

Sławomir SZYMCZYK¹

**SEASONAL VARIATION IN THE CONCENTRATIONS
AND LOADS OF MINERAL NITROGEN COMPOUNDS
IN ATMOSPHERIC PRECIPITATION
IN THE VICINITY OF OLSZTYN (NE POLAND)**

**SEZONOWA ZMIENNOŚĆ STĘŻEŃ
I ŁADUNKÓW MINERALNYCH ZWIĄZKÓW AZOTU
W OPADACH ATMOSFERYCZNYCH W OKOLICACH OLSZTYNA**

Abstract: The present study was conducted during the hydrological years 1993–2008 at the meteorological station in Tomaszkowo near Olsztyn (NE Poland). The study involved the determination of daily precipitation levels, water sampling after each precipitation event, and the measurement of pH, electrolytic conductivity (EC), the concentrations and loads of mineral nitrogen compounds: N-NO₂, N-NO₃, N-NH₄. It was found that the 1993–2008 period was characterized by the average amount of precipitation in the vicinity of the city of Olsztyn. Three years were classified as wet, three years were dry and one year was very dry. The majority of the annual precipitation (77 % on average) occurred in the summer half-year. Summer was the wettest season (37 % of the total annual precipitation on average), and winter was the driest season (17 %). The pH of precipitation water ranged from 3.8 to 8.12 (pH 5.6 on average). Rainfall was usually slightly acidic (72 %) to acidic (21 %). The total nitrogen load in precipitation was determined by precipitation levels and the concentrations of mineral nitrogen compounds in precipitation. As regards nitrogen concentrations and loads, the predominant compound was N-NH₄, while N-NO₂ was present in low quantities. In the vicinity of Olsztyn, the input of mineral nitrogen via precipitation per ha, per year ranged from 5.34 to 9.74 kg, including 5.17 kg · ha⁻¹ N-NH₄, 2.27 kg · ha⁻¹ N-NO₃ and 0.05 kg · ha⁻¹ N-NO₂ on average. The highest mineral nitrogen load was noted in wet years (8.87 kg · ha⁻¹ on average), while the lowest – in years with normal precipitation (4.80 kg · ha⁻¹ on average). Most nitrogen was deposited from the atmosphere in precipitation over the growing season, which supported its accumulation in plants and soil, thus reducing groundwater and surface water pollution.

Keywords: precipitation water, nitrogen, atmospheric deposition

In recent years the natural process of soil acidification has intensified due to improper agricultural practices and the application of high mineral fertilizer rates. Another important reason is anthropogenic atmospheric pollution with sulfur compounds and nitrogen oxides, which are the principal cause of acid rain [1]. Due to

¹ Department of Land Improvement and Environmental Management, University of Warmia and Mazury in Olsztyn, pl. Łódzki 2, 10–719 Olsztyn, Poland, email: szymek@uwm.edu.pl

natural air pollution, the pH of rain is at a level of 5.65. Atmospheric precipitation whose pH is lower is referred to as acid rain. The pH of precipitation is determined by the content of sulfuric acid and nitric acid in ambient air in 60–70 % and 30–40 %, respectively [2]. Soil acidification has harmful effects on the environment as it induces and accelerates many processes that lead to soil impoverishment caused by the loss of basic calcium, magnesium and potassium ions, increased release of aluminum and manganese ions toxic to plants, as well as increased mobility and availability of other heavy metals [1]. Atmospheric precipitation is a significant source of non-point pollution in soil and surface water. In contrast to mineral fertilizers, precipitation water contains dissolved components which facilitates their migration in the environment. During intensive precipitation nitrogen quickly migrates to groundwater with surface and subsurface runoff [3, 4]. The input of mineral nitrogen load to the catchment varies in time and space. It is higher in areas exposed to strong human pressure and in regions characterized by high levels of precipitation. Atmospheric deposition is a valuable source of nitrogen in farmlands, where it ensures a grain yield of $2 \text{ Mg} \cdot \text{ha}^{-1}$. However, in natural areas (nature reserves) high nitrogen loads may contribute to the rapid growth of nitrophilous plants and the disappearance of plants characteristic of nutrient-poor habitats [5]. The runoff from agricultural catchments is affected primarily by the intensity and distribution of atmospheric precipitation, land use type, the properties and type of soils, vegetation cover, the growth stage of vegetation as well as soil reclamation and drainage systems [6, 7].

