dose in fertigation form by using computer program DSS was established. The doses of water and dates of their application by using tensiometer were established. The soil for examination was taken from the layer of 0–30 and 30–60 cm. Analyses of nitrate and ammonium ions contents were carried out by reflection spectroscopy using RQ flex Merck reflectometr. The yield of tubers on irrigated object by using fertilizer program DSS was about 47 % higher than on the control object but content of mineral nitrogen in the soil on this object was smaller than on the control. Application nitrogen dose of 150 kg N $\cdot$ ha^{-1} on non-irrigated object, in all investigation years was the cause high cumulation of mineral nitrogen in the soil after harvest of potato. In second years of investigation (2007) already after applied dose of 100 kg N $\cdot$ ha^{-1} on non-irrigated conditions high level of mineral nitrogen in the soil was faound. Nitrogen surplus may be leached from the soil into groundwater in the autumn and winter period.

Keywords: potato, drip irrigation, fertigation, yield of tubers, soil, mineral nitrogen

A low coefficient of nitrogen utilization by the potato plant from the applied fertilizers, amounting to up to 50 % [1, 2], results in more and more attention being paid to the effects of mineral forms of nitrogen on the soil environment, principally after the end of the plant vegetation period. A large amount of mineral nitrogen remaining after the plant harvesting presents a hazard of washing out of this component during the autumn/winter season, which poses a risk to groundwater [3, 4]. Lability of the mineral forms of nitrogen in the soils is the reason why nitrogen should ideally be applied during the stages of the highest potato plants' demand for this component. Application

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of several supplementary doses of nitrogen during the plant vegetation period is considered to be one of the factors optimizing fertilization with this component and creates favourable conditions for both the appropriate yield to be obtained and accumulation of nitrates in the soil to be reduced [5–7]. The factors which significantly limit nitrogen utilization by the plants from the applied fertilizers may include rainfall deficiency as well as unfavourable rainfall distribution during the period of tuber weight increase [8]. In order to limit the unfavourable effects of the water factor, irrigation of potato plantations is introduced. Drip irrigation is considered to be the most precise since it does not result in washing away of furrows; moreover, water is not poured over the aboveground parts of the potato plant and the devices incorporated in the system allow precise fertilization at the time of irrigation [9].

The aim of the research was to compare tubers yield and content of mineral nitrogen in the soil after harvest of potatoes by different doses of solid and liquid nitrogen form (fertigation established by using computer program DSS) in drip irrigation conditions and natural soil moisture.

Material and methods

The field experiment was conducted in the years 2006–2008 at Plant Breeding and Acclimatization Institute, Division Jadwisin on the light and acid soil by light loamy sand soil texture. Top layer of the soil contained high amounts of available phosphorus, low to medium of potassium and low to high of magnesium forms. The content of mineral nitrogen in spring in soil layer of 0–60 cm ranged from 40.9 to 67.1 kg $\cdot$ ha^{-1}. The research years rainfall deficit in accumulation period of potato tubers yield were recorded. In the years of 2006 and 2008 rainfall deficit in June and July was recorded, but in 2007 years only in July was found (Table 1).

Table 1

The climate conditions of the vegetation periods in Jadwisin. Years 2006–2008

Year	Deviations from long term average									
	Rainfalls in mm and month					Temperature in °C and month				
	V	VI	VII	VIII	IX	V	VI	VII	VIII	IX
2006	−0.6	−26.1	−63.8	94.1	−37.5	−0.9	−1.3	3.6	−0.7	1.6
2007	26.4	32.6	−18.9	12.3	52.7	−0.5	−0.8	−0.8	0.0	−2.3
2008	10.9	−33.5	−4.2	18.9	−2.2	0.0	0.6	−0.3	−0.1	−1.5

Combinations system was following: A. Without NPK, without irrigation (control object); B. 100 kg N $\cdot$ ha^{-1} + 34.9 kg P $\cdot$ ha^{-1} + 99.6 kg K $\cdot$ ha^{-1}, without irrigation; C. 150 kg N $\cdot$ ha^{-1} + 34.9 kg P $\cdot$ ha^{-1} + 99.6 kg K $\cdot$ ha^{-1}, without irrigation; D. Dose of N according to DSS system (fertigation) + 34.9 kg P $\cdot$ ha^{-1} + 99.6 kg K $\cdot$ ha^{-1} + irrigation; E. 100 kg N $\cdot$ ha^{-1} + 34.9 kg P $\cdot$ ha^{-1} + 99.6 kg K $\cdot$ ha^{-1} + irrigation; F. 150 kg N $\cdot$ ha^{-1} + + 34.9 kg P $\cdot$ ha^{-1} + 99.6 kg K $\cdot$ ha^{-1} + irrigation.

The organic fertilization consisted in using straw in dose about 5 Mg $\cdot$ ha^{-1} and aftercrop of white mustard in dose about 23.4 Mg $\cdot$ ha^{-1}. The phosphorus (triple

superphosphate) and potassium (potassium salt) fertilization in spring before potato planting were applied. Mineral nitrogen fertilization (ammonium nitrate – 34 % N) into soil in solid and liquid form with water (fertigation) was applied. The nitrogen in solid form of 50 kg $\cdot$ ha^{-1} before planting and the rest before emergence of potatoes was applied. The nitrogen doses in fertigation form (years of 2006 – 57.7 kg $\cdot$ ha^{-1}, years of 2007 – 31.7 kg $\cdot$ ha^{-1}, years of 2008 – 39.7 kg $\cdot$ ha^{-1}) and term their application on object of D by using computer program DSS were established [10]. Drip irrigation system by using of drip lines with compensation of pressure was used. The drip lines with emitters (distance between emitters 35 cm) on each top ridge were located. Fertilizer pump application ammonium nitrate solution during irrigation practices. The doses of water (year of 2006 – 110.3 mm, year of 2007 – 20.0 mm, year of 2008 – 68.9 mm) and dates of their application on a base soil moisture by using tensiometer were established. When soil water potential decreasing under –40 kPa irrigation practices were started [11].

Medium early potatoes of Triada cultivar in row spacing of 75 × 33 cm were planted. Plot area amounts to 56. 4 m^2. A harvest after end of vegetation plants period was performed. During harvest yield of tubers on each plot was determined. The soil for examination was taken in spring before fertilizers application and in autumn after end of vegetation period, before harvest of potato tubers. Soil sampling were taken from the layer 0–30 and 30–60 cm. Analyses of nitrate and ammonium ions contents were carried out by reflection spectroscopy using RQ flex Merck reflectometr [12]. The significantly differences using Fisher test at the significance level p = 0.05 was estimated.

Results and discussion

A significant diversity was demonstrated in tuber yield in relation to the form and dose of nitrogen fertilization (Table 2). Indeed, the highest tuber yield was obtained following application of the dose of 150 kg $\cdot$ ha^{-1} nitrogen through an irrigation system; the difference with regard to the untreated control amounted to 60 %. With application of nitrogen fertigation the tuber yield was found to be bigger by 13.2 Mg $\cdot$ ha^{-1}, ie by approx. 47 % compared with the untreated control; moreover, it was demonstrated that the obtained tuber yield was similar to the one from a combination with application of nitrogen at a dose of 100 kg $\cdot$ ha^{-1} in a solid form.

Table 2

Influence fertilization on the yield of potato tubers [Mg $\cdot$ ha^{-1}] in study years

Year	Objects						Average
	A	B	C	D	E	F	
2006	27.0	33.0	37.6	48.8	47.7	51.2	40.8
2007	18.4	23.1	23.9	23.3	23.0	24.0	22.6
2008	38.4	45.9	54.3	51.2	53.3	58.8	50.3
Average	27.9	33.9	38.5	41.1	41.3	44.6	
LSD$_{0.05}$	2.1						1.9

In the experiments by Mazurczyk et al [13] the difference in the tuber yield between the control object and the object under drip irrigation amounted to 53.4 %, while for the irrigated and fertigated with nitrogen the difference increased up to 88 %.

Diversified fertilization with nitrogen as well as many years' experiments had a significant influence on the level of mineral forms of nitrogen in the soil after the end of the plant vegetation period. In both own experiments [14] and experiments by other researchers [15–17] it was confirmed that the content of mineral nitrogen in the soil after the end of the plant vegetation period increases with the increase in the applied doses of nitrogen. Experiments revealed a significant positive effect of increasing nitrogen fertilization on the content of mineral forms of nitrogen in both the surface soil layer of 0–30 cm and in the layer of 30–60 cm (Tables 3 and 4). In the soils kept in good condition the predominant form of mineral nitrogen are nitrate ions which in turn are more labile than ammonium ions, hence in the assessment of the environmental effects of fertilization a particular attention must be paid to the content of this form of nitrogen in the soil [3]. Experiments demonstrated that the bigger diversity of mineral nitrogen in the soil was related to the nitrate form rather than to the ammonium form. Moreover, a higher content of the nitrate form in the soil layers of 0–30 cm and 30–60 cm was found under non-irrigated conditions (Tables 3 and 4), therefore it can be concluded with greater probability that under irrigated conditions the level of washing out of the mineral nitrogen to the deeper layers of soil at the time after the end of plant vegetation period can be lower. It should be emphasized that the level of the nitrate form in the soil under irrigation and nitrogen fertigation treatment was lower than the same level found in the untreated control (Table 3).

Table 3

Content of $N-NO_3^-$ form [kg · ha^{-1}] in the soil depending on study years and fertilization

Soil layer	Year	Objects						Average
		A	B	C	D	E	F	
0–30 cm	2006	12.1	17.0	56.7	10.9	12.4	17.0	21.0
	2007	22.7	31.4	39.2	21.6	23.6	28.5	26.3
	2008	10.3	15.0	36.3	9.5	9.8	12.7	17.9
Average		15.0	21.1	44.1	14.0	15.2	19.4	
LSD$_{0.05}$		4.2						3.3
30–60 cm	2006	13.0	12.4	30.9	7.8	8.6	11.1	14.0
	2007	15.7	22.2	25.8	14.6	18.7	23.8	18.7
	2008	7.8	10.3	15.4	6.7	8.1	7.5	11.4
Average		12.2	15.0	24.0	9.7	11.8	14.1	
LSD$_{0.05}$		3.2						2.5
0–60 cm	2006	25.1	29.4	87.6	18.8	21.0	28.1	35.1
	2007	38.4	53.6	64.9	36.2	42.3	52.4	45.0
	2008	18.1	25.3	51.7	16.3	17.9	20.2	29.4
Average		27.3	36.1	68.1	23.7	27.1	33.5	
LSD$_{0.05}$		5.8						5.0

Table 4

Content of N-NH$_4^+$ form [kg $\cdot$ ha^{-1}] in the soil depending on study years and fertilization

Soil layer	Year	Objects						Average
		A	B	C	D	E	F	
0–30 cm	2006	3.1	3.2	3.6	7.9	6.7	9.1	6.9
	2007	6.7	8.3	8.3	9.5	12.7	13.5	9.5
	2008	5.1	6.3	10.3	7.1	5.5	7.5	6.3
Average		5.0	5.9	7.4	8.1	8.3	10.0	
LSD$_{0.05}$		2.0						0.9
30–60 cm	2006	2.6	5.2	7.0	5.2	5.6	8.2	7.2
	2007	7.0	8.5	7.4	8.2	10.8	11.9	8.6
	2008	4.8	6.3	7.4	5.2	6.7	5.9	5.5
Average		4.8	6.7	7.3	6.2	7.7	8.7	
LSD$_{0.05}$		1.7						0.8
0–60 cm	2006	5.7	8.4	10.6	13.1	12.3	17.3	14.1
	2007	13.8	16.9	15.7	17.7	23.5	25.4	18.1
	2008	9.9	12.6	17.7	12.3	12.2	13.4	11.9
Average		9.8	12.6	14.7	14.3	16.0	18.7	
LSD$_{0.05}$		2.6						1.3

According to Fotyma [18] the content of the nitrate form N-NO$_3^-$ in the light soil in the layer of 0–30 cm, amounting to 31 kg $\cdot$ ha^{-1}, as well as this content in the layer of 30–60 cm, amounting to 16–17 kg $\cdot$ ha^{-1}, is considered to be safe, which means that the potential hazard of groundwater contamination with excess nitrates is excluded. The results obtained indicate that application of nitrogen at a dose of 150 kg $\cdot$ ha^{-1} under non-irrigated conditions may lead to excessive accumulation of mineral nitrogen in the soil after potato harvesting, while in the second year of experiments application of as low a dose of nitrogen as 100 kg $\cdot$ ha^{-1} under non-irrigated conditions made it possible for some part of nitrogen to be washed out to groundwater. Samples for assessment of the content of mineral nitrogen were taken during September and in the beginning of October, and it is highly probable that due to absence of nitrogen uptake by the plants as well as to mineralization of the organic nitrogen the content of this component in the soil could increase significantly until the winter season. Therefore Müller and Gorlitz [19] suggest that appropriate measures should be taken to decrease the level of mineral nitrogen in the soil after the harvesting by means of sowing aftercrops or cultivation of winter crops.

Research revealed that after the end of vegetation period the content of the nitrate form in the soil layer of 0–60 cm under irrigated conditions amounted to approx. 62–64 %, while under the non-irrigation conditions it oscillated between 73 % in the untreated control and approx. 82 % following application of nitrogen at a dose of 150 kg $\cdot$ ha^{-1}. In earlier experiments [20, 21] a similar percentage of N-NO$_3^-$ and N-NH$_4^+$ in the mineral nitrogen was demonstrated. According to research by Fotyma and Boguszewska [22], the content of nitrate ions in the soil in the autumn season may amount to 60–80 % of the total content of mineral nitrogen. Fotyma and Boguszewska

[22] also emphasized that in a case of a high percentage of nitrate form in the soil in the autumn season one should take into account the possibility of more intense washing away of this form than in case of a lower percentage of this form in the total content of the mineral nitrogen in the soil.

Conclusion

1. The yield of tubers on irrigated object by using fertilizer program DSS was about 47 % higher than on the control object (without fertilization and irrigation).

2. The irrigation significantly decreased content of mineral nitrogen, mainly nitrate form in the soil after end of vegetation period.

3. The nitrogen application in fertigation form decreased level of mineral nitrogen in the soil and reduced risk nitrates leached from the soil into groundwater in the autumn and winter period.

4. Application nitrogen dose of 150 kg $\cdot$ ha^{-1} in all investigation years and dose of 100 kg $\cdot$ ha^{-1} (years of 2007) without irrigation was the cause high cumulate of mineral nitrogen in the soil after harvest of potatoes.

References

[1] Lis B., Mazurczyk W., Trawczyński C. and Wierzbicka A.: Zesz. Probl. Post. Nauk Roln. 2002, **489**, 165–174.
[2] Neeteson J.J.: Netherlands J. Agric. Sci. 1989, **37**, 143–155.
[3] Fotyma E., Wilkos G. and Pietruch Cz.: Test glebowy azotu mineralnego – możliwości praktycznego wykorzystania. Mat. szkol. 1998, **69/98**, 48 pp.
[4] Vos. J. and Mackerron D.K.L.: *Basic concepts of the management of supply of nitrogen and water in potato production*, [in:] Management of nitrogen and water in potato production. Haverkart A.J., Mackerron D.K.L. (eds). Wageningen Pres, Wageningen 2000, 136–154.
[5] Czuba R.: Zesz. Probl. Post. Nauk Roln. 1996, **440**, 65–73.
[6] Goffart J.P. and Guiot J.: *Influence of timing and type of N-fertilization on N-uptake and yield of potato and on soil mineral nitrogen status in Belgian Loam soil*. 13th Trien. Conf. EAPR, Veldhoven, Netherlands 1996, 391–392.
[7] Trawczyński C. and Grześkiewicz H.: Biul. Inst. Hodow. Aklimat. Rośl. 2000, **213**, 149–155.
[8] Lis B. and Wierzejska-Bujakowska A.: Biul. Inst. Hodow. Aklimat. Rośl. 2000, **213**, 87–98.
[9] Łuszczyk K.: Ziemniak Polski 2004, **2**, 16–19.
[10] Batillani A., Hansen S. and Plauborg F.: Decision Support System (DSS), 2006 <fertorganic.org>.
[11] Haverkort A.J. and MacKerron D.K.L.: Management of nitrogen and water in potato production. Wageningen. Pres., Wageningen 2000, 353 pp.
[12] Instrukcja do reflektometrycznej metody oznaczania jonów azotanowych i amonowych. Merck Sp. z o.o., 8 pp.
[13] Mazurczyk W., Głuska A., Trawczyński C., Nowacki W. and Zarzyńska K.: Roczn. AR Poznan. 2006, CCCLXXX, Roln. **66**, 235–241.
[14] Trawczyński C.: Biul. Inst. Hodow. Aklimat. Rośl. 2001, **217**, 177–185.
[15] Ciećko Z., Wyszkowski M. and Szagała J.: Zesz. Probl. Post. Nauk Roln. 1996, **440**, 27–33.
[16] Fotyma M., Fotyma E. and Stuczyński T.: Naw. Nawoż. 1999, **1**, 44–58.
[17] Łabętowicz J.: Zesz. Probl. Post. Nauk Roln. 1995, **421a**, 245–251.
[18] Fotyma E.: Naw. Nawoż. 2000, **3a**, 17–37.
[19] Müller S. and Gorlitz H.: Fragm. Agronom. 1990, **1**, 23–35.
[20] Trawczyński C.: Ann. UMCS 2004, Sec. E, **59**(2), 687–696.
[21] Trawczyński C.: Biul. Inst. Hodow. Aklimat. Rośl. 2007, **246**, 83–93.