The objective of this study was to estimate the concentrations and loads of mineral nitrogen compounds in precipitation water, deposited on the land surface, and to determine their potential effect on the natural environment in the Olsztyn Lakeland.

Materials and methods

The study was conducted during the hydrological years 1993–2008 at the meteorological and hydrological station in Tomaszkowo near Olsztyn, in the Olsztyn Lakeland, in the western part of the Masurian Lakeland – the most westward macroregion among Eastern Baltic Lakelands. The Olsztyn Lakeland covers an area of approximately 3820 km². The local landscape was shaped in the Poznan and Pomeranian phases of the Vistulian glaciation during the last glacial period. The axis of symmetry of seven concentric arcs of end moraines is the Lyna River flowing south to north. Olsztyn, the main city of the province of Warmia and Mazury, is situated on the Lyna River, in the central part of the region. The climate of the Masurian Lakeland is cooler than in the neighboring macroregions. It is affected by topographic features and the proximity of numerous water bodies, forests and peatlands. Brown soils used as arable land and grassland dominate in this Lakeland [8].

The study involved the determination of daily precipitation levels – with a Hellmann rain gauge, water sampling after each precipitation event – with a precipitation collector design based on a model [7], the measurement of pH – with a potentiometer, electrolytic conductivity (EC) – with a conductometer, the concentrations of mineral nitrogen compounds: nitrate(III) nitrogen (N-NO₃) – colorimetrically, using sulfanilic acid,

nitrate(V) nitrogen (N-NO₃) – using disulfophenolic acid, ammonium nitrogen (N-NH₄) – colorimetrically, using Nessler's reagent. The loads of N-NH₄, N-NO₃ and N-NO₂ were calculated as the product of their concentrations and the volume of each precipitation event in a given month, expressed as kg · ha⁻¹. As the loads of N-NO₂ were very low (below 0.01 kg · ha⁻¹), their values are not listed in the table, but they were used for calculating the total mineral nitrogen load (N-NH₄ + N-NO₃ + N-NO₂). The results are presented for individual months, years, half-years (winter half-year: November – April and summer half-year: May – October) and seasons (fall: September – November, winter: December – February, spring: March – May and summer: June – August). The obtained precipitation data were compared with the long-term average of 1951–2000 (615.9 mm), and the analyzed years, periods (half-years) and seasons were classified according to the system proposed by Kaczorowska [9] as: extremely wet (above 155 % of the long-term average), very wet (136–155 %), wet (111–135 %), normal (90–110 %), dry (75–89 %), very dry (51–74 %) and extremely dry (below 50 % of the long-term average).

Results and discussion

During the hydrological years 1993–2008, the annual precipitation totals in the vicinity of Olsztyn ranged from 408.2 to 827.2 mm (Table 1).

Table 1

Annual precipitation totals and mean air temperatures in the vicinity of Olsztyn in the years 1993–2008

Year	Precipitation		Temperature [°C]
	[mm]	Kind of year	
1993	679.0	normal	7.8
1994	649.3	normal	8.6
1995	716.9	wet	8.2
1996	408.2	very dry	5.8
1997	556.1	normal	7.3
1998	550.0	dry	7.3
1999	671.3	normal	8.2
2000	558.2	normal	8.6
2001	653.6	normal	7.4
2002	640.1	normal	8.4
2003	477.8	dry	7.5
2004	696.3	wet	7.3
2005	460.5	dry	8.3
2006	645.0	normal	7.9
2007	827.5	wet	8.5
2008	561.5	normal	8.9
Mean	609.5	normal	7.9
1951–2000	615.9	—	7.1

In comparison with the long-term average of 1951–2000, according to the classification proposed by Kaczorowska [8], three years were found to be wet, nine years were normal, three years were dry and one year was very dry. Over the experimental period, the mean annual air temperature ranged from 5.8 to 8.9 °C (7.9 °C on average), and it was by 0.8 °C higher than the long-term average of 1951–2000.

In the years 1993–2008, monthly precipitation totals varied widely in time (Fig. 1). Extremely low (3.1 mm – December) and high (188.4 mm – July) values were noted in 1997. However, during the 16-year period February was the driest month (26.3 mm on average), and July was the wettest month (86.0 mm on average). As regards precipitation amounts, months with normal precipitation (39 %) and dry months (19 %) dominated over this period. The hydrological year 1996 was found to be driest (annual precipitation total of 408.2 mm) and coolest (mean temperature of 5.8 °C), the year 2007 was wettest (827.2 mm) and the year 2008 was hottest (8.9 °C).

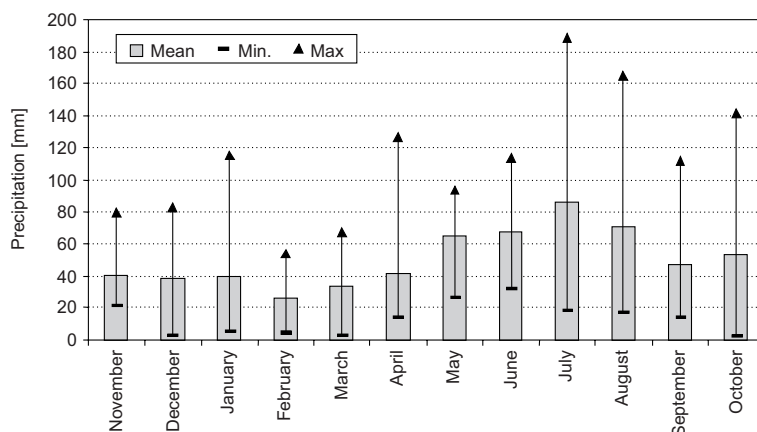


Fig. 1. Dynamics of monthly precipitation totals in the vicinity of Olsztyn in the years 1993–2008

Compared with the analogous periods in 1951–2000, the winter half-years were characterized by lower amounts of precipitation, by 10.5 mm on average. The lowest precipitation total was recorded in the winter half-year of 1996 – by 126.7 mm lower than the long-term average, while the highest precipitation total was noted in the winter half-year of 1994 – by 104.6 mm higher than the long-term average (Table 2).

In the summer half-years of the experimental period mean precipitation was by 4.1 mm higher than the long-term average, varying from 121.3 mm below to 125.8 mm above this average. As regards the seasons, mean precipitation during the experimental period was lower compared with the long-term average, by 17.4 mm in the fall, by 3.3 mm in the summer and by 2.8 mm in the winter. Higher precipitation levels, by 17.0 mm on average, were observed only in the spring. The winter and summer half-years as well as all seasons were warmer (from 0.3 °C in the fall to 1.0 °C in the winter) in the experimental period, as compared with the analogous periods in 1951–2000. The values of calculated means and medians revealed different trends with

Table 2

Seasonal variation in precipitation totals and mean air temperatures
in the vicinity of Olsztyn in the years 1993–2008

Season	Precipitation [mm]				Temperature [°C]			
	Min.–Max	Median	V (%)	Average	Min.–Max	Median	SD	Average
Half year								
Winter	103.6–334.9	215.9	30	219.8	–1.9–3.2	1.1	1.2	1.3
Summer	264.3–511.4	409.6	17	389.7	13.4–15.5	14.5	0.7	14.5
Season of year								
Autumn	67.0–243.3	137.9	32	140.4	5.4–11.2	7.8	1.4	7.9
Winter	35.0–184.3	116.9	38	104.4	–6.7–1.0	–1.2	1.8	–1.3
Spring	80.6–232.7	134.1	29	140.1	5.6–9.2	7.6	1.2	7.4
Summer	99.0–329.8	237.5	28	224.6	16.1–19.0	17.7	1.0	17.5

SD – Standard deviation; V – coefficient of variation; Min.–Max – the lowest and the highest monthly values.

respect to both precipitation totals and air temperatures in the summer and winter half-years. The amounts of precipitation were characterized by considerably greater variation in the winter half-years ($V = 30\%$) than in the summer half-years ($V = 17\%$). However, in the winter half-years of the analyzed 16-year period wet and dry periods remained in a relative equilibrium, whereas in the summer half-years wet periods dominated over dry periods. With regard to seasons, winter months showed the greatest variation ($V = 38\%$) in rainfall amount. Similarly as in the summer and spring, humid periods dominated also in the winter, and dry periods were more frequent only in the fall.