[22] Fotyma E. and Boguszewska M.: *Zawartość azotu mineralnego w glebach Polski jako wskaźnik stanu środowiska rolniczego*. Mat. Konf. Nauk. nt. "Dobre praktyki w produkcji rolniczej" 1, IUNG, Puławy 1998, 61–70.

WPŁYW NAWADNIANIA KROPLOWEGO I FERTYGACJI NA PLON BULW ZIEMNIAKA I ZAWARTOŚĆ AZOTU MINERALNEGO W GLEBIE

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Abstrakt: Doświadczenie polowe przeprowadzono w latach 2006–2008 w Instytucie Hodowli i Aklimatyzacji Roślin, Oddział Jadwisin na glebie lekkiej, kwaśnej. Celem badań było porównanie wpływu na plon bulw i zawartość azotu mineralnego w glebie po zakończeniu wegetacji ziemniaków zróżnicowanego nawożenia azotem stosowanego do gleby w formie stałej (100 i 150 kg N · ha^{-1}) i płynnej – fertygacja (średnio 43.0 kg N · ha^{-1}). Kontrolę stanowił obiekt bez nawożenia NPK i nienawadniany. Kombinacje podzielono na: nawadniane i nienawadniane. Nawadnianie prowadzono metodą kroplową. Dawkę azotu w formie fertygacji ustalono przy wykorzystaniu komputerowego programu nawozowego DSS. Dawki wody oraz terminy ich stosowania ustalono na podstawie wilgotności gleby przy użyciu tensjometrów. Glebę do badań pobierano z warstwy gleby 0–30 i 30–60 cm. Oznaczenie zawartości jonów azotanowych i amonowych wykonano reflektometrycznie przy użyciu reflektometru RQ flex Merck. Plon bulw uzyskany na kombinacji nawadnianej z wykorzystaniem programu nawozowego DSS był o około 47 % większy niż na kontroli, a zawartość azotu mineralnego w glebie na tej kombinacji mniejsza w porównaniu do kontroli. Zastosowanie dawki azotu 150 kg N · ha^{-1} bez nawadniania, we wszystkich badanych latach, przyczyniło się do dużej kumulacji azotu mineralnego w glebie po zbiorze ziemniaków. W drugim roku badań (2007) już po zastosowaniu dawki 100 kg N · ha^{-1} bez nawadniania stwierdzono wysoki poziom azotu mineralnego w glebie. Nadmiar tego azotu może być wypłukany z gleby do wód gruntowych w okresie jesienno--zimowym.

Słowa kluczowe: ziemniak, nawadnianie kroplowe, fertygacja, plon bulw, gleba, azot mineralny

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DIURNAL AND SEASONAL VARIATIONS IN THE NO$_2$ PHOTOLYSIS RATE CONSTANT, NO TITRATION RATE CONSTANT AND THE NO$_2$/NO RATIO IN AMBIENT AIR IN THE CITY OF OLSZTYN

DOBOWA I SEZONOWA ZMIENNOŚĆ STAŁYCH SZYBKOŚCI REAKCJI FOTOLIZY NO$_2$ I TITRACJI NO ORAZ STOSUNKU NO$_2$/NO W POWIETRZU ATMOSFERYCZNYM OLSZTYNA

Abstract: The paper presents diurnal and seasonal variations in the NO$_2$ photolysis rate constant (J_{NO_2}), NO titration rate constant (k_3) and the NO$_2$/NO molecular ratio determined experimentally and calculated for the photostationary state in atmospheric air in the city of Olsztyn (NE Poland). Diurnal variations in the titration rate constant ranged from 20.8 to 25.3 ppm^{-1} min^{-1} in the summer (June 2008), and from 16.5 to 17.2 ppm^{-1} min^{-1} in the winter (December 2008). The values of the J_{NO_2} constant, which is dependent on the total solar radiation (TSR) and the solar zenith angle (SZA), ranged from zero in night hours to 0.071 min^{-1} at 12:00 noon local time in the winter and to 0.254 min^{-1} 11:00 a.m. local time in the summer. The NO$_2$/NO ratio (both observed and calculated) showed characteristic diurnal variations, reaching a minimum around noon. The determined NO$_2$/NO ratio was found to be higher than the calculated NO$_2$/NO ratio both in the summer and winter. The lowest values of the calculated NO$_2$/NO ratio were noted in June, with an average of 0.0407 at 12:00 noon, which was 176-fold lower than the value determined experimentally. This points to the significance of NO oxidation to NO$_2$ with the participation of volatile organic compounds (VOCs) and/or carbon monoxide.

Keywords: NO$_2$ photolysis, NO titration, rate constant, NO$_2$/NO ratio, tropospheric photochemistry, tropospheric ozone

Nitrogen oxides (NO$_x$), including nitric oxide (NO) and nitrogen dioxide (NO$_2$), are the primary air pollutants [1, 2]. The largest global sources of nitrogen oxides are fossil fuel combustion (20–25 Tg N-NO$_x$ per year) and biomass combustion in tropical and subtropical regions (2–13 Tg N-NO$_x$ per year) [3, 4]. Natural sources also contribute to the total NO$_x$ balance (eg soil emissions and atmospheric discharges – 3–21 and 2–20

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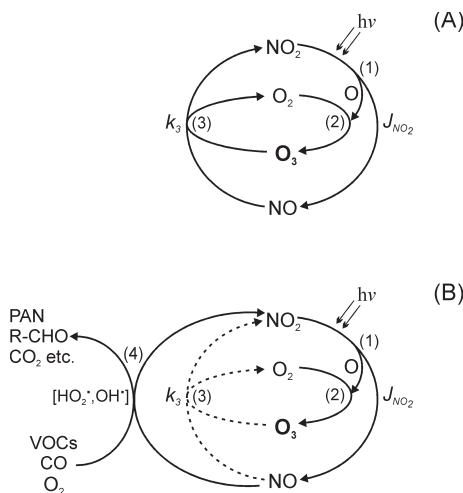
Fig. 1. Pattern of NO_x and O_3 transformations in the atmospheric air, in the presence of sunlight. Solid line –
predominant reactions, broken line – second-order reactions. Fig. 1A – main NO_2-NO-O_3 cycle in the
air not polluted with organic compounds. Fig. 1B – inclusion of volatile organic compounds (VOCs)
and carbon monoxide (CO) in the cycle of transformations. Reaction (1) – NO_2 photolysis, reaction
(2) – ozone synthesis, reaction (3) – NO titration, reactions (4) represent an alternative – in relation to
reaction (3) pathway of NO_2 production, leading to an increase in the NO_2/NO ratio and to O_3
accumulation

Tg N-NO_x per year, respectively) [5–8]. Nitrogen oxides cause adverse health and
environmental impacts. Human health concerns include effects on breathing and
respiratory system. Besides, nitrogen oxides react with other compounds to form acid
rains and a strong oxidant, tropospheric ozone [9–11]. Until the 1970s, it was believed
that tropospheric ozone originated from the stratosphere. Today we know that air mass
transfer from the stratosphere to the troposphere is one of the two reasons for the
presence of ozone in the lower atmosphere near the ground [4, 12]. The other, more
important, reason are photochemical processes with the participation of NO_x, volatile
organic compounds (VOCs) and carbon monoxide (CO) [1, 13, 14]. Reactions between
O_3, NO_2 and NO in the troposphere in the absence of VOCs are the predominant cycle
of photochemical transformations proceeding according to the pattern shown in Figure
1A. First, NO and O are produced as a result of nitrogen dioxide photolysis in the
presence of sunlight (reaction R1). Next atomic oxygen (O) reacts with a molecule of
diatomic oxygen (O_2) to form ozone (O_3), a highly reactive gas (reaction R2). Ozone
may oxidize a variety of substances in the air, including nitric oxide. The reaction of
nitric oxide oxidation with ozone (R3) is known as nitric oxide titration. As illustrated
in Figure 1A, an equilibrium between NO_2, NO and O_3, referred to as a photostationary
state, is reached. This equilibrium is described by the following equation [2, 15]:

$$\frac{[NO][O_3]}{[NO_2]} = \frac{J_{NO_2}}{k_3} \qquad \text{(Eq. 1)}$$

where: J_{NO_2} – NO_2 photolysis rate constant dependent on the intensity of solar radiation at the photochemically active wavelengths, k_3 – titration rate constant, [NO], [NO_2] and [O_3] – volume concentrations of NO, NO_2 and O_3 [ppm] respectively.

Apart from the above reactions, there occur many other photochemical processes involving CO and VOCs. All reactions that cause a decrease in NO concentrations in favor of NO_2 lead to an increase in O_3 concentrations to a level that can no longer be calculated based on equation 1. Such reactions include, among others, photochemical oxidation of VOCs, CH_4 and CO, with OH and HO_2 radicals as catalytic agents (Fig. 1B, reaction 4). This is an alternative NO oxidation pathway which upsets the photostationary state, thus leading to increased tropospheric ozone concentrations [15–19].

In view of the above, the observed NO_2/NO molecular ratio in the air polluted by VOCs must be higher than the NO_2/NO molecular ratio calculated from the photostationary state equation:

$$\left(\frac{[NO_2]}{[NO]}\right)_{calculated} = \frac{k_3}{J_{NO_2}} \cdot [O_3]_{observed} \qquad \text{(Eq. 2)}$$

This suggests that the greater the differences between these values, the higher the rates of photochemical processes involving NO_x and VOCs. In order to perform such an analysis, we have to know the values of reaction rate constants J_{NO_2} and k_3 and the actual concentrations of NO_2, NO and O_3.

The objective of this study was to determine diurnal variations in the values of reaction rate constants J_{NO_2} and k_3, and the observed and calculated NO_2/NO ratio in ambient air in the city of Olsztyn (NE Poland) in the summer and winter.

Material and methods

Measurement methods

The study was conducted in the summer (June 2008) and winter (December 2008), at the air quality monitoring station of the Department of Air Protection and Environmental Toxicology, University of Warmia and Mazury in Olsztyn. The station is situated in the south-western part of the city, on Lake Kortowskie. The geographical location of the measurement point is as follows: 53°45′39″N, 20°27′27″E. Continuous measurements of NO and NO_2 concentrations were performed by the chemiluminescence method, and ozone concentrations were measured by ultraviolet absorption analysis (MLU 200E and MLU 400E analyzers, Teledyne API, Inc. USA). The MLU 200E analyzer was checked for accuracy every 23 hours, against a standard mixture of NO_2 (350 ppb) and N_2 (Messer Group GmbH) and against zero air with activated carbon and Purafil® (Purafil, Inc. USA). The MLU 400E analyzer is equipped with an ozone and zero air generator, which enables to check its accuracy. Temperature was measured with a DMA580 electronic thermo-hygrometer, and total solar radiation (TSR) was

determined with a DPA 559 pyranometer (LSI s.p.a., Italy). Instantaneous data were recorded every five seconds, validated and averaged to hourly values using a data logger with CS5 v. 5.3 software (CSMS, Poland).

Computational methods

The NO_2 photolysis rate constant may be calculated by various methods, which were found to provide comparable results [20]. One of the methods is based on the dependence of J_{NO_2} on TSR and solar zenith angle (α). Wratt et al [21] modified three equations developed by other authors:

for $\alpha < 47^o$:
$$J_{NO_2} = TSR \cdot \left(4.23 \cdot 10^{-4} + 1.09 \cdot \frac{10^{-4}}{\cos \alpha} \right)$$
(Eq. 3)

for $47^o \leq \alpha < 64^o$:
$$J_{NO_2} = TSR \cdot 5.82 \cdot 10^{-4}$$
(Eq. 4)

for $\alpha \geq 64^o$:
$$J_{NO_2} = TSR \cdot (-0.997 \cdot 10^{-4} + 1.2 \cdot 10^{-3} \cdot (1 - \cos \alpha))$$
(Eq. 5)

Average hourly values of TSR > 10 W/m^2 were used in calculations. The solar zenith angle was determined using an on-line calculator, "Altitude and Azimuth of the Sun or Moon During One Day" (Astronomical Applications Department of the U.S. Naval Observatory, http://aa.usno.navy.mil/). According to this procedure, α is calculated based on latitude, longitude, date and local time. This method was applied, among others, by Sozzi et al [22].

The nitric oxide titration rate constant (k_3) was calculated from the following equation [23]:

$$k_3 = 3.23 \cdot 10^3 \exp\left(\frac{-1430}{T} \right) \quad [\text{ppm}^{-1} \ \text{min}^{-1}]$$
(Eq. 6)

where: T – air temperature [K].

The observed NO_2/NO molecular ratio was determined based on the measured concentrations of NO_2 and NO [ppb], only when [NO] > 0. The NO_2/NO ratio calculated for the photostationary state was determined from equation 2. Points in Figures 2, 3 and 4 denote average values calculated for each hour over a month ($\pm$ standard error).

Results and discussion

The greatest diurnal variations in the NO titration rate constant (k_3) were observed in the summer (June 2008). The maximum and minimum hourly average value of k_3 was noted at 3:00 p.m. and 5:00 a.m. local time (25.3 and 20.8 ppm$^{-1} \cdot$ min^{-1}, respectively, Fig. 2). In December 2008 the values of k_3 oscillated within a narrower range of 16.5 to 17.2 ppm$^{-1} \cdot$ min^{-1}, due to lower air temperatures. These results are similar to our
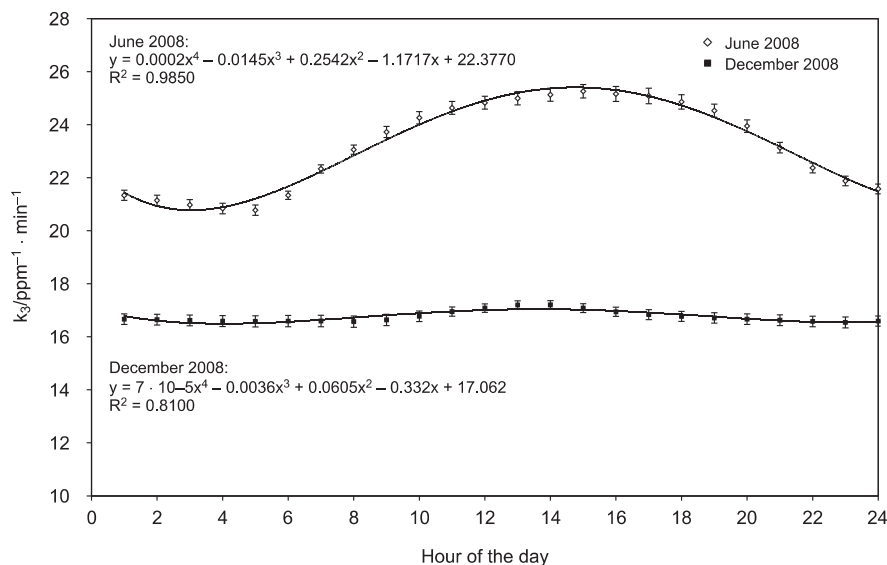
Fig. 2. Daily variations in the NO titration rate constant k$_3$ in June and December 2008 (means ± SE)

previous findings [24]. Wiegand and Bofinger [20], and Mazzeo et al [2] noted lower values of k$_3$ in Australia and Argentina (from 21.5 to 23.0 ppm^{-1} · min^{-1}).

Nitrogen dioxide photolysis occurs only during the daytime, when solar UV radiation reaches the Earth. The cosinus function proposed by the authors of the present study adequately describes variations in the NO$_2$ photolysis rate constant:

$$J_{NO_2} = f(x) = a + b \cdot \cos (c + d \cdot x) \qquad \text{(Eq. 7)}$$

where: x – hour; a, b, c, d – equation constants.

The determination coefficients (R^2) for June and December are 0.9813 and 0.9988, respectively (Fig. 3). The highest average value of J_{NO_2} (0.254 min^{-1}) was noted in June 2008 at 11:00 a.m. local time. The values of $J_{NO_2} > 0.2$ were observed between 10:00 a.m. and 3:00 p.m., while above-zero values were recorded from 5:00 a.m. to 9:00 p.m. The highest values, noted around noon, were characterized by considerable variation throughout the month. The standard error of the mean (SEM) was approximately 0.03 min^{-1} between 10:00 a.m. and 3:00 p.m., and below 0.01 min^{-1} in the morning and in the evening. In December 2008, the J_{NO_2} constant remained low (Fig. 3), reaching a maximum (0.071 ± 0.009 min^{-1}) at 12:00 noon. Above-zero values were noted between 9:00 a.m. and 3:00 p.m. The values of the NO$_2$ photolysis rate constant determined in this study in the summer and winter are lower than those reported by Castro et al [25], Wiegand and Bofinger [20] and Mazzeo et al [2], and comparable with the findings of Barnard et al [26]. In eastern Australia, the maximum value of J_{NO_2} was 0.55 min^{-1} in summertime (January–February) and 0.4 min^{-1} during the winter (July) [20], whereas in Argentine – 0.3 min^{-1} [2] and in Mexico – 0.42 min^{-1} in wintertime [25].
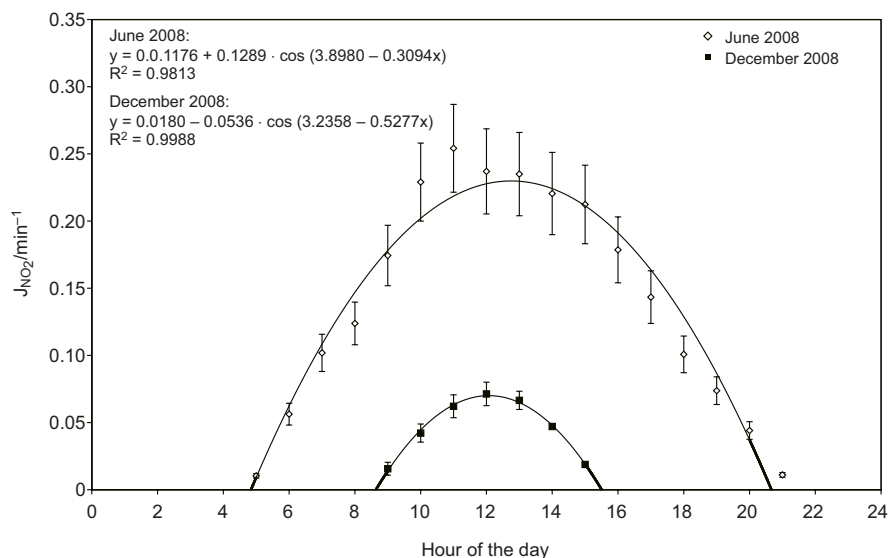
Fig. 3. Daily variations in the NO_2 phytolysis rate constant J_{NO_2} in June and December 2008 (means ± SE)

The fact that higher values of k_3 and J_{NO_2} were recorded in Australia and Argentina than in Poland results from latitude differences. Poland is situated farther from the equator than Australia and Argentina, and therefore the altitude of the Sun and the intensity of UV (actinic) radiation are lower in Poland. The results obtained by Barnard et al [26] are comparable with our findings because Arizona (USA) and Poland are situated at a similar latitude.