During the experimental period, the pH of precipitation water ranged from 3.8 to 8.12 (pH 5.6 on average) and electrolytic conductivity (EC) ranged from 7 to $103 \mu\text{S} \cdot \text{cm}^{-1}$ ($29 \mu\text{S} \cdot \text{cm}^{-1}$ on average) (Table 3).

Rainfall was usually slightly acidic (72 %) to acidic (21 %), with a low proportion of slightly basic (5 %) and neutral (approx. 2 %) samples. As a result, precipitation water was slightly acidic (pH 5.3 to pH 6.0 on average) and only in 2004 – acidic (pH 4.9 on average). The amount of precipitation had no significant effect on the pH and EC of precipitation water. However, a trend was noted towards lower pH values in wetter years and greater variation in EC in drier years, in comparison with the mean values throughout the entire experimental period. Statistically significant correlations between precipitation and pH levels (Table 4) were observed only in one dry year (1998 – $r = 0.67$) and one wet year (2004 – $r = -0.68$), while a significant correlation between precipitation and EC was reported in one of the normal years (1999 – $r = -0.69$). In the winter half-years, the pH of precipitation water was somewhat lower (pH 5.5 on average, ranging from 4.9 to 6.0) and less variable than in the summer half-years (pH 5.7 on average, ranging from 4.4 to 6.3).

Table 3

Variation in the pH and electrolytic conductivity of precipitation water in the vicinity of Olsztyn in the years 1993–2008

Year	Reaction pH				EC [$\mu\text{S} \cdot \text{cm}^{-2}$]				
	Min.–Max	Median	SD	Average	Min.–Max	Median	V (%)	Average	
1993	4.6–6.7	5.7	0.6	5.8	19–64	29	40	32	
1994	5.4–6.6	5.7	0.4	5.9	15–50	26	35	29	
1995	5.3–6.7	5.6	0.5	5.7	17–50	27	36	31	
1996	5.0–6.9	6.0	0.5	5.9	20–65	33	38	33	
1997	5.0–6.5	5.8	0.5	5.7	13–51	36	34	33	
1998	4.7–6.6	5.9	0.6	5.8	13–67	33	48	37	
1999	4.6–8.1	5.8	0.9	6.0	17–66	32	41	33	
2000	4.1–6.2	5.6	0.6	5.5	3–61	29	48	29	
2001	3.8–7.3	5.3	1.1	5.5	7–72	32	45	35	
2002	4.6–6.1	5.5	0.5	5.4	14–64	32	35	34	
2003	4.0–6.8	5.4	0.9	5.3	20–63	36	34	39	
2004	3.9–6.2	4.8	0.9	4.9	10–49	29	37	30	
2005	4.2–7.5	5.1	1.0	5.4	20–103	38	55	41	
2006	3.9–7.0	5.5	0.9	5.5	18–48	31	30	33	
2007	4.2–7.7	5.0	1.0	5.4	19–75	36	42	37	
2008	4.0–7.5	6.0	1.3	5.9	18–62	31	45	34	
Average					5.6				29
Half year									
Winter	4.9–6.0	5.5	0.3	5.5	26–43	35	14	35	
Summer	4.4–6.3	5.8	0.4	5.7	21–41	32	14	33	
Season of year									
Autumn	4.9–7.0	5.6	0.5	5.6	18–39	27	24	28	
Winter	4.6–6.1	5.2	0.5	5.3	20–42	34	17	34	
Spring	5.4–7.3	5.7	0.5	5.8	31–49	36	14	38	
Summer	4.0–6.6	5.8	0.6	5.7	23–50	36	18	35	

SD – Standard deviation; V – coefficient of variation; Min.–Max – the lowest and the highest monthly values.

The values and the range of variation of EC in particular years of the study (V from 30 to 55 %) are indicative of relatively high differences in the concentrations of substances in atmospheric precipitation, resulting from various intensity of pollutant emissions throughout the year. The above variation was affected by the amount and distribution of annual precipitation, although this effect was statistically non-significant. The relatively low variation in EC values in the analyzed half-years (V = 14 %) and seasons (V = 14–24 %) points to a low level of air pollution dynamics in the vicinity of Olsztyn.

Variable weather conditions during the experimental period contributed to high differences in the concentrations and loads of mineral nitrogen compounds in precipitation water in the vicinity of Olsztyn, which were strongly affected by the

Table 4
Correlations between the concentrations and loads of mineral nitrogen compounds in atmospheric precipitation at N = 192 and p < 0.05

Variable	Precipitation	Temperature	Reaction pH	EC	Concentration N-NH ₄	Concentration N-NO ₃	Concentration N-NO ₂	Load N-NH ₄	Load N-NO ₃	Load N-NO ₂
Temperature	0.44*									
Reaction pH	-0.01	0.22*								
EC	-0.07	-0.03	0.17*							
Concentration N-NH ₄	-0.14	-0.01	0.09	0.07						
Concentration N-NO ₃	-0.25*	-0.21*	0.08	0.17*	0.59*					
Concentration N-NO ₂	-0.06	0.08	0.12	-0.02	0.01	-0.01				
Load N-NH ₄	0.48*	0.33*	-0.02	-0.01	0.63*	0.10	-0.03			
Load N-NO ₃	0.60*	0.22*	0.03	0.10	0.18	0.47*	-0.02	0.44*		
Load N-NO ₂	0.33*	0.22*	0.08	-0.02	-0.06	-0.09	0.87*	0.16*	0.23*	
Load N mineral	0.58*	0.34*	-0.01	0.02	0.58*	0.22*	-0.02	0.97*	0.66*	0.21*

* - essential correlations; EC - electrolytic conductivity.

distribution and intensity of precipitation in particular years. A comparison of mean values obtained in the studied 16 years showed that N-NH₄ dominated in precipitation water (0.924 mg · dm⁻³ on average) – its concentration was over twofold higher than the concentration of N-NO₃ (0.42 mg · dm⁻³ on average). N-NO₂ concentrations were very low (0.009 mg · dm⁻³), compared with the other compounds (Table 5). The mean monthly concentrations of N-NH₄ ranged from 0.036 to 6.195 mg · dm⁻³, of N-NO₃ – from 0.005 to 1.889 mg · dm⁻³, and of N-NO₂ – from 0.001 to 0.036 mg · dm⁻³. Among the analyzed nitrogen forms, N-NH₄ concentrations were characterized by the greatest annual variation, which reached the highest level (V = 138 %) in precipitation water in the dry year 2005. This was probably related to the low amount of precipitation which therefore contained a low concentration of ammonia absorbed from ambient air. However, as shown by the coefficients of variation in the concentrations of the investigated nitrogen forms during the 16-year experimental period, N-NO₃ concentrations were most variable (V from 42 to 97 %).

The concentrations of mineral nitrogen in precipitation water tended to decrease along with an increase in the amount of precipitation, as indicated by the negative values of correlation coefficients. However, due to high variation in precipitation totals and air pollution levels over the 1993–2008 period, a significant correlation ($r = -0.25$) was found only between the amount of precipitation and N-NO₃ concentrations. The concentrations of N-NH₄ (by 13 % on average) and N-NO₃ (by 34 % on average) were higher in the winter half-years, marked by lower precipitation totals, than in the summer half-years.

The highest concentrations of mineral nitrogen compounds in precipitation water were noted in the spring (1.397 mg · dm⁻³ N-NH₄, 0.673 mg · dm⁻³ N-NO₃ and 0.010 mg · dm⁻³ N-NO₂ on average). The high concentrations of ammonia nitrogen and nitrate(V) nitrogen in atmospheric precipitation over spring months could result from a higher level of air pollution with ammonia from organic fertilizers (slurry and manure) applied at that time in grassland and arable land. Another source of nitrogen compounds in precipitation water could be soil processes leading to the release of ammonia formed during organic matter decomposition.