At the next stage of our study, we compared the experimentally determined NO_2/NO molecular ratio with that calculated for the photostationary state. It was found that the NO_2/NO ratio (both measured and calculated) showed characteristic diurnal variations, reaching a minimum around noon (Figs. 4 and 5). The measured NO_2/NO ratio was higher than the calculated NO_2/NO ratio both in the summer and winter, which is indicative of photochemical reactions with the participation of VOCs and NO_x. In June 2008, the lowest value of the calculated NO_2/NO ratio (0.0407) was noted at 12:00 noon. It was 176-fold lower than the value determined experimentally (Fig. 4). In December 2008 these differences were much smaller. The lowest calculated NO_2/NO ratio (< 0.40) was recorded at 12:00 noon and 1:00 p.m., and it was only twofold lower than the actual value (Fig. 5). Warmiński and Rogalski [24] reported higher NO_2/NO ratios, but the differences determined between the measured and calculated values in summertime (July 2006) were smaller than in this study.

Both NO_2 photolysis and NO oxidation to NO_2 occur at a faster rate in the summer than in the winter. The lowest differences between the observed and calculated NO_2/NO ratio are observed in the morning and in the evening, when the rate of photochemical reactions is slow. In the atmosphere free from hydrocarbon pollution, both parameters should be at a similar level, even around noon. The relationships between O_3, NO_2 and
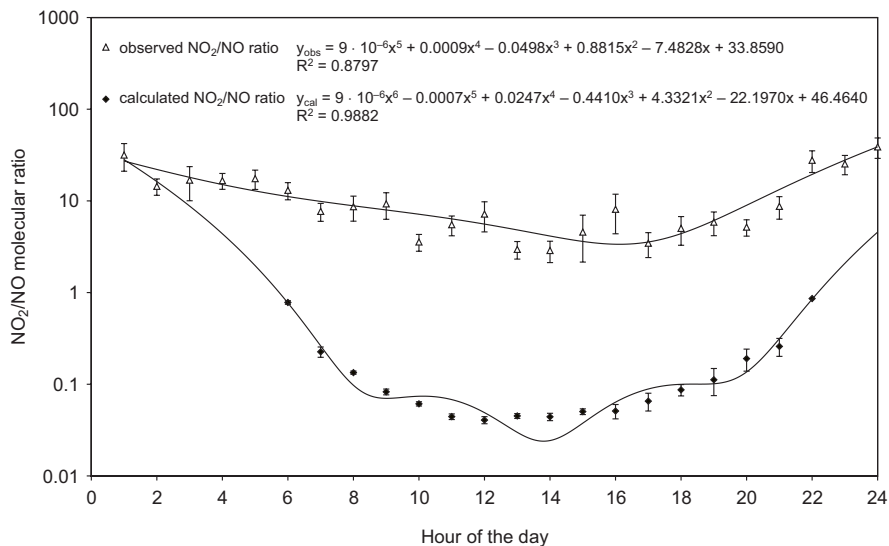
Fig. 4. Daily variations in the observed and calculated NO$_2$/NO molecular ratio in June 2008 (means ± SE)

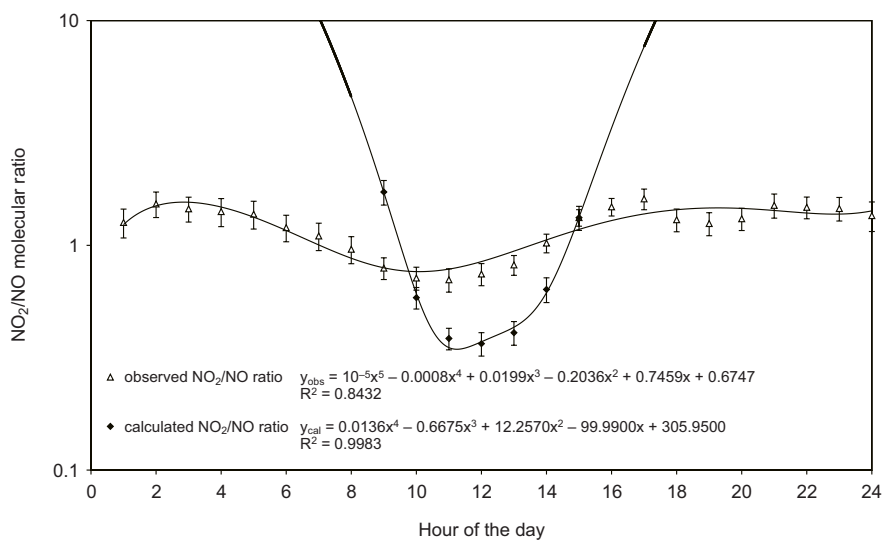Fig. 5. Daily variations in the observed and calculated NO$_2$/NO molecular ratio in December 2008 (means ± SE)

NO in unpolluted air (Fig. 1A) can be described by equation 1. However, such a situation was not encountered in this study, probably due to the occurrence of additional reactions involving VOCs and CO, which accelerated NO oxidation to NO$_2$ and increased the concentrations of O$_3$ (Fig. 1B).

Conclusions

1. The titration rate constant (k_3) was almost 1.5-fold higher in the summer than in the winter (23.2 and 16.8 $ppm^{-1} \cdot min^{-1}$, respectively daily means).

2. Diurnal variations in the values of k_3 were small, particularly in the cold period. In June 2008, the lowest (20.8 $ppm^{-1} \cdot min^{-1}$) and the highest (25.3 $ppm^{-1} \cdot min^{-1}$) value of k_3 was noted at 4:00 a.m. and at 3:00 p.m., respectively.

3. The NO_2 photolysis rate constant (J_{NO_2}) depended primarily on insolation, and it ranged from zero at night to approximately 0.07 and 0.25 min^{-1} at noon, in December and June 2008, respectively.

4. The theoretical (calculated) value of the NO_2/NO molecular ratio was much lower than that determined experimentally, which points to the high significance of NO to NO_2 transformation processes other than NO oxidation with ozone and diatomic oxygen. The greatest differences were observed in the summer, between 9.00 a.m. and 6.00 p.m., when the calculated NO_2/NO ratio was approximately 100-fold higher than the theoretical value determined for the photostationary state.

5. An analysis of variations in the values of J_{NO_2} and k_3 and the relationships between O_3, NO_2 and NO may provide a basis for a preliminary estimation of the rate of photochemical reactions with the participation of tropospheric ozone precursors other than nitrogen oxides.

References

[1] Winer A.M.: Air pollution chemistry. In: Harrison R.M. and Perry R. (eds.) Handbook of Air Pollution Analysis. Chapman and Hall, London–New York 1986.

[2] Mazzeo N.A., Venegas L.E. and Choren H.: Atmos. Environ. 2005, **39**, 3055–3068.

[3] Benkovitz C.M, Scholtz M.T., Pacyna J., Tarrason L., Dignon J., Voldner E.C., Spiro P.A., Logan J.A. and Graedel T.E.: J. Geophys. Res. 1996, **101**(D22), 29239–29253,.

[4] Crutzen P.J., Lawrence M.G. and Pőschl U.: Tellus 1999, **51A-B**, 123–146.

[5] Yienger J.J. and Levy H. II: J. Geophys. Res. 1995, **100**(D6), 11447–11464.

[6] Davidson E.A. and Kingerlee W.: Nutr. Cycl. Agroecosys. 1997, **48**, 37–50.

[7] Price C., Penner J. and Prather M.: J. Geophys. Res. 1997, **102**, 5929–5941.

[8] Meijer E.W., van Velthoven P.F.J., Brunner D.W., Huntrieser H. and Kelder H.: Phys. Chem. Earth (C) 2001, **26**(8), 577–583.

[9] Juda-Rezler K.: Effect of Air Pollution on Environment. Warsaw University of Technology Press, Warsaw, Poland 2000 [in Polish].

[10] Manahan S.E.: Environmental Science and Technology. A Sustainable Approach to Green Science and Technology, 2nd ed. CRC Press/Taylor & Francis, Boca Raton, USA 2007.

[11] Zhang M., Wang S., Wu F., Yuan X. and Zhang Y.: Atmos. Res., 2007, **84**, 311–322.

[12] Fabian P. and Junge C.E.: Arch. Met. Geoph. Biokl., Serie A 1970, **19**, 161–172.

[13] Nicholson J.P., Weston K.J. and Fowler D.: Atmos. Environ. 2001, **35**, 2009–2022.

[14] Falkowska L. and Korzeniewski K.: Atmospheric Chemistry. Wyd. Uniwer. Gdańskiego, Gdańsk, Poland 1998 [in Polish].

[15] Kleinman L.I.: Atmos. Environ. 2000, **34**, 2023–2033.

[16] Carter W.P.L., Pierce J.A., Luo D. and Malkina I.L.: Atmos. Environ. 1995, **29**, 2499–2511.

[17] Chang T.Y., Nance B.I. and Kelly N.A.: Atmos. Environ. 1999, **33**, 4695–4708.

[18] Sillman S.: Atmos. Environ. 1999, **33**, 1821–1845.

[19] Kleinman L.I.: Atmos. Environ. 2005, **39**, 575–586.

[20] Wiegand A.N. and Bofinger N.D.: Atmos. Environ. 2000, **34**, 99–108.

[21] Wratt D.S., Hadfield M.G., Jones M.T., Johnson G.M. and McBurney I.: Ecol. Modell. 1992, **64**, 185–203.

[22] Sozzi R., Salcido A, Flores R.S. and Georgiadis T.: Atmos. Res. 1999, **50**, 53–68.

[23] Seinfeld J.H. and Pandis S.N.: Atmospheric Chemistry and Physics. From Air Pollution to Climate Changes. Wiley, New York 1998.

[24] Warmiński K. and Rogalski L.: Polish J. Environ. Stud. 2007, **16**(3B), 497–502.

[25] Castro T., Ruiz-Suarez L.G., Ruiz-Suarez J.C., Molina M.J. and Montero M.: Atmos. Environ. 1997, **31**, 609–620.

[26] Barnard J.C., Chapman E.G., Fast J.D., Schmelzer J.R., Slusser J.R. and Shetter R.E.: Atmos. Environ. 2004, **38**, 3393–3403.

DOBOWA I SEZONOWA ZMIENNOŚĆ STAŁYCH SZYBKOŚCI REAKCJI FOTOLIZY NO$_2$ I TITRACJI NO ORAZ STOSUNKU NO$_2$/NO W POWIETRZU ATMOSFERYCZNYM OLSZTYNA

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Abstrakt: W pracy przedstawiono wyniki zmienności stałych szybkości reakcji fotolizy NO$_2$ (J$_{NO_2}$) i titracji NO (k$_3$), a także stosunku stężeń NO$_2$/NO wyznaczonego eksperymentalnie oraz obliczonego dla stanu fotostacjonarnego w powietrzu atmosferycznym Olsztyna. Stała titracji w miesiącu letnim (czerwiec 2008 r.) wahała się w ciągu doby w zakresie od 20.8 do 25.3 ppm^{-1} · min^{-1}, natomiast w miesiącu zimowym (grudzień 2008 r.) – w zakresie od 16.5 do 17.2 ppm^{-1} · min^{-1}. Z kolei stała J$_{NO_2}$, która zależy od natężenia całkowitego promieniowania słonecznego i kąta zenitalnego Słońca, wahała się od zera w godzinach nocnych do 0.071 min^{-1} o godzinie 12:00 czasu lokalnego zimą i 0.254 min^{-1} o godz. 11:00 latem. Stosunek NO$_2$/NO wykazuje charakterystyczną zmienność dobową z minimum przypadającym na godziny południowe. Zarówno latem, jak i zimą obserwowany stosunek NO$_2$/NO jest większy niż obliczony. W czerwcu stwierdzono najmniejsze wartości obliczonego stosunku NO$_2$/NO, którego średnia o godzinie 12:00 wynosiła 0.0407 i była aż 176 razy mniejsza niż wartość NO$_2$/NO wyznaczona eksperymentalnie. Wskazuje to na duże znaczenie reakcji utleniania NO do NO$_2$ z udziałem lotnych związków organicznych (VOC) i/lub tlenku węgla.

Słowa kluczowe: fotoliza NO$_2$, titracja NO, stałe szybkości reakcji, stosunek NO$_2$/NO, fotochemia troposfery, ozon troposferyczny

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CONTENT OF NITROGEN COMPOUNDS IN SOIL POLLUTED WITH CHROMIUM(III) AND CHROMIUM(VI) AFTER APPLICATION OF COMPOST, ZEOLITE AND CALCIUM OXIDE

ZAWARTOŚĆ ZWIĄZKÓW AZOTOWYCH W GLEBIE ZANIECZYSZCZONEJ CHROMEM(III) I CHROMEM(VI) PO APLIKACJI KOMPOSTU, ZEOLITU I TLENKU WAPNIA

Abstract: The present study has been undertaken in order to determine the influence of tri- and hexavalent chromium compounds – 25, 50, 100 and 150 mg $\cdot$ kg^{-1} of soil on the concentration of nitrogen compounds in soil after crop harvest, and the effectiveness of neutralizing substances, such as compost, zeolite and calcium oxide, on alleviating results of chromium pollution. Soil contamination with chromium(III) and chromium(VI) significantly modified the content of nitrogen compounds in soil after plant harvests. Under the influence of trivalent chromium, in a series lacking any neutralising substances, the total nitrogen content decreased while the ammonia nitrogen level rose after plant harvest. Chromium(VI) had a similar influence on N-NH$_4^+$. The neutralising substances added to soil, such as compost, zeolite and calcium oxide had a significant effect on the content of total nitrogen in soil. Calcium oxide in the objects polluted with chromium(III) and chromium(VI) caused a significant decrease in the content of N-total in soil. Compost, zeolite and calcium oxide caused an increase in the average content of N-NO$_3^-$ in soil, with the effect being stronger in post polluted with chromium(VI) than with chromium(III). As for chromium(VI), the content of N-NO$_3^-$ was most strongly affected by calcium oxide added as a soil amending substances. All the tested neutralising substances had a weaker influence on the content of N-NH$_4^+$ in soil.

Keywords: chromium(III), chromium(VI), soil, compost, zeolite, CaO, N-NH$_4^+$, N-NO$_3^-$

Contamination of the natural environment with xenobiotics, including heavy metals, leads to modifications of the basic physiochemical properties of soil. Chromium is one of the heavy metals that can appear excessively in the environment due to human activity. Various derivatives of this element are emitted to the nature, where they undergo further transformations, creating a wide range of chemical and physical forms [1]. The most widespread in nature are chromium compounds which have an oxidation

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state of +3 or +6. These compounds differ from each other in the chemical properties as well as chemical and biological reactivity [2]. Research on reducing the effect of chromium on soils or plants, which are an intermediary link in the trophic chain between sources of chromium pollution and humans, seems important in all scientific disciplines connected with nature conservation.

Thus, the present study has been undertaken in order to determine the influence of tri- and hexavalent chromium compounds on the concentration of nitrogen compounds in soil after crop harvest, and the effectiveness of neutralizing substances, such as compost, zeolite and calcium oxide, on alleviating results of chromium pollution.

Material and methods

The experimental part of the study was conducted as a series of pot trials established in a greenhouse belonging to the University of Warmia and Mazury in Olsztyn. The soil used for the trials had a grain size distribution of light loamy sand and the following properties: pH_{KCl} 4.8, hydrolytic acidity (HA) – 33.75 mmol $(H^+) \cdot kg^{-1}$, exchangeable base cations (EBC) – 62.20 mmol(+) $\cdot kg^{-1}$, cation exchange capacity (CEC) – 95.95 mmol(+) $\cdot kg^{-1}$; base saturation with base cations (BS) – 64.8 %, content of C_{org} – 7.13 g $\cdot kg^{-1}$, content of available phosphorus 46.6 mg $\cdot kg^{-1}$, potassium 8.2 mg $\cdot kg^{-1}$, and magnesium 33.9 mg $\cdot kg^{-1}$, content of total nitrogen 0.27 mg $\cdot kg^{-1}$, $N-NH_4^+$ 16.20 mg $\cdot kg^{-1}$, and $N-NO_3^-$ 3.52 mg $\cdot kg^{-1}$. Before being placed in polyethylene pots, each holding 9.5 kg, soil was amended with neutralising substances, such as compost and zeolite in the amount 3 % relative to the soil mass and calcium oxide in the amount equal 1 hydrolytic acidity (HA). Additionally, the following quantities of basic macro- and micronutrients were added to soil: N-110 $[CO(NH_2)_2 + (NH_4)_6 Mo_7O_{24} \cdot 4H_2O + (NH_4)_2HO_4]$, P-50 $[(NH_4)_2HPO_4]$, K-110 $[KCl + KCr(SO_4)_2 \cdot 12H_2O + K_2Cr_2O_7]$, Mg-50 $[MgSO_4 \cdot 7H_2O]$, B-0.33 $[H_3BO_3]$, Mn-5 $[MnCl_2 \cdot 4H_2O]$, Mo-5 $[(NH_4)_6Mo_7O_{24} \times \times 4H_2O]$ mg $\cdot kg^{-1}$ soil. Soil was artificially polluted with aqueous solutions of chromium(III) as $KCr(SO_4)_2 \cdot 12H_2O$ and chromium(VI) as $K_2Cr_2O_7$, in the following rates: 0, 25, 50, 100 and 150 mg $Cr \cdot kg^{-1}$ of soil. Two crops were grown: spring barley (*Hordeum vulgare* L.) cv. Ortega (main crop) and maize (*Zea mays* L.) cv. Fripon (aftercrop). The sowing density of barley was 15, while that of maize was 8 plants per pot. During the growth of the crops, the soil moisture content was maintained at 60 % capillary water capacity. Spring barley was harvested during the heading phase and maize was collected in the intensive stem elongation phase, ie on days 56 and 67 of vegetative growth, respectively. Soil material was sampled during the maize harvest.

Soil samples were tested to determine total nitrogen content with Kjeldahl's method in concentrated sulphuric(VI) acid and hydrogen peroxide as a catalyser [3], $N-NH_4^+$ by colorimetric method with Nessler's reagent [4], $N-NO_3^-$ by colorimetric method using phenoldisulfonic acid [4]. The results of the determinations were processed statistically with an aid of Statistica software programme [5], applying three-factor analysis of variance ANOVA. Besides, Pearson's simple correlation coefficients were used to test the relationships between soil pollution with chromium(III) and chromium(VI) versus the content of nitrogen compounds in soil.

Results and discussion

Nitrogen which enters soil undergoes complex and dynamic transformations. Its chemical form and amount present in soil depends on a number of factors including climatic conditions, content of organic matter, mineral fertilization and man-made conditions [6–9]. When present in soil in excessive amounts, heavy metals can retard mineralization of organic compounds, which are a source of nitrogen [10]. In the present pot experiment, soil contamination with chromium(III) and chromium(VI) significantly modified the content of nitrogen compounds in soil after spring barley and maize harvests. In the series without neutralising substances, soil from the objects polluted with hexavalent chromium rather than trivalent chromium contained more total nitrogen (7 % more on average) (Table 1). Higher rates of trivalent chromium had a negative effect on the total nitrogen content in analysed soil (r = –0.967), with the highest dose of Cr(III), ie 150 mg · kg^{-1} soil, depressing the concentration of N-total by 36 % relative to the control series (no pollution). The effect of Cr(VI) on the concentration of nitrate(V) nitrogen in the analysed soil was less unambiguous.

Microbiological and chemical reactions involved in the mineralization processes of organic nitrogen forms generate mineral forms of this element: ammonium cation NH_4^+ and nitrate anion NO_3^- [11]. In soil, these two ions are the primary source of nitrogen for plants [12]. Under the soil and climatic conditions occurring in Poland, $N-NH_4^+$ is typically the dominant form of mineral nitrogen [6, 13]. Mineralization of organic nitrogen bonds depends on the decomposition of organic soil matter components, C:N ratio and moisture within the soil profile [14, 15]. The process is made possible by various groups of soil borne microorganisms, which produce enzymes involved in deamination of organic nitrogen compounds [16, 17]. In a study performed by Wyszkowska [18], hexavalent chromium strongly affected transformations of organic and mineral forms of nitrogen in soil, inhibiting the processes of ammonification and nitrification. According to Rudnicki and Galezewski [19], growing plants take up nitrogen mainly in its nitrate form, thus depleting nitrogen supply in soil. In the present experiment, increasing rates of tri- and hexavalent chromium in the series with unamended soil positively shaped the content of $N-NH_4^+$ in analysed soil. In the series with Cr(III), the rate of 150 mg · kg^{-1} had the strongest effect, doubling the concentration of $N-NH_4^+$. Hexavalent chromium had a positive effect on the content of ammonia nitrogen, initially raising its concentration in soil and later maintaining it on an approximately same level. In the series without neutralising substances, under the influence of the lowest Cr(VI) rate, ie 25 mg · kg^{-1} soil, ammonia nitrogen was observed to have increased by 51 %. In contrast, the highest dose of hexavalent chromium (150 mg · kg^{-1}) resulted in a nearly two-fold decrease in the concentration of $N-NO_3^-$ versus the control.

The concentration of nitrogen compounds in soil was also affected by the neutralising substances such as compost, zeolite and calcium oxide (Table 1). The strongest negative effect on the average total nitrogen content in soil after crop harvests was produced by calcium oxide, both in the tri- and hexavalent trials. Under the influence of this substance, the average total nitrogen content fell by 23 and 51 %,

Table 1

Content of total-N, N-NO$_3^-$ and N-NH$_4^+$ in 1 kg d.m. of soil after plants harvest

Total-N [g · kg⁻¹ d.m.]

Cr dose [mg · kg⁻¹ of soil]	Chromium(III)					Chromium(VI)				
	without additives	compost	zeolite	CaO	average	without additives	compost	zeolite	CaO	average
0	0.97	0.78	0.64	0.63	0.76	0.97	0.78	0.64	0.63	0.76
25	0.86	0.98	0.85	0.65	0.84	0.87	0.99	0.98	0.51	0.84
50	0.85	0.78	0.88	0.64	0.79	0.85	0.98	0.91	0.42	0.79
100	0.79	0.98	0.88	0.64	0.82	0.77	0.88	0.80	0.32	0.69
150	0.62	0.88	0.91	0.60	0.75	0.96	0.81	0.92	0.25	0.74
r	–0.967**	0.310	0.737**	–0.624*	–0.169	–0.089	–0.266	0.373	–0.971**	–0.582
Average	0.82	0.88	0.83	0.63	0.79	0.88	0.89	0.85	0.43	0.76

LSD: a – 0.02**, b – 0.02**, c – 0.02**, a · b – 0.04**, a · c – 0.03**, b · c – 0.05**, a · b · c – 0.07**

N-NH$_4^+$ [mg · kg⁻¹ d.m.]

Cr dose [mg · kg⁻¹ of soil]	Chromium(III)					Chromium(VI)				
	without additives	compost	zeolite	CaO	average	without additives	compost	zeolite	CaO	average
0	12.19	21.66	19.52	17.20	17.64	12.19	21.66	19.52	17.20	17.64
25	13.29	21.80	16.01	15.59	16.67	15.63	22.82	13.76	13.88	16.52
50	13.92	22.77	14.51	15.65	16.71	16.99	20.14	19.91	16.75	18.45
100	17.04	20.02	15.32	20.92	18.33	16.90	20.07	20.17	17.66	18.70
150	24.83	18.06	19.16	20.83	20.72	16.92	19.58	25.37	32.97	23.71
r	0.952**	–0.865**	0.068	0.818**	0.845**	0.722*	–0.789**	0.751**	0.821**	0.880**
Average	16.25	20.86	16.90	18.04	18.01	15.73	20.85	19.75	19.69	19.00

LSD: a – 0.54**, b – 0.85**, c – 0.76**, a · b – 1.20*, a · c – 1.08**, b · c – 1.70**, a · b · c – 2.41**

Table 1 contd.

Cr dose [mg · kg⁻¹ of soil]	Chromium(III)					Chromium(VI)				
	Type of neutralizing substance									
	without additives	compost	zeolite	CaO	average	without additives	compost	zeolite	CaO	average
	$N-NO_3^-$ [mg · kg⁻¹ d.m.]									
0	0.55	1.11	0.62	0.58	0.72	0.55	1.11	0.62	0.58	0.72
25	0.70	0.82	0.71	1.05	0.82	0.83	0.94	0.95	0.82	0.89
50	0.34	0.64	0.47	0.80	0.56	0.64	0.99	0.77	2.65	1.26
100	0.17	0.53	0.47	0.89	0.52	0.64	0.99	0.77	2.87	1.32
150	0.53	0.50	0.78	0.54	0.59	0.27	0.61	0.67	3.90	1.36
r	−0.368	−0.885**	0.221	−0.289	−0.657*	−0.676*	−0.833**	−0.183	0.941**	0.875**
Average	0.46	0.72	0.61	0.77	0.64	0.59	0.93	0.76	2.16	1.11
LSD	a − 0.04**, b − 0.06**, c − 0.05**, a · b − 0.09**, a · c − 0.08**, b · c − 0.12**, a · b · c − 0.18**									

LSD for: a – contamination kind, b – chromium dose, c – kind of neutralizing substance; * – significant for p = 0.05, ** – significant for p = 0.01; r – correlation coefficient.

respectively, relative to the control variant (unamended soil). When chromium(III) was tested as a pollutant, the total nitrogen content was significantly affected by compost, as it increased by several per cent compared with the control (no soil improving substances). The level of ammonia nitrogen was most significantly influenced by the introduction of compost, both to tri- and hexavalent chromium polluted pots, where this neutraliser increased the average $N-NH_4^+$ by 28 and 33 %, respectively, versus the control without any neutralising substances. In the series with hexavalent chromium, zeolite and calcium oxide produced weaker effect. The application of compost, zeolite and calcium oxide to soil under spring barley and maize increased the content of nitrate nitrogen, with the rise being higher in objects polluted with Cr(VI) versus to pots with Cr(III). When soil was contaminated with hexavalent chromium, the content of $N-NO_3^-$ was most strongly affected by calcium oxide added to soil, which raised the amount of this form of nitrogen by nearly four-fold compared with the control. Compost added to soil produced weaker influence on the analysed properties of soil. Application of composts improves physical, chemical and biological properties of soil [20], but can also be effective in reducing the negative influence of chromium on the content of nitrogen compounds, which has been confirmed by the present experiment. In another experiment, Wyszkowski and Ziółkowska [21, 22] concluded that soil liming caused a decrease in the amount of ammonia nitrogen.

Conclusions

1. Under the influence of trivalent chromium, in a series lacking any neutralising substances, the total nitrogen content decreased while the ammonia nitrogen level rose after plant harvest. Chromium(VI) had a similar influence on $N-NH_4^+$.

2. The neutralising substances added to soil, such as compost, zeolite and calcium oxide had a significant effect on the content of total nitrogen in soil.

3. Calcium oxide in the objects polluted with chromium(III) and chromium(VI) caused a significant decrease in the content of N-total in soil.

4. Compost, zeolite and calcium oxide caused an increase in the average content of $N-NO_3^-$ in soil, with the effect being stronger in post polluted with chromium(VI) than with chromium(III). As for chromium(VI), the content of $N-NO_3^-$ was most strongly affected by calcium oxide added as a soil amending substances. All the tested neutralising substances had a weaker influence on the content of $N-NH_4^+$ in soil.

References

[1] Richard F.C. and Bourg A.C.M.: Water Res. 1991, **25**(7), 807–816.
[2] Shupac S.I.: Environ. Health Perspect. 1991, **92**, 7–11.
[3] Bremner J.M.: Amer. Soc. Agron. 1965, **2**, 1149–1178.

[4] Panak H. (ed.): Przewodnik metodyczny do ćwiczeń z chemii rolnej. Wyd. ART., Olsztyn 1997, 242 pp.

[5] StatSoft, Inc.: STATISTICA (data analysis software system), version 8.0. www.statsoft.com, 2007.

[6] Czępińska-Kamińska D., Rutkowski A. and Zakrzewski S.: Roczn. Glebozn. 1999, **50**(4), 47–56.

[7] Scholefield D., Lockyer D.R. Whitehead D.C. and Tyson K.C.: Plant Soil 1991, **132**, 165–171.

[8] Fotyma E.: Zesz. Probl. Post. Nauk Roln. 1996, **440**, 89–100.

[9] Czekała J.: Zesz. Probl. Post. Nauk. Roln. 2003, **493**, 585–590.

[10] Benbi D.K., Richter J., Vermoesen A. and Van-Cleemput O.: Proc. of the 8th nitrogen workshop held at the University of Ghent, 5–8 September 1996, 17–22.

[11] Sapek B.: Mat. Inf., Wyd. IMUZ 1995, **30**, 31 pp.

[12] Fotyma E., Fotyma M. and Pietruch: Nawozy Nawoż. 2005, **2**(23), 39–48.

[13] Łabętowicz J. and Rutkowska B.: Zesz. Probl. Post. Nauk Roln. 1996, **440**, 224–229.

[14] Gotkiewicz J. and Gotkiewicz M.: Wiad. IMUZ 1991, **77**, 59–76.

[15] Paul E.A. and Clark F.E.: Mikrobiologia i biochemia gleb, Wyd. UMCS, Lublin 2000, 400 pp.

[16] Barabasz W.: Post. Mikrobiol. 1992, **31**, 3–33.

[17] Brzezińska M., Stępniewska Z. and Stępniewski W.: Soil Biol. Biochem. 1998, **30**(13), 1783–1790.

[18] Wyszkowska J.: Rozprawy i monografie, Wyd. UWM, Olsztyn 2002, 134 pp.

[19] Rudnicki F. and Gałęzewski L.: Roczn. AR Poznań 2006, **66**, 323–329

[20] Szulc W., Rutkowska B., Łabętowicz J. and Ożarowski G.: Zesz. Probl. Post. Nauk Roln. 2003, **494**, 445–451.

[21] Wyszkowski M. and Ziółkowska A.: Zesz. Probl. Post. Nauk. Roln. 2006, **513**, 563–573.

[22] Wyszkowski M. and Ziółkowska A.: Ochr. Środow. Zasob. Natur. 2007, **31**, 154–159.

ZAWARTOŚĆ ZWIĄZKÓW AZOTOWYCH W GLEBIE ZANIECZYSZCZONEJ CHROMEM(III) I CHROMEM(VI) PO APLIKACJI KOMPOSTU, ZEOLITU I TLENKU WAPNIA

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Abstrakt: Celem przeprowadzonych badań było określenie wpływu wzrastającego zanieczyszczenia związkami chromu(III) i chromu(VI) – 25, 50, 100, 150 mg · kg^{-1} gleby oraz kompostu, zeolitu i tlenku wapnia na zawartość związków azotowych w glebie po zbiorze jęczmienia jarego i kukurydzy. Zanieczyszczenie chromem(III) i chromem(VI) znacząco modyfikowało zawartość związków azotowych w glebach po zbiorze roślin. Pod wpływem chromu trójwartościowego w serii bez dodatków łagodzących nastąpiło zmniejszenie zawartości N-ogólnego, natomiast zwiększenie stężenia N-amonowego w glebie po zbiorze roślin. Podobny wpływ miał chrom(VI) w przypadku N-NH$_4^+$. Zastosowane dodatki neutralizujące w postaci kompostu, zeolitu i tlenku wapnia miały znaczący wpływ na zawartość badanych form azotu w glebie. Tlenek wapnia w obiektach z chromem(III) i chromem(VI) wywołał znaczące zmniejszenie zawartości N-ogólnego w glebie. Kompost, zeolit i tlenek wapnia spowodował zwiększenie średniej zawartości N-NO$_3^-$ w glebie, przy czym działanie to było większe w wazonach z chromem(VI) niż w obiektach z chromem(III). W przypadku chromu(VI) na zawartość N-NO$_3^-$ najsilniej wpływał dodatek do gleby tlenku wapnia. Zastosowane substancje najsłabiej działały na zawartość N-NH$_4^+$ w glebie.

Słowa kluczowe: chrom(III), chrom(VI), gleba, kompost, zeolit, CaO, N-NH$_4^+$, N-NO$_3^-$

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EFFECT OF COMPOST, BENTONITE, ZEOLITE AND CALCIUM OXIDE ON MINERAL NITROGEN CONTENT IN NICKEL CONTAMINATED SOIL

WPŁYW KOMPOSTU, BENTONITU, ZEOLITU I TLENKU WAPNIA NA ZAWARTOŚĆ AZOTU MINERALNEGO W GLEBIE ZANIECZYSZCZONEJ NIKLEM

Abstract: The purpose of this study has been to determine the effect of compost, bentonite, zeolite and calcium oxide on the concentration of nitrogen in nickel contaminated soil (0, 100, 200 and 300 mg Ni $\cdot$ kg^{-1} of soil). The level of mineral nitrogen in soil depended on the soil contamination with nickel, addition of pollution neutralizing substances and crop species. The effect of nickel on the content of mineral nitrogen in soil was closely connected with the crop species. In the series of trials without substances alleviating nickel contamination, the metal pollution depressed the share and content of N-NO$_3^-$ in mineral nitrogen in soil under oats, but raised its concentration and percentage in soil under yellow lupine. The effect of nickel was much stronger in soil under yellow lupine than under oats. Nickel had an adverse effect on the content of N-NH$_4^+$ in soil under yellow lupine. Application of bentonite, zeolite and calcium oxide limited the content of ammonia nitrogen in soil, as compared with the average concentration from the unamended series. Bentonite had the strongest effect on the content of N-NH$_4^+$ in soil under oats, while in soil under yellow lupine zeolite and calcium oxide were the most effective. The neutralising substances added to soil had a contrary influence on the content of nitrate(V) nitrogen when compared with that produced on ammonia nitrogen. They all favoured increased concentration of this form of nitrogen in soil. The strongest effect on the average content of N-NO$_3^-$ was produced by bentonite. Bentonite, zeolite and calcium oxide resulted in increased ratios of nitrate nitrogen in total mineral nitrogen in soil, with bentonite producing a stronger effect in soil under oats while zeolite and calcium oxide being more effective in soil under yellow lupine. Zeolite and calcium oxide had a stronger effect on the ratio of N-NO$_3^-$ in soil under yellow lupine than in soil under oats. Compost produced similar results, but only in soil under yellow lupine.

Keywords: contamination, nickel, compost, bentonite, zeolite, calcium oxide, soil, mineral nitrogen

Under the soil and climatic conditions prevailing in Poland, nitrogen is one of the major nutrients essential for the proper growth and development of crops. The element plays a critical role in soil fertility and volume of crop yields [1]. Atmosphere is the

main source of nitrogen, which, bound either biologically or chemically, enters soils, where it undergoes various transformations [2]. Plants take up mineral nitrogen as NH_4^+ and NO_3^- ions [3]. The rate of releasing mineral nitrogen in soil depends on environmental conditions and varies between years and different periods of the vegetative season [4]. The most important source of nitrogen for the crops grown in Poland is mineral fertilization, and the way it is utilized depends on crop species, fertilization rates and techniques as well as soil and climatic conditions [5]. Crops use up to 50–70 % of nitrogen from mineral fertilizers but much less, about 30 %, from organic fertilizers [6]. Organic compounds from organic fertilizers undergo mineralization, which results in the generation of ammonia nitrogen NH_4^+; mineral fertilizers are a source of nitrogen in the form of NH_4^+ and NO_3^- ions. Through nitrification, NH_4^+ is transformed to NO_3^- [7]. These mineral forms are a source of nitrogen for plants, but when taken up in excess can disturb their homeostasis due to the excessive accumulation of nitrates(V) compounded by the limited content of total nitrogen, proteins, free amino acids and sugars in plant tissues [8]. The forms of nitrogen which have not been absorbed by plants, particularly nitrates(V), can migrate downwards through the soil profile and threaten the soil environment, including soil and ground waters [9]. The content of mineral nitrogen in soil can fluctuate depending on a number of factors such as, for example, trace elements in soil, including nickel. The effect of nickel can be inhibited by adding to soil various substances, eg post-production waste. However, application of such soil supplements can have beneficial as well as adverse influence on natural environment, including soil, or on the growth and development of crops [10].

The purpose of this study has been to determine the effect of compost, bentonite, zeolite and calcium oxide on the concentration of nitrogen in nickel contaminated soil.

Material and methods

The experiment has been conducted in a greenhouse belonging to the University of Warmia and Mazury in Olsztyn. The trials were established in polyethylene pots containing 9.5 kg of soil of the grain size distribution corresponding to loamy sand. Soil was polluted with nickel in the following amounts: 0, 100, 200 and 300 mg Ni $\cdot$ kg^{-1} soil. The following substances were added to soil to alleviate the effects of nickel pollution: compost (3 % of soil mass), bentonite and zeolite (2 % of soil mass) and calcium oxide (60 %) in the amount equal 1 hydrolytic acidity (HA). In order to ensure proper nourishment of the crops, basic nutrients were added to all the pots in the following quantities [mg $\cdot$ kg^{-1} of soil]: N-150 (oats) and 25 (yellow lupine) [$CO(NH_2)_2$ + $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$], P-30 [$KH_2PO_4$]; K-75 [$KH_2PO_4$ + KCl], Mg-50 [$MgSO_4 \times \times 7H_2O$], Mn-5 [$MnCl_2 \cdot 4H_2O$], Mo-5 [$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$], B-0.33 [$H_3BO_3$]. Nickel was introduced to soil as $NiCl_2 \cdot 6H_2O$. The effect of nickel and neutralising substances was tested on oats (*Avena sativa* L.) cv. Borowiak and yellow lupine (*Lupinus luteus* L.) cv. Mister. The sowing density of oats was 15 plants per pot and that of yellow lupine – 8 plants per pot. During the plants' growing season, the soil moisture content was maintained at 60 % of capillary water capacity. The crops were harvested during the inflorescence stage, after 58 days of vegetative growth.

The following were determined in soil samples: $N-NH_4^+$ by colorimetry with Nessler's reagent [11] and $N-NO_3^-$ by colorimetry with phenyldisulfonic acid [11]. The results were processed statistically using a three-factor analysis of variance ANOVA in a software programme Statistica [12]. In addition, Pearson's correlation coefficients were calculated between the rate of nickel and content of mineral nitrogen in soil.

Results and discussion

The level of mineral nitrogen in soil depended on the soil contamination with nickel, addition of pollution neutralizing substances and crop species (Tables 1 and 2). The effect of nickel on the content of mineral nitrogen in soil was closely connected with the crop species. In the series without neutralizing substances, nickel contamination of soil depressed the content of $N-NO_3^-$ in soil under oats but increased it under yellow lupine. It needs to be added that the influence of nickel in soil under yellow lupine was evidently much stronger than under oats. The highest rate of nickel (300 mg Ni · kg^{-1} soil) caused a 57 % decrease (r = –0.602) in the content of nitrates(V) in soil under oats and their 11-fold increase (r = 0.881) in soil under yellow lupine. Besides, nickel had a negative effect on the content of $N-NH_4^+$ in soil under yellow lupine, while in soil under oats its influence on this form of nitrogen did not have unidirectional character. The highest rate of nickel in soil under yellow lupine caused a 65 % decrease (r = –0.942) in the concentration of ammonia nitrogen. The content of $N-NO_3^-$ in the objects not amended with neutralising substances was nearly four-fold higher in soil under yellow lupine than oats whereas the concentration of $N-NH_4^+$ was similar in both soils.

Table 1

$N-NH_4^+$ content in soil after plants harvest [mg · kg^{-1}]

Nickel dose [mg · kg^{-1} of soil]	Kind of substance neutralizing effect of nickel					
	without additions	compost	bentonite	zeolite	calcium oxide	average
Oats (*Avena sativa* L.)						
0	33.95	31.72	8.83	8.40	33.52	23.29
100	29.44	38.81	9.43	14.77	31.72	24.83
200	25.13	40.53	8.44	15.93	33.52	24.71
300	54.73	36.06	7.11	32.83	26.68	31.48
r	0.571	0.495	–0.807**	0.921**	–0.747**	0.861**
Yellow lupine (*Lupinus luteus* L.)						
0	55.50	11.54	23.72	8.57	12.32	22.33
100	38.34	13.43	35.76	10.72	11.80	22.01
200	18.98	50.26	25.87	11.54	9.52	23.23
300	19.59	55.03	10.72	13.69	12.27	22.26
r	–0.942**	0.928**	–0.613	0.987**	–0.235	0.245
LSD	a − 1.31**, b − 1.46**, c − 0.92**, a · b − 2.92**, a · c − 1.84**, b · c − 2.07**, a · b · c − 4.13**					

LSD for: a – nickel dose, b – kind of neutralizing substance, c – plant species; * – significant for p = 0.05, ** – significant for p = 0.01; r – correlation coefficient.

Table 2

N-NO$_3^-$ content in soil after plants harvest [mg · kg^{-1}]

Nickel dose [mg · kg^{-1} of soil]	Kind of substance neutralizing effect of nickel					
	without additions	compost	bentonite	zeolite	calcium oxide	average
Oats (*Avena sativa* L.)						
0	18.15	4.30	26.85	9.11	3.87	12.46
100	4.07	10.98	41.03	27.12	2.97	17.23
200	4.67	8.37	57.14	43.26	29.39	28.57
300	7.81	6.44	55.20	13.34	38.13	24.18
r	−0.602	0.173	0.926**	0.242	0.933**	0.838**
Yellow lupine (*Lupinus luteus* L.)						
0	5.27	62.91	88.06	28.52	94.16	55.78
100	4.47	51.33	84.69	124.28	141.73	81.30
200	63.04	160.74	171.48	132.55	112.94	128.15
300	60.51	104.80	120.08	120.48	75.22	96.22
r	0.881**	0.613	0.587	0.750**	−0.390	0.718*
LSD	a − 2.33**, b − 2.61**, c − 1.65**, a · b − 5.22**, a · c − 3.30**, b · c − 3.69**, a · b · c − 7.38**					

LSD for: a – nickel dose, b – kind of neutralizing substance, c – plant species; * – significant for p = 0.05, ** – significant for p = 0.01; r – correlation coefficient.

The substances introduced to soil in order to reduce the effect of nickel on the content of mineral nitrogen included organic compost and mineral substances, such as bentonite, zeolite and calcium oxide. Analogously to organic or natural fertilizers, composts contain large amounts of macro- and micronutrients, which are essential for the proper growth and development of plants [13]. Bentonites are distinguishable by many specific properties, such as ionic exchange ability, water dispersibility, excellent sorption characteristics, swellability and ability to create thixotropic suspensions [14]. Having porous structure, zeolites can absorb and release water as well as exchange the cations they possess without losing their characteristic structure [10]. Liming is used to enhance the microbiological activity of soil, activate the mineralisation process, improve availability of nutrients and regulate the soil reaction. Mineral fertilization and liming of soil have a direct influence on the volume and quality of crop yields [1]. Nickel contamination of soil inhibits nitrification [15] and ammonification [16], acting more strongly in light than in medium heavy soil [15, 16].

The application of bentonite, zeolite and calcium oxide to soil depressed the concentration of ammonia nitrogen in soil compared with the average content from the series without soil amendments, with the effect produced by calcium oxide and zeolite being stronger in soil under yellow lupine than in soil under oats, unlike the influence of bentonite, which was more evident in soil under oats than under yellow lupine (Fig. 1). The most profound effect on the content of N-NH$_4^-$ in soil under yellow lupine was produced by bentonite. In soil under oats, zeolite and calcium oxide were more effective. Compost did not produce large changes in the concentration of ammonia
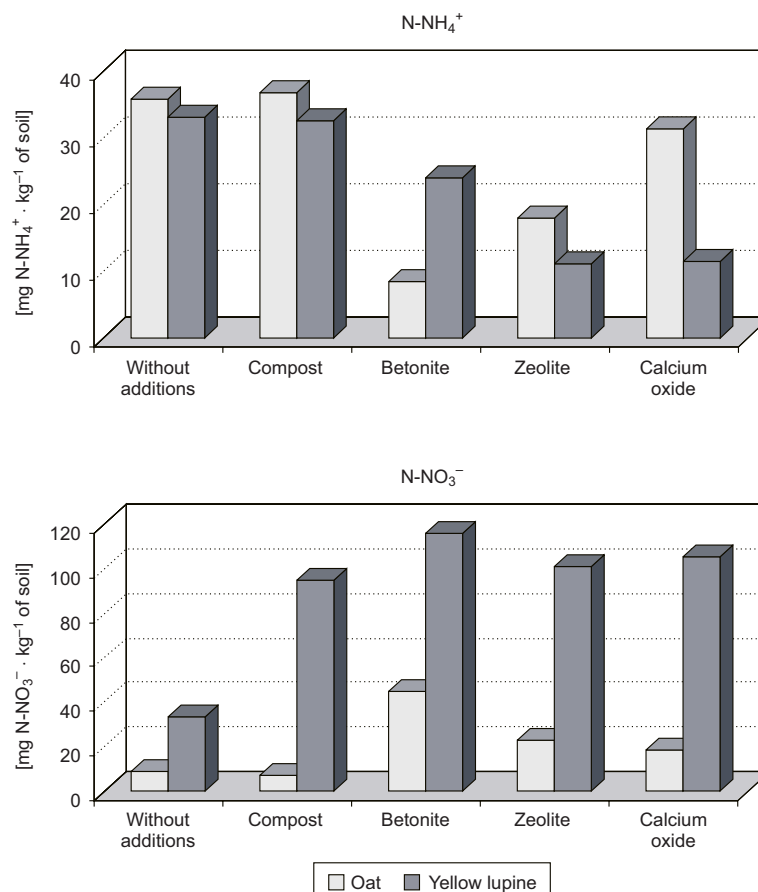
N-NH$_4^+$

N-NO$_3^-$

□ Oat   ■ Yellow lupine

Fig. 1. Average content of mineral nitrogen in soil after plants harvest, in dependence from addition of a different substances [mg · kg^{-1} of soil]

nitrogen in soil. The influence of bentonite in soil under oats depressed the content of N-NH$_4^+$ by 27 % relative to unamended soil. The average concentration of N-NH$_4^+$ in the bentonite series was three-fold higher in soil under yellow lupine than in soil under oats. The content of N-NH$_4^+$ in soil with added zeolite was two-fold (oats) or three-fold (yellow lupine) lower than in the objects without neutralising substances. The effect of CaO on the concentration of N-NH$_4^+$ in soil under oats was relatively weak, causing a 65 % decrease in ammonia nitrogen compared with the unamended series. Similar results have been reported by Tkaczyk and Bednarek [1] in their studies involving spring barley, where the uptake of nitrogen from limed soil was significantly higher from acidic soil, leading to a depressed level of mineral nitrogen in soil.

The neutralising substances had a reverse effect on the content of nitrate nitrogen (Fig. 1). They favoured the increased concentration of this form of nitrogen in soil. The most important effect on average content of N-NO$_3^-$ had bentonite. Bentonite produced

stronger effect of the average concentration of N-NO$_3^-$ in soil under oats, whereas zeolite and calcium oxide were more effective in soil under yellow lupine. In soil under oats, bentonite raised the average level of N-NO$_3^-$ two-fold compared with the soils with added zeolite and calcium oxide, as much as six-fold relative to the soils with compost and five-fold versus the unamended soils. The application of calcium oxide to soil under oats increased the concentration of N-NO$_3^-$ three-fold. When zeolite was added, the content of this form of nitrogen rose three-fold. Additionally, it has been observed that the average content of this form of mineral nitrogen in soil under yellow lupine tended to rise under the effect of compost, in contrast to soil under oats. When yellow lupine was grown, bentonite, zeolite and calcium oxide added to soil had similar influence on the content of nitrate nitrogen, as in each case the latter increased over three-fold compared with unamended soil, although the effect of bentonite was slightly stronger than that of calcium oxide or zeolite.
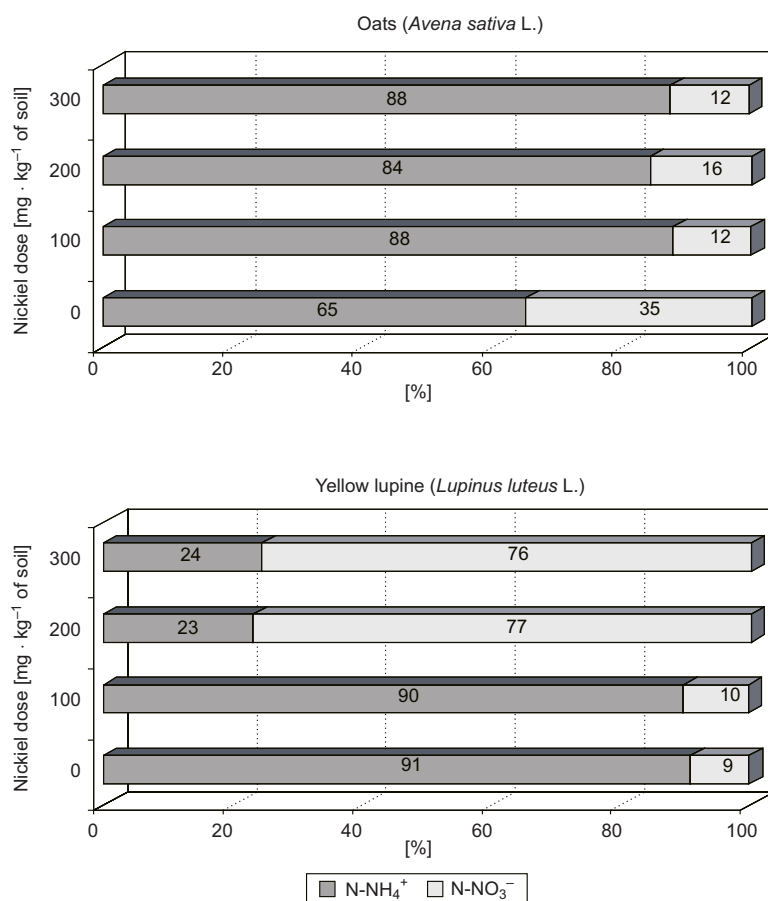

Fig. 2. Effect of soil contamination with nickel on proportion between N-NH$_4^+$ and N-NO$_3^-$ in soil mineral nitrogen after plants harvest [%]

In another experiment conducted by Wyszkowski and Ziolkowska [17, 18] with the same neutralising substances but in soil contaminated with petrol and diesel oil, the added substances were also noticed to affect the content of the mineral forms of nitrogen. Bentonite and lime depressed the level of ammonia nitrogen in soil, analogously to the present experiment, in which $N-NH_4^+$ in soil under oats and yellow lupine occurred in smaller quantities. All the neutralisers, however, favoured accumulation of $N-NO_3^-$ in soil, whether under oats or yellow lupine, with compost producing the weakest effect. In contrast, the application of bentonite or calcium oxide raised three-fold the content of ammonia nitrogen. This dependence has been confirmed in another study by Wyszkowski and Ziolkowska [17], in which introduction of neutralising substances caused a 2.5-fold increase in the content of nitrate nitrogen in soils polluted with petroleum substances.

When comparing percentages of ammonia and nitrate nitrogen in total nitrogen (Figs. 2 and 3), it is possible to observe that they depend on a crop species and soil

Oats (*Avena sativa* L.)

Yellow lupine (*Lupinus luteus* L.)
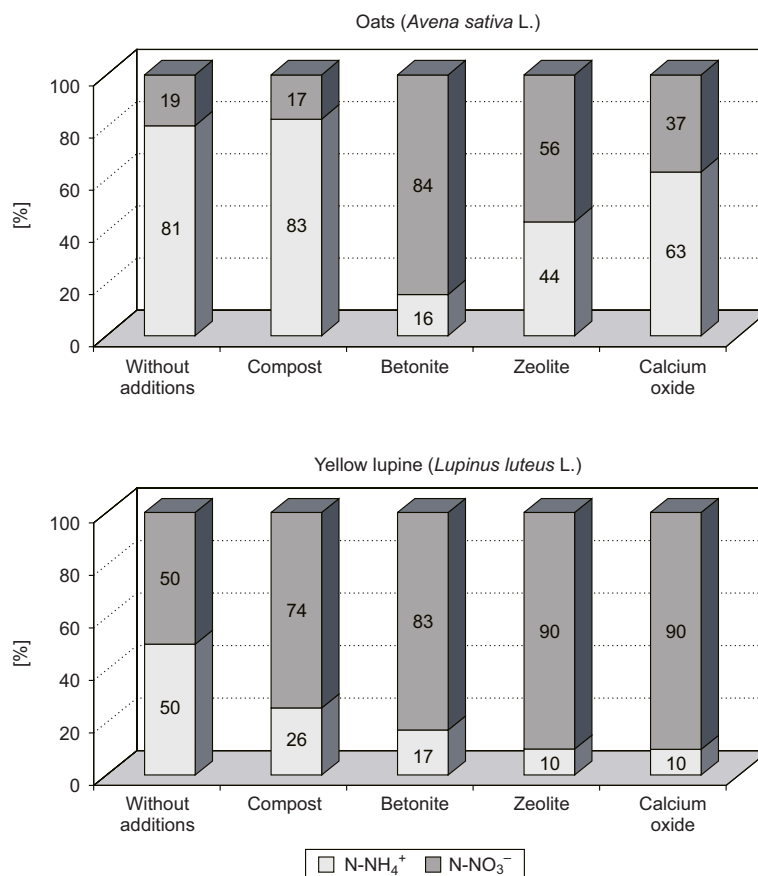
N-NH$_4^+$ N-NO$_3^-$

Fig. 3. Effect of compost, bentonite, zeolite and calcium oxide on proportion between $N-NH_4^+$ and $N-NO_3^-$ in soil mineral nitrogen after plants harvest (average for series) [%]

amending substances. It is very important to know the percentage of nitrate nitrogen in total mineral nitrogen present in soil as it is $N-NO_3^-$ that functions as the main source of nitrogen available to plants. In unamended soil, ammonia nitrogen was on average four-fold more abundant but in soil under lupine the ratio between both forms of nitrogen was approximately 50/50. These observations seem to be verified by a study reported by Rudnicki and Galezewski [19]. Oats seriously depleted the soil supply of nitrogen, although the crop took up nitrate more readily than ammonia nitrogen forms. It should be added that under the influence of nickel contamination, the ratio of ammonia nitrogen in soil under oats tended to rise (Fig. 2). Reverse relationships occurred in soil under lupine polluted with 200 and 300 mg Ni $\cdot$ kg^{-1}. Adding compost to soil which was then sown with oats did not modify these values, but when yellow lupine was grown the share of nitrate nitrogen increased (Fig. 3). The application of bentonite to soil under both oats and yellow lupine, under nearly identical conditions, increased the percentage of $N-NO_3^-$ while depressing that of $N-NH_4^+$ relative to unamended soil ($N-NH_4^+$ fell from 81 or 50 % to 16 and 17 %, respectively) The effect of zeolite and calcium oxide to soil under yellow lupine was similar, increasing the share of $N-NO_3^-$ to 90 % of total mineral nitrogen in soil, at the expense of $N-NH_4^+$. When zeolite and calcium oxide were added to soil under oats the ammonia nitrogen decreased relative to unamended soil, particularly when zeolite was added to soil, although the overall range of modifications was smaller than in soil under oats. Pecio et al [9] reported that in their experiment the nitrate of nitrogen constituted around 65 % of the total mineral nitrogen content in the profile of soil which was amended with farmyard manure under corn and around 80 % in objects without FYM in dry years. In the present experiment, the share of nitrate nitrogen under the effect of compost reached 17 % when oats was grown and 74 % under yellow lupine.

Conclusions

1. In the series of trials without substances alleviating nickel contamination, the metal pollution depressed the share and content of $N-NO_3^-$ in mineral nitrogen in soil under oats, but raised its concentration and percentage in soil under yellow lupine. The effect of nickel was much stronger in soil under yellow lupine than under oats. Nickel had an adverse effect on the content of $N-NH_4^+$ in soil under yellow lupine.

2. Application of bentonite, zeolite and calcium oxide limited the content of ammonia nitrogen in soil, as compared with the average concentration from the unamended series. Bentonite had the strongest effect on the content of $N-NH_4^+$ in soil under oats, while in soil under yellow lupine zeolite and calcium oxide were the most effective.

3. The neutralising substances added to soil had a contrary influence on the content of nitrate nitrogen when compared with that produced on ammonia nitrogen. They all favoured increased concentration of this form of nitrogen in soil. The strongest effect on the average content of $N-NO_3^-$ was produced by bentonite.

4. Bentonite, zeolite and calcium oxide resulted in increased ratios of nitrate nitrogen in total mineral nitrogen in soil, with bentonite producing a stronger effect in soil under

oats while zeolite and calcium oxide being more effective in soil under yellow lupine. Zeolite and calcium oxide had a stronger effect on the ratio of $N\text{-}NO_3^-$ in soil under yellow lupine than in soil under oats. Compost produced similar results, but only in soil under yellow lupine.

References

[1] Tkaczyk P. and Bednarek W.: Zesz. Probl. Post. Nauk Roln. 2006, **513**, 485–491.
[2] Szczepaniak W. and Musolf R.: Agrotechnika 2005, **10**, 4–8.
[3] Michałojć Z.M.: Zesz. Probl. Post. Nauk Roln. 2006, **513**, 277–283.
[4] Orzechowski M.: Zesz. Probl. Post. Nauk Roln. 2006, **513**, 285–292.
[5] Sosulski T., Mercik S. and Szara E.: Ann. UMSC., Sec. E 2004, **59**(2), 589–597.
[6] Mercik S., Łabętowicz J., Sosulski T. and Stępień W.: Nawozy Nawoż. 2002, **IV**, 1(10), 228–237.
[7] Sosulski T. and Łabętowicz J.: Zesz. Probl. Post. Nauk Roln. 2006, **513**, 423–432.
[8] Jasiewicz Cz., Antonowicz J. and Baran A.: Zesz. Probl. Post. Nauk Roln. 2006, **513**, 149–159.
[9] Pecio A., Rutkowska A. and Leszczyńska D.: Fragm. Agronom. 2005, **1**(85), 214–224.
[10] Rumpel J.: Zesz. Probl. Post. Nauk Roln. 1998, **461**, 47–66.
[11] Panak H. (ed.): Przewodnik metodyczny do ćwiczeń z chemii rolnej. Wyd. ART., Olsztyn 1997, 242 pp.
[12] StatSoft, Inc.: STATISTICA (data analysis software system), version 8.0. www.statsoft.com, 2007.
[13] Filipek-Mazur B. and Gondek K.: Zesz. Probl. Post. Nauk Roln. 2006, **512**, 111–120.
[14] Wyszomirski P. and Lewicka E.: Gospod. Surowcami Mineral. 2005, **21**(3), 5–19.
[15] Wyszkowska J., Kucharski J. and Boros E.: Polish J. Natur. Sci. 2006, **20**(1), 111–120.
[16] Wyszkowska J., Boros E. and Kucharski J.: Polish J. Natur. Sci. 2007, **22**(3), 382–394.
[17] Wyszkowski M. and Ziółkowska A.: Zesz. Probl. Post. Nauk Roln. 2006, **513**, 563–573.
[18] Wyszkowski M. and Ziółkowska A.: Ochr. Środow. Zasob. Natural. 2007, **31**, 154–159.
[19] Rudnicki F. and Gałęzewski L.: Rocz. Akad. Roln. Poznań, Roln. 2006, **66**, 323–329.

WPŁYW KOMPOSTU, BENTONITU, ZEOLITU I TLENKU WAPNIA NA ZAWARTOŚĆ AZOTU MINERALNEGO W GLEBIE ZANIECZYSZCZONEJ NIKLEM

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Abstrakt: Celem badań było określenie oddziaływania kompostu, bentonitu, zeolitu i tlenku wapnia na zawartość azotu mineralnego w glebie zanieczyszczonej niklem (0, 100, 200 i 300 mg Ni · kg^{-1} gleby). Zawartość azotu mineralnego w glebie była uzależniona od zanieczyszczenia gleby niklem, dodatku substancji łagodzących i gatunku rośliny. Wpływ niklu na zawartość azotu mineralnego w glebie był ściśle związany z gatunkiem roślin. W serii bez dodatków łagodzących zanieczyszczenie gleby niklem wywołało zmniejszenie zawartości i udziału $N\text{-}NO_3^-$ w azocie mineralnym gleby spod owsa oraz zwiększenie jego zawartości i udziału w glebie spod łubinu żółtego. Wpływ w glebie spod łubinu żółtego był znacznie większy niż w glebie spod owsa. Nikiel oddziaływał negatywnie na zawartość $N\text{-}NH_4^+$ w glebie spod łubinu żółtego. Aplikacja bentonitu, zeolitu i tlenku wapnia do gleby ograniczyła zawartość azotu amonowego w glebie, w porównaniu do średniej z serii bez dodatków. Najsilniej na zawartość $N\text{-}NH_4^+$ w glebie spod owsa działał bentonit, a w glebie spod łubinu żółtego zeolit i tlenek wapnia. Zastosowane substancje miały odwrotny wpływ na zawartość azotu azotanowego(V) niż azotu amonowego w glebie. Sprzyjały one zwiększeniu zawartości tej formy azotu w glebie. Największy wpływ na średnią zawartość $N\text{-}NO_3^-$ miał bentonit. Bentonit, zeolit i tlenek wapnia wywołały zwiększenie udziału azotu azotanowego w azocie mineralnym gleby, przy czym bentonit działał silniej w glebie spod owsa, a zeolit i tlenek wapnia w glebie spod łubinu żółtego. Zeolit i tlenek wapnia miały większy wpływ na udział $N\text{-}NO_3^-$ w glebie spod łubinu żółtego niż w glebie spod owsa. Podobny wpływ miał kompost, ale tylko w glebie spod łubinu żółtego.

Słowa kluczowe: zanieczyszczenie, nikiel, kompost, bentonit, zeolit, tlenek wapnia, gleba, azot mineralny

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RELATIONSHIPS BETWEEN PETROL AND DIESEL OIL CONTAMINATION VERSUS MINERAL NITROGEN CONTENT IN SOIL FOLLOWING APPLICATION OF COMPOST, BENTONITE AND CALCIUM OXIDE

RELACJE MIĘDZY ZANIECZYSZCZENIEM BENZYNĄ I OLEJEM NAPĘDOWYM A ZAWARTOŚCIĄ AZOTU MINERALNEGO W GLEBIE PO APLIKACJI KOMPOSTU, BENTONITU I TLENKU WAPNIA

Abstarct: A study has been conducted to identify the effect of soil pollution with petrol and diesel oil on the content of $N-NH_4^+$ and $N-NO_3^-$ in soil treated with compost, bentonite and CaO as the substances neutralising the influence of petroleum substances. Soil pollution with petroleum substances as well as introduction of substances neutralising the effect of petrol and diesel strongly modified the content of ammonia and nitrate nitrogen in soil after crop harvest. The effect of petroleum substances on soil properties was dependent on the rate of pollutants. In a series without neutralising substances, petrol or diesel oil pollution up to the rate of 2.5 or 5 $cm^3 \cdot kg^{-1}$ of soil, in contrast to the highest rate (10 $cm^3 \cdot kg^{-1}$), caused a very high and significant increase in the content of ammonia nitrogen in the analysed soil. Petroleum substances raised the ratio of ammonia nitrogen in soil to the detriment of the level of $N-NO_3^-$ compared with the variant free from contamination. Bentonite and calcium oxide produced an evidently stronger effect on soil properties than compost, typically increasing the concentration of $N-NO_3^-$; in addition, they contributed to a decline in the content of $N-NH_4^+$; CaO produced such effect in the series polluted with petrol while compost and bentonite were effective in objects contaminated with diesel oil. Bentonite and CaO caused a significant decrease in the ratio of $N-NH_4^+$ or a decrease in the ratio of $N-NH_4^+$ in soil in the objects polluted with petrol and diesel oil as compared with the series without such neutralising substances. Compost produced a similar effect in pots polluted with diesel oil.

Keywords: petrol, diesel oil, soil, compost, bentonite, CaO, $N-NH_4^+$, $N-NO_3^-$

The issues related to environmental pollution caused by nitrogen compounds have become very important in many countries around the world, in Europe and in Poland. It seems that nitrogen entering aqueous environment (particularly closed water bodies)

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poses a very severe threat, although excessive quantities of nitrogen in soils and groundwater cannot be neglected either, as they are taken up by plants [1]. Plants absorb nitrogen from soil in the mineral form, mainly as NO_3^- [2]. The level of nitrogen in soil is conditioned primarily by fertilizers used in agriculture [3] and environmental pollution with nitrogen oxides, but some other sources may be involved as well [4]. Additionally, the concentration of nitrogen in soil can be modified by several factors. It seems interesting to investigate relationships between some pollutants (ie petroleum products) and the content of mineral nitrogen in soil. There are certain reasons to suggest that such relationships do exist [5, 6].

For this purpose, a study has been conducted to identify the effect of soil pollution with petrol and diesel oil on the content of $N-NH_4^+$ and $N-NO_3^-$ in soil treated with compost, bentonite and CaO as the substances neutralising the influence of petroleum substances.

Material and methods

The study, conducted in a greenhouse at the University of Warmia and Mazury in Olsztyn, has been established in four replicates on soil which under natural conditions was proper brown soil formed from loamy sand. The soil was characterised by the following properties: pH in 1 mol $KCl \cdot dm^{-3}$ – 5.20; hydrolytic acidity (HA) – 27.0 mmol $(H^+) \cdot kg^{-1}$; exchangeable base cations Ca^{2+}, Mg^{2+}, K^+ and Na^+ (EBC) – 100.0 mmol$(+) \cdot kg^{-1}$; cation exchange capacity (CEC) – 127.0 mmol(+)/kg; base saturation (BS) – 78.7 %; content of C_{org} – 5.5 $g \cdot kg^{-1}$, content of mineral nitrogen – $N-NH_4^+$ – 8.3 mg $\cdot$ kg^{-1} and $N-NO_3^-$ – 19.2 mg $\cdot$ kg^{-1}, content of available phosphorus – 21.7 mg $\cdot$ kg^{-1}, potassium – 55.5 mg $\cdot$ kg^{-1} and magnesium – 32.5 mg $\cdot$ kg^{-1}. The polluting substances consisted of unleaded petrol 95 and diesel oil, introduced to soil in the following quantities: 0, 2.5, 5 and 10 $cm^3 \cdot kg^{-1}$ d.m. The tests were carried out in four series: without added substances (control), and with the application of compost (3 % relative to the soil mass), bentonite (2 %) and 60 % calcium oxide (in a rate corresponding to 1 HA). In addition, each pot was enriched with macro- and micronutrients in the following rates [mg $\cdot$ kg^{-1} soil]: N – 150 $CO(NH_2)_2$, P – 30 (KH_2PO_4); K – 75 $(KH_2PO_4 + KCl)$; Mg – 50 $(MgSO_4 \cdot 7H_2O)$; Mn – 5 $(MnCl_2 \cdot 4H_2O)$; Mo – 5 $[(NH_4)_6Mo_7O_{24} \cdot 4H_2O]$; B – 0.33 (H_3BO_3). The petrol substances, compost, bentonite, calcium oxide and mineral fertilizers were carefully mixed with 9.5 kg soil and transferred to polyethylene pots. Spring barley (*Hordeum vulgare* L.) cv. Ortega was the test plant. Soil moisture was maintained at 60 % capillary water capacity throughout the whole experiment. Soil samples for analyses were collected during barley harvest.

The following determinations were performed in the soil samples: concentration of $N-NH_4^+$ by colorimetry using Nessler's reagent [7] and $N-NO_3^-$ – by colorimetry using phenoldisulfonic acid [7]. The results of the determinations underwent statistical processing using a three-factor analysis of variance ANOVA from the computer software Statistica 8.0 [8].

Results and discussion

The contamination of soil with petroleum substances as well as the application of the neutralising substances strongly modified the content of ammonia and nitrate nitrogen in soil after harvest (Table 1). In the soil sampled after barley harvest, more $N-NH_4^+$ accumulated in soil contaminated with petrol than with diesel oil. Higher concentrations of $N-NO_3^-$ were found in soil polluted with diesel oil than with petrol.

The content of $N-NH_4^+$ in soil under sprig barley was positively correlated with the rate of petrol or diesel oil, except the series neutralised with CaO, where for both pollutants negative correlation occurred (Table 1). In the series without neutralising substances, both petrol and diesel oil up to 5 $cm^3 \cdot kg^{-1}$ of soil caused a very high and significant increase in the content of ammonia nitrogen in soil, in contrast to the highest rate. In the experimental series where no neutralising substances were added, the rate of 5 cm^3 of petrol per kg soil caused a considerable and statistically significant (about four-fold) rise in the level of $N-NO_3^-$ in soil after barley harvest compared with the control. The analogous series with diesel oil proved that the lowest rate of this pollutant (2.5 $cm^3 kg^{-1}$ soil) caused a nearly 3-fold increase in the content of nitrates(V) in soil, while the subsequently higher rates resulted in the successively decreasing concentration of this form of nitrogen in soil.

The accumulation of ammonia nitrogen in soil after harvesting the test crops was to a certain extent shaped by the type of a neutralising substance introduced to soil (Table 1). Among the three neutralising substances tested under spring barley grown in soil polluted with petroleum products, calcium oxide produced the strongest effect in soil contaminated with petroleum while compost and bentonite were the most effective in the objects polluted with diesel oil. The application of these substances resulted in the concentration of ammonia nitrogen being depressed by 11 %, 35 % and 42 %, respectively, as compared with the series without these neutralising substances.

The substances added to soil in order to neutralise the pollution significantly affected the content of $N-NO_3^-$ in soil after the harvest of the test plant (Table 1). All the neutralising substances favoured the accumulation of nitrates(V) in soil under spring barley. Both in petroleum and in diesel oil polluted objects, bentonite proved to be the most effective neutraliser. Its application contributed to the highest increase in the average content of $N-NO_3^-$ in soil versus the series without any neutralising substance.

It should also be emphasised that increasing rates of petroleum derived pollutants modified the ratio of the tested nitrogen forms in soil after harvest of spring barley (Fig. 1). When 10 cm^3 of petrol or diesel oil per kg of soil was introduced, the ratio of ammonia nitrogen in soil increased while that of $N-NO_3^-$ decreased compared with the variant free from the pollutants. The neutralising substances added to soil significantly affected the content of mineral nitrogen forms in soil after harvest. Bentonite and CaO caused a significant decline in the ratio of $N-NH_4^+$ in soil after spring barley harvest, both in petrol and in diesel polluted soil. Additionally, in the pots contaminated with diesel oil also compost that depressed the ratio of $N-NH_4^+$ versus the series without the neutralising substances (Fig. 2). As for the contribution of nitrates(V), reverse relationships were discovered.

Table 1

Mineral nitrogen content in soil after plants harvest [mg · kg^{-1}]

Dose [cm³ · kg^{-1} of soil]	Kind of contamination									
	Petrol (Pet)					Diesel oil (DO)				
	Kind of substance neutralizing effect of Pet and DO									
	without additions	compost	bentonite	CaO	average	without additions	compost	bentonite	CaO	average
N-NH$_4^+$										
0	6.18	6.31	9.49	24.96	11.74	6.18	6.31	9.49	24.96	11.74
2.5	19.69	21.58	11.38	16.28	17.23	18.24	18.40	13.57	9.16	14.84
5	24.13	39.17	18.87	10.25	23.11	27.98	12.67	8.40	15.79	16.21
10	16.58	27.31	25.76	8.10	19.44	21.38	10.42	11.45	18.83	15.52
Average	16.65	23.59	16.37	14.90	17.88	18.44	11.95	10.73	17.19	15.24
r	0.454	0.629*	0.983**	–0.908**	0.658*	0.655*	0.068	0.092	–0.126	0.722*
LSD	a – 0.36**, b – 0.38***, c – 0.38**, a · b – 0.42**, a · c – 0.42*, b · c – 0.46**, a · b · c – 0.54**									
N-NO$_3^-$										
0	10.41	27.04	30.62	40.82	27.23	10.41	27.04	30.62	40.82	27.23
2,5	20.24	18.41	31.36	25.94	23.99	30.26	37.15	76.60	72.05	54.01
5	39.90	24.93	58.41	19.60	35.71	20.61	52.30	67.32	48.81	47.26
10	21.07	53.36	67.14	67.32	52.22	13.72	27.59	37.61	30.12	27.26
Average	22.91	30.93	46.88	38.42	34.79	18.75	36.02	53.04	47.95	38.94
r	0.380	0.826**	0.924**	0.602	0.939**	–0.109	0.000	–0.084	–0.499	–0.212
LSD	a – n.s., b – 0.56**, c – 0.56**, a · b – 0.79**, a · c – 0.79**, b · c – 1.12**, a · b · c – 1.58**									

LSD for: a – kind of petroleum substance, b – petroleum substance dose, c – kind of neutralizing substance; ** – significant for p = 0.01; * – significant for p = 0.05; n.s. – non-significant; r – correlation coefficient.

0 (control)　　　　　　10 cm³ petrol · kg⁻¹ of soil　　　　　10 cm³ diesel oil · kg⁻¹ of soil

62.7 %	37.3 %
56.0 %	44.0 %
39.1 %	60.9 %

N-NH$_4^+$　　　N-NH$_3^-$
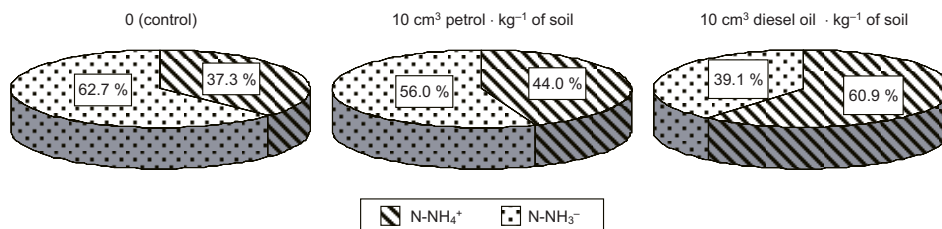
Fig. 1. The effect of petrol and diesel oil on proportion between N-NH$_4^+$ and N-NO$_3^-$ in soil [%]

Petrol　　　　　　　　**Diesel oil**

Without additions

| 57.9 % | 42.1 % |
| 50.4 % | 49.6 % |

Compost

| 56.7 % | 43.3 % |
| 75.1 % | 24.9 % |

Batonite

| 74.1 % | 25.9 % |
| 83.2 % | 16.8 % |

CaO

| 72.1 % | 27.9 % |
| 73.6 % | 26.4 % |

N-NH$_4^+$　　　N-NH$_3^-$

Fig. 2. Effect of compost, bentonite and CaO on proportion between N-NH$_4^+$ and N-NO$_3^-$ in soil (average for series) [%]

Nitrogen plays an important role in degradation of hydrocarbons in soil. Particularly important influence on the rate of degradation is produced by ammonia nitrogen [9]. As a result, its concentration in polluted soils may be depressed, which has been confirmed in the authors' own research when the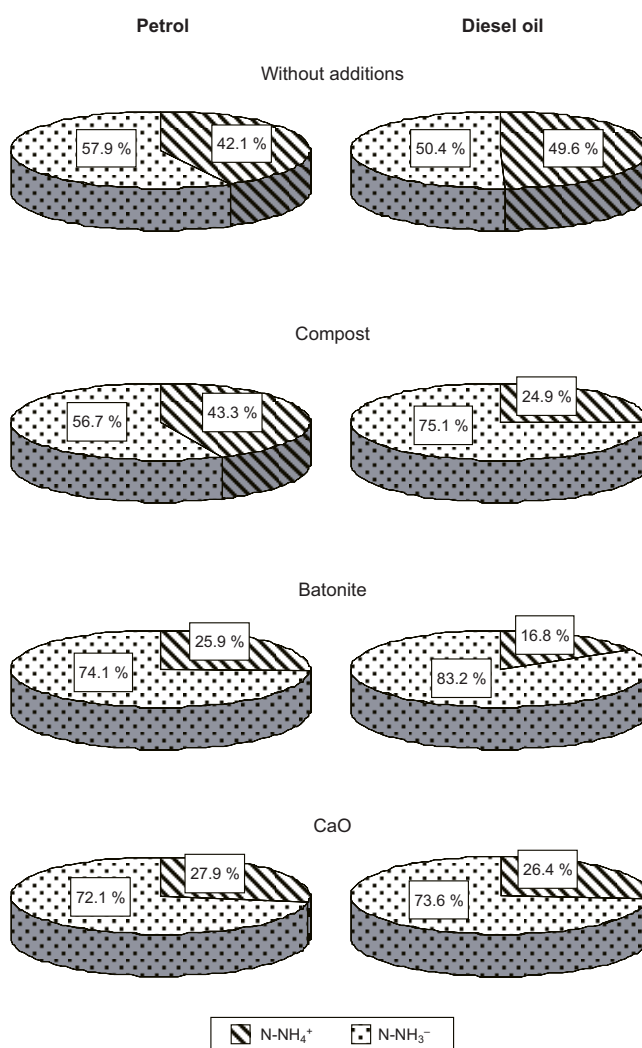 highest level of contamination with petroleum substances was examined. Positive correlation between the degree of soil pollution with diesel oil and the concentration of $N-NH_4^+$ and $N-NO_3^-$ in soil has also been indicated by Dimitrov and Markov [10]. Such observations are in accord with the effect produced by lower rates of the petroleum pollutants observed in the authors' own study. Similar results were obtained our earlier experiments [5, 6]. In contrast, Rivera-Espinoza and Dendooven [11] demonstrated that diesel oil did not have significant influence on the content of mineral nitrogen forms in soil, but these two researchers tested very low rates of pollution (4 g C $\cdot$ kg^{-1} soil). Initially, they were even able to observe a slight increase in the content of $N-NO_3^-$ in soil, although later its level was similar to that determined in unpolluted objects and after 100 days from the establishment of the experiment both forms of nitrogen (and $N-NO_3^-$ particularly) increased significantly. Obire and Nwaubeta [12] found out that the total nitrogen concentration fell in soil polluted with petroleum-derived substances, although the latter had no effect on the concentrations of ammonia and nitrate nitrogen. Deni and Pennickx [13] proved that by introducing hydrocarbons in the amount of 4 g C $\cdot$ kg^{-1} soil it was possible to stimulate nitrogen immobilization. Petroleum substances inhibit processes of nitrification [14, 15], especially when leaded or unleaded petrol is nitrified [15] and can limit ammonification [15].

Application of different substances to soil affects soil properties that have been modified by petroleum or diesel oil. Organic substance, which increases sorption of petroleum substances while simultaneously limiting their effect on the biological life of soil [16] and nitrogen metabolism in soil, is of special importance in this respect. In the previous studies by Wyszkowski and Ziółkowska [5, 6], bentonite, calcium oxide and partly compost caused a significant decrease in the content of $N-NH_4^+$ in soil, especially in objects polluted with diesel oil. Bentonite, calcium oxide and compost created favourable conditions for accumulation of $N-NO_3^-$ in petrol polluted soil whereas bentonite and calcium oxide produced similar effects in pots contaminated with diesel oil. Introduction of petroleum-based substances as well as substances neutralising the pollution caused an increase in the ratio of $N-NO_3^-$ to N-mineral.

Conclusions

1. Soil pollution with petroleum substances as well as introduction of substances neutralising the effect of petrol and diesel strongly modified the content of ammonia and nitrate nitrogen in soil after crop harvest.

2. The effect of petroleum substances on soil properties was dependent on the rate of pollutants. In a series without neutralising substances, petrol or diesel oil pollution up to the rate of 2.5 or 5 cm^3 $\cdot$ kg^{-1} of soil, in contrast to the highest rate (10 cm^3 $\cdot$ kg^{-1}), caused a very high and significant increase in the content of ammonia nitrogen in the analysed soil.

3. Petroleum substances raised the ratio of ammonia nitrogen in soil to the detriment of the level of $N\text{-}NO_3^-$ compared with the variant free from contamination.

4. Bentonite and calcium oxide produced an evidently stronger effect on soil properties than compost, typically increasing the concentration of $N\text{-}NO_3^-$; in addition, they contributed to a decline in the content of $N\text{-}NH_4^+$; CaO produced such effect in the series polluted with petrol while compost and bentonite were effective in objects contaminated with diesel oil.

5. Bentonite and CaO caused a significant decrease in the ratio of $N\text{-}NH_4^+$ or a decrease in the ratio of $N\text{-}NH_4^+$ in soil in the objects polluted with petrol and diesel oil as compared with the series without such neutralising substances. Compost produced a similar effect in pots polluted with diesel oil.

Acknowledgements

References

[1] Pecio A., Rutkowska A. and Leszczyńska D.: Fragm. Agron. 2005, **XXII**, 1(85), 214–225.
[2] Michałojć Z.M.: Zesz. Probl. Post. Nauk Roln. 2006, **513**, 277–283.
[3] Łabętowicz J. and Rutkowska B.: Zesz. Probl. Post. Nauk Roln. 1996, **440**, 223–229.
[4] Czekała J.: Zesz. Probl. Post. Nauk Roln. 2003, **493**, 585–590.
[5] Wyszkowski M. and Ziółkowska A.: Zesz. Probl. Post. Nauk Roln. 2006, **513**, 563–573.
[6] Wyszkowski M. and Ziółkowska A.: Ochr. Środow. Zasob. Natural. 2007, **31**, 154–159.
[7] Panak H. (ed.): Przewodnik metodyczny do ćwiczeń z chemii rolnej. Wyd. ART., Olsztyn 1997, 242 pp.
[8] StatSoft, Inc.: STATISTICA (data analysis software system), version 8.0. www.statsoft.com, 2007.
[9] Brook T.R., Stiver W.H. and Zytner R.G.: Soil Sediment Contam. 2001, **10**(5), 539–553.
[10] Dimitrov D.N. and Markov E.: Pochvoznanie, Agrokhimiya, Ekologiya 2000, **35**(3), 3–8.
[11] Rivera-Espinoza Y. and Dendooven L.: Chemosphere 2004, **54**(3), 379–386.
[12] Obire O. and Nwaubeta O.J.: Appl. Sci. Environ. Manage. 2002, **6**(1), 39–44.
[13] Deni J. and Penninckx M.J.: Appl. Environ. Microbiol. 1999, **65**, 4008–4013.
[14] Amadi A., Abbey S.D. and Nma A.: Water, Air, Soil, Pollut. 1996, **86**, 1–11.
[15] Kucharski J., Jastrzębska E. and Wyszkowska J.: Acta Agrar. et Silv., Ser. Agraria 2004, **XLII**, 249–255.
[16] Małachowska-Jutsz A., Mrozowska J., Kozielska M. and Miksch K.: Biotechnologia 1997, **1**(36), 79–91.

RELACJE MIĘDZY ZANIECZYSZCZENIEM BENZYNĄ I OLEJEM NAPĘDOWYM A ZAWARTOŚCIĄ AZOTU MINERALNEGO W GLEBIE PO APLIKACJI KOMPOSTU, BENTONITU I TLENKU WAPNIA

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Abstrakt: Celem badań było określenie oddziaływania zanieczyszczenia gleby benzyną i olejem napędowym na zawartość $N\text{-}NH_4^+$ i $N\text{-}NO_3^-$ w glebie w warunkach zastosowania kompostu, bentonitu i CaO, jako substancji łagodzących wpływ substancji ropopochodnych. Zanieczyszczenie gleby substancjami ropopochodnymi oraz zastosowanie dodatków łagodzących wpływ benzyny i oleju napędowego silnie modyfikowało zawartość azotu amonowego i azotanowego w glebie po zbiorze roślin Oddziaływanie substancji ropopochodnych na właściwości gleby zależało od ich dawki. W serii bez dodatków łagodzących, zanieczyszczenie

benzyną i olejem napędowym do dawki 2,5 lub 5 cm^3 · kg^{-1} gleby, w odróżnieniu od dawki największej (10 cm^3 · kg^{-1}) powodowało bardzo duży i znaczący wzrost zawartości azotu amonowego w badanej glebie. Największa dawka substancji ropopochodnych działała zdecydowanie ujemnie. Substancje ropopochodne zwiększyły udział azotu amonowego w glebie, kosztem N-NO$_3^-$, w porównaniu do wariantu bez zanie-czyszczeń. Bentonit i tlenek wapnia zdecydowanie silniej wpływały na właściwości gleby niż kompost, powodując na ogół wzrost zawartości: N-NO$_3^-$, przyczyniły się także do zmniejszenia zawartości N-NH$_4^+$: CaO – w serii z benzyną oraz kompost i bentonit w obiektach zanieczyszczonych olejem napędowym. Bentonit i CaO wywołały znaczne zmniejszenie udziału N-NH$_4^+$ oraz zmniejszenie udziału w N-NH$_4^+$ glebie w obiektach z benzyną i olejem napędowym, w porównaniu do serii bez dodatków. W wazonach zanieczyszczonych olejem napędowym podobny wpływ miał także kompost.

Słowa kluczowe: benzyna, olej napędowy, gleba, kompost, bentonit, CaO, N-NH$_4^+$, N-NO$_3^-$

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EFFECT OF AGRICULTURAL TREATMENTS
ON THE CONTENT OF TOTAL AND PROTEIN NITROGEN IN POTATO TUBERS

WPŁYW ZABIEGÓW AGROTECHNICZNYCH NA ZAWARTOŚĆ AZOTU OGÓLNEGO I BIAŁKOWEGO W BULWACH ZIEMNIAKA

Abstract: The research was conducted in the years 2002–2004 in Agricultural Experimental Station Zawady. The experiment was set on the soil of the rye very good complex in three replications. The aim of the present paper was to determine the effect of soil tillage and weed control methods using herbicides on the content of total nitrogen and protein nitrogen in the edible potato tubers. The weeding chemical agents used in the potato treatment increased the total nitrogen content and protein nitrogen content in the tubers, as compared with the control. The statistical analysis also revealed a significant effect of the soil tillage and meteorological conditions over the experimental years on the parameters investigated.

Keywords: potato, herbicides, tillage systems, total nitrogen, protein nitrogen

Potato plays a very significant role in human diet. As a result, an impact of plant protection agents, on potato quality characteristic in an important issue [1]. According to many authors, the content of particular macroelements in potato tubers is determined by cultivar properties [2–4], agrotechnical factors [5–8] and climatic conditions during the potato growing period [9–11]. According to Mazurczyk [2] and Mazurczyk and Lis [12], the content of total and protein nitrogen in tubers depends on less stabile characteristics, tightly connected with climate conditions during the vegetation. When it comes to the influence of herbicides on the quality of the crop, their opinion diverge [6, 7, 13]. That is why, the aim of the experiments was to define the influence of some herbicides and their mixtures and soil tillage on the total and protein nitrogen in potato tubers.

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Material and methods

Studies were carried out on potato tubers cv. Wiking obtained from a field experiment conducted in the years 2002–2004 in Agricultural Experimental Station Zawady owned by the University of Podlasie in Siedlce. The soil originating from light clay sands and strong clay sands belonging to the rye very good complex. The selected soil chemical properties prior to the experiment are shown in Table 1. The experiment was a randomized sub-block design including two factors: factors I – two soil tillage systems – traditional and simplified and factors II – seven weed control methods for herbicides:

   1. control object – mechanical weeding,

   2. Plateen 41.5 WG 2.0 kg/ha,

   3. Plateen 41.5 WG 2.0 kg/ha + Fusilade Forte 150 EC 2.5 dm^3/ha (mixture),

   4. Plateen 41.5 WG 1.6 kg/ha + Fusilade Forte 150 EC 2.0 dm^3/ha + adjuvant Atpolan 80 EC 1.5 dm^3/ha (mixture),

   5. Barox 460 SL 3.0 dm^3/ha,

   6. Barox 460 SL 3.0 dm^3/ha + Fusilade Forte 150 EC 2.5 dm^3/ha (mixture),

   7. Barox 460 SL 2.4 dm^3/ha + Fusilade Forte 150 EC 2.0 dm^3/ha + adjuvant Atpolan 80 EC 1.5 dm^3/ha (mixture).

Table 1

Chemical properties of the soil

Years	pH 1 mol KCl^{-3}	Macroelements content [mg/kg^{-1}]				Hh	S	T	V [%]
		N total	P	K	Mg	[mm(+)kg^{-1}]			
2002	6.50	0.92	38.8	150.3	70.0	9.16	106.10	115.26	92.05
2003	6.44	0.89	43.0	102.2	157.0	8.70	130.70	139.40	93.75
2004	5.60	0.91	62.5	103.9	159.0	8.15	132.60	140.75	94.21

Hh – hydrolitic acidity; S – total base exchangeable cations; T – sorptive complex exchange capacity; V – saturation with base cations.

The mechanical treatment was applied on the referential experimental cultures 2 to 7 until the plant germination. Herbicides and their mixtures were applied just before the germination of potato (treatments 2–4) and after potato germination (treatments 5–7). Farmyard manure (25 Mg/ha) and mineral fertilization in the amounts of: 90 kg N, 32.9 kg P and 112.1 kg K per hectare were applied on a regular basis. The area of one plot was 25 m^2. Potato tubers were planted manual in the third decade of April at the spacing of 67.5 cm × 37 cm. Potato were harvested in technological maturity phase in the first decade of September. Chemical analyses were done on dry material in 3 replications. The total and protein nitrogen were determined with Kjeldahl method on the 2300 Kjeltec Analyzer Unit [14]. The results of the analyses were worked out statistically with the help of the variance analysis and, the significance of the difference was tested with Tukey at the significance level p = 0.05. Precipitation sums and mean air temperatures during the period of potato growth (April–September) were the following

(percentages of the multiyear mean): 90.3 and 115.7 for 2002, 38.6 and 110.7 in 2003, and 93.4 and 100.7 in 2004.

Results and discussion

The total nitrogen content in potato tubers was within 14.65–18.14 g/kg and significantly depended on methods of tillage and weed control methods as well as precipitation and temperature of the research years (Table 2, 3). Total nitrogen concentration in tubers was similar to the values reported by other authors [2, 15–17]. An introduction of soil tillage simplification worsened the conditions of the nitrogen accumulation in tubers, compared with the traditional tillage. It was reflected in the studies by Kraska and Palys [10]. Herbicides and their mixtures caused the growth of total nitrogen content comparing with the tubers of the control object. They significantly increase the concentration of the given component after the use of the following herbicides: Plateen 41.5 WG, Plateen 41.5 WG + Fusilade Forte 150 EC, Barox 460 SL and Barox 460 SL + Fusilade Forte 150 EC. The growth of the total nitrogen content in tubers from fields sprayed with herbicides was also noticed by other authors [8, 12, 18, 19]. On the other hand, Klikocka [6] claimed that the chemical and mechanical--chemical treatments decreased the total nitrogen level in potato tubers.

Table 2

Content of total nitrogen in the dry matter [g/kg]

Weed control methods	Tillage system		Years			Average
	traditional	simplified	2002	2003	2004	
1. Control object – mechanical weeding	15.92	15.66	14.65	17.27	15.46	15.79
2. Plateen 41,5 WG	16.70	16.04	15.31	18.09	15.71	16.37
3. Plateen 41,5 WG + Fusilade Forte 150 EC	17.27	16.31	15.87	18.47	16.04	16.79
4. Plateen 41,5 WG + Fusilade Forte 150 EC + Atpolan 80 EC	16.52	15.90	15.44	17.29	15.91	16.21
5. Barox 460 SL	16.58	16.08	15.63	17.51	15.85	16.33
6. Barox 460 SL + Fusilade Forte 150 EC	17.12	16.55	17.00	17.50	16.02	16.84
7. Barox 460 SL + Fusilade Forte 150 EC + Atpolan 80 EC	16.48	15.92	15.40	17.42	15.77	16.20
Average	16.66	16.07	15.62	17.65	15.83	16.37
LSD$_{0.05}$						
weed control methods						0.48
tillage systems						0.13
years						0.24
interaction: weed control methods × tillage systems						n.s.
weed control methods × years						0.83

n.s. – no significant difference.

Table 3

Content of total and protein nitrogen in potato tubers depending on tillage systems [g/kg]

Years	Total nitrogen		Average	Protein nitrogen		Average
	traditional	simplified		traditional	simplified	
2002	16.28	14.95	15.62	10.81	10.55	10.68
2003	17.80	17.50	17.65	11.79	11.39	11.59
2004	15.90	15.75	15.83	11.00	10.98	10.99
Average	16.66	16.07	16.37	11.20	10.97	11.09
LSD$_{0.05}$						
years			0.24			0.09
tillage systems			0.13			0.06
interaction: tillage systems × years			0.22			0.10

Weather conditions during the experimental years significantly differentiated the total nitrogen content. The tubers of the warm and dry year 2003 gathered the highest content of the element but a lot less during the humid seasons of vegetation (2002 and 2004). The influence of weather conditions on total nitrogen content was proven in many scientific works [11, 13, 17]. Klikocka [6] claimed that during the dry year, nitrogen was more for about 5% (a relative results) than in the cold year. The experiment carried out revealed that there is an interaction between weed control methods and the years. It means different influence of weather conditions on the activity of herbicides.

Table 4

Content of protein nitrogen in the dry matter [g/kg]

Weed control methods	Tillage system		Years			Average
	traditional	simplified	2002	2003	2004	
1. Control object – mechanical weeding	10.98	10.58	10.01	11.43	10.90	10.78
2. Plateen 41,5 WG	11.14	10.97	10.70	11.58	10.90	11.06
3. Plateen 41,5 WG + Fusilade Forte 150 EC	11.46	11.19	11.01	11.79	11.18	11.33
4. Plateen 41,5 WG + Fusilade Forte 150 EC + Atpolan 80 EC	11.11	10.89	10.56	11.49	10.94	11.00
5. Barox 460 SL	11.18	11.04	10.79	11.61	10.94	11.11
6. Barox 460 SL + Fusilade Forte 150 EC	11.38	11.19	11.02	11.70	11.14	11.29
7. Barox 460 SL + Fusilade Forte 150 EC + Atpolan 80 EC	11.18	10.95	10.68	11.54	10.98	11.07
Average	11.20	10.97	10.68	11.59	10.99	11.09
LSD$_{0.05}$						
weed control methods						0.18
tillage systems						0.06
years						0.09
interaction: weed control methods × tillage systems						n.s.
weed control methods × years						0.32

n.s. – no significant difference.

The chemical analysis of tubers revealed that the protein nitrogen content in potato tubers significantly depended on methods of tillage, weed control methods and weather conditions during the experimental years (Table 3, 4). More nitrogen was accumulated by weeds sampled from the traditional tillage than from the simplified tillage. Sawicka and Kus [20] observed similar changes. The years, in which the experiments were carried out, the discussed characteristics were different. In the mild drought year 2003, tubers gathered the highest rate of protein nitrogen. The growth in the protein nitrogen content during the drought was also observed by other authors [11, 17].

Conclusion

1. Simplifications of soil tillage created poorer conditions for total nitrogen content in potato tubers compared with the traditional tillage.

2. When potatoes were cultivated using herbicide weed control, the total and protein nitrogen content in their tubers was bigger than in the tubers of potatoes whose cultivation included mechanical weed control.

References

[1] Leszczyński W.: Zesz. Probl. Post. Nauk Rol. 2002, **489**, 47–64.
[2] Mazurczyk W.: Biul. Inst. Ziemn. 1988, **37**, 55–63.
[3] Roztropowicz S.: Fragm. Agron. 1989, **1**(21), 33–75.
[4] Tekalign T. and Hammes P.S.: Sci. Horticult. 2005, **105**(1), 29–44.
[5] Boligłowa E. and Dzienia S.: Electron. J. Polish Agricult. Universities 1999, **2**(2), 1–8.
[6] Klikocka H.: Biul. Inst. Hodow. Aklimatyz. Rośl. 2001, **217**, 197–203.
[7] Lachman J., Hamouz K., Dvořák P. and Orsák M.: Plant Soil Environ. **51**(10), 431–438.
[8] Zarzecka K. and Gąsiorowska B.: Zesz. Probl. Post. Nauk Rol. 2002, **489**, 301–308.
[9] Kołodziejczyk M. and Szmigiel A.: Fragm. Agron. 2005, **1**(85), 436–445.
[10] Kraska P. and Pałys E.: Fragm. Agron. 2004, **2**(82), 91–99.
[11] Mazurczyk W. and Lis B.: Polish J. Food Nutr. Sci. 2001, **10/51**, 27–30.
[12] Mężykowska B. and Mazurczyk W.: Biul. Inst. Ziemn. 1979, **23**, 132–142.
[13] Zarzecka K. and Gugała M.: Plant Soil Environ. 2005, **51**(11), 517–522.
[14] Ostrowska A., Gawliński S. and Szczubiałka S. [in:] Metody analizy i oceny właściwości gleb i roślin. Wyd. Inst. Ochr. Środow., Warszawa 1991, 237–240.
[15] Kołodziejczyk M., Szmigiel A. and Kiełbasa A.: Fragm. Agron. 2007, **2**(94), 142–150.
[16] Sądej W., Przekwas K. and Bartoszewicz J.: Annales UMCS, 2004, **59**(1), Sec. E, 83–92.
[17] Zrust J. and Hola Z.: Rostl. Vyroba 1994, **40**, 271–279.
[18] Ceglarek F. and Księżak J.: Fragm. Agron. 1992, **3**(35), 58–64.
[19] Mazur T. and Smoczyńska A.: Zesz. Nauk. ART w Olsztynie, Rolnictwo 1982, **34**, 173–185.
[20] Sawicka B. and Kuś.: Zesz. Probl. Post. Nauk Roln. 2002, **489**, 273–282.

WPŁYW ZABIEGÓW AGROTECHNICZNYCH NA ZAWARTOŚĆ AZOTU OGÓLNEGO I BIAŁKOWEGO W BULWACH ZIEMNIAKA

Katedra Szczegółowej Uprawy Roślin, Akademia Podlaska w Siedlcach

Abstrakt: Badania przeprowadzono w latach 2002–2004 w Rolniczej Stacji Doświadczalnej Zawady. Doświadczenie założono na glebie kompleksu żytniego bardzo dobrego w trzech powtórzeniach. Celem pracy

było określenie wpływu sposobów uprawy roli i sposobów odchwaszczania z zastosowaniem herbicydów na zawartość azotu ogólnego i białkowego w bulwach ziemniaka jadalnego. Chemiczne środki chwastobójcze zastosowane w pielęgnacji ziemniaka znacznie zwiększały zawartość azotu ogólnego i białkowego w porównaniu do bulw z obiektu kontrolnego. Analiza statystyczna wykazała również znaczny wpływ sposobów uprawy roli i warunków meteorologicznych w latach prowadzenia badań na omawiane cechy.

Słowa kluczowe: ziemniak, herbicydy, sposoby uprawy roli, azot ogólny, azot białkowy

Varia

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On the first day the debates of sections SI and SII will take place. The second day will be started with an ecological excursion. Afterwards the plenary Session with lectures on **environmental education** as well as **grants within the EU Programmes** and presentation of **EU Centres of Excellence** will be held. Then the **Forum of Young Scientists** – the presentation (lectures and posters) of young scientists work will take place.

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The Conference language is English.

Contributions to the Conference will be published as:

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Additional information one could find on the Conference website:

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The deadline for sending the Abstracts is **31.08.2009** and for the Extended Abstracts: **1.10.2009**. The actualised list (and the Abstracts) of the Conference contributions

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The Conference fee is 300 € (covering hotel, meals and transportation during the Conference). It could be reduced (to 170 €) for young people actively participating in the Forum of Young Scientists. But the colleague has to deliver earlier the Extended Abstract (4-6 pages) of his/her contribution (deadline is on 15.08.2009), and a recommendation of his/her Professor.

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Further information is available from:
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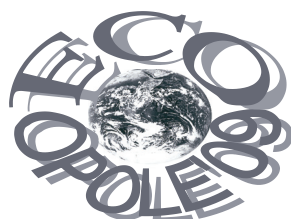
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Materiały konferencyjne będą opublikowane w postaci:
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Termin nadsyłania angielskiego i polskiego streszczenia o objętości 0,5–1,0 strony (wersja cyfrowa + wydruk) planowanych wystąpień upływa w dniu 31 sierpnia 2009 r. Lista prac zakwalifikowanych przez Radę Naukową Konferencji do prezentacji będzie sukcesywnie publikowana od 15 lipca 2009 r. na stronie webowej konferencji

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Koszt uczestnictwa w całej konferencji wynosi 1000 zł i pokrywa opłatę za udział, koszt noclegów i wyżywienia oraz rocznej prenumeraty Ecol. Chem. Eng. (razem blisko 2000 ss.) łącznie z materiałami Konferencji. Jest możliwość udziału tylko w jednym wybranym przez siebie dniu, wówczas opłata wyniesie 650 zł i będzie upoważniała do uzyskania wszystkich materiałów konferencyjnych, jednego noclegu i trzech posiłków (śniadanie, obiad, kolacja), natomiast osoby zainteresowane udziałem w dwóch dniach, tj. w pierwszym i drugim lub drugim i trzecim, winny wnieść opłatę w wysokości 800 zł. Opłata dla magistrantów i doktorantów oraz młodych doktorów biorących aktyw-ny udział w Forum Młodych może być zmniejszona do 600 zł, przy zachowaniu takich samych świadczeń. Osoby te winny dodatkowo dostarczyć: rozszerzone streszczenia (4–6 stron) swoich wystąpień (**do 15.08.2009 r.**). Jest także wymagana opinia opiekuna naukowego. Sprawy te będą rozpatrywane indywidualnie przez Radę Naukową oraz Komitet Organizacyjny Konferencji. Członkowie Towarzystwa Chemii i Inżynierii Ekologicznej i Polskiego Towarzystwa Chemicznego (z opłaconymi na bieżąco skład-kami) mają prawo do obniżonej opłaty konferencyjnej o 25 zł. Opłaty wnoszone po dniu 15 września 2009 r. są większe o 10% od kwot podanych powyżej. Wszystkie wpłaty winne być dokonane na konto w Banku Śląskim:

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15th ICHMET

15th International Conference on Heavy Metals in the Environment
September 19–23, 2010
Gdańsk, Poland

Organized by
Chemical Faculty, Gdańsk University of Technology (GUT)
together with
Committee on Analytical Chemistry of the Polish Academy Sciences (PAS)

15th ICHMET – is a continuation of a series of highly successful conferences that have been held in major cities of the world since 1975. These conferences typically draw 500–1000 participants from countries in many parts of the world. Well over 5000 scientists have taken part in this series of conferences including most leaders in the field. Apart from the city's natural beauty, Gdansk is logical choice for the 15th Conference to highlight the outstanding work that is being done on heavy metals in central Europe. The venue for the meeting will be the Gdansk University of Technology (GUT) which features many tourist attractions.

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- Life cycle analysis for metalliferous consumer products
- Soil quality criteria
- Remediation technologies
- Control strategies for heavy metal emissions and deposition
- Metal mixtures – mechanistic and epidemiological studies
- Nutrient-metal interactions
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– Toxicology of heavy metals, from cellular and genomic to ecosystem levels
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