The input of mineral nitrogen via precipitation per ha of catchment area ranged from 5.34 to 9.74 kg, including 3.48–8.09 kg N-NH₄, 1.42–3.88 kg N-NO₃ and 0.03–0.08 kg N-NO₂ (Table 6). These quantities do not pose a threat to contamination in agricultural land where nitrogen from atmospheric deposition may contribute to soil enrichment, in particular under conditions of low fertilization rates [5].

The amount of mineral nitrogen deposited by precipitation was determined by precipitation totals and by nitrogen concentrations in precipitation water, although the concentrations of N-NH₄ and N-NO₃ decreased in precipitation water along with an increase in its amount. The variation in the load of total mineral nitrogen and its forms was very low, compared with the variation in mineral nitrogen concentrations. Similarly as in the case of nitrogen concentrations, the greatest variation in the atmospheric deposition of N-NH₄ was noted in the dry year 2005 (V = 18 %), and of N-NO₃ – in 2006 (V = 11 %). The highest mineral nitrogen load (9.74 kg · ha⁻¹) was recorded in the wet year 1995, and the lowest (5.34 kg · ha⁻¹) – in the normal year 2001.

Table 5
Variation in the concentrations of mineral nitrogen compounds [$\text{mg} \cdot \text{dm}^{-3}$] in precipitation water in the vicinity of Olsztyn in the years 1993–2008

Year	N-NH ₄				N-NO ₃				N-NO ₂			
	Min.–Max	Median	V (%)	Average	Min.–Max	Median	V (%)	Average	Min.–Max	Median	V (%)	Average
1993	0.48–1.13	0.71	28	0.74	0.05–0.84	0.37	58	0.38	0.002–0.016	0.008	46	0.008
1994	0.49–1.27	0.79	28	0.79	0.10–0.57	0.36	44	0.31	0.004–0.014	0.009	35	0.009
1995	0.48–1.48	0.93	36	0.93	0.04–0.50	0.35	50	0.31	0.002–0.012	0.006	49	0.006
1996	0.68–2.95	1.95	58	1.85	0.23–1.90	0.64	77	0.79	0.002–0.016	0.007	53	0.008
1997	0.46–1.51	0.90	38	0.93	0.09–0.93	0.45	60	0.46	0.002–0.018	0.010	51	0.009
1998	0.21–1.33	0.64	43	0.70	0.05–0.86	0.31	69	0.38	0.002–0.013	0.006	55	0.007
1999	0.21–1.52	0.65	56	0.75	0.12–0.67	0.42	42	0.39	0.001–0.018	0.006	61	0.007
2000	0.17–1.71	0.54	63	0.63	0.07–1.38	0.29	87	0.41	0.001–0.011	0.005	53	0.005
2001	0.04–2.03	0.42	92	0.61	0.03–0.80	0.35	69	0.33	0.002–0.009	0.003	51	0.004
2002	0.16–1.50	0.62	58	0.69	0.15–1.12	0.40	67	0.44	0.004–0.036	0.009	79	0.013
2003	0.25–2.69	0.82	77	0.97	0.19–1.14	0.31	70	0.48	0.007–0.018	0.009	31	0.011
2004	0.14–1.20	0.75	50	0.72	0.01–0.90	0.17	97	0.29	0.003–0.078	0.007	57	0.013
2005	0.09–6.20	0.50	138	1.24	0.13–1.05	0.24	78	0.35	0.003–0.016	0.008	41	0.009
2006	0.10–4.58	0.58	116	1.28	0.02–1.26	0.30	96	0.47	0.004–0.033	0.010	67	0.014
2007	0.10–2.35	0.60	80	0.78	0.25–1.15	0.43	53	0.52	0.004–0.018	0.010	41	0.011
2008	0.22–2.95	0.66	86	1.17	0.22–1.02	0.41	52	0.48	0.006–0.019	0.012	31	0.012
Average				0.92				0.42				0.009

Table 5 contd.

Year	N-NH ₄				N-NO ₃				N-NO ₂			
	Min.-Max	Median	V (%)	Average	Min.-Max	Median	V (%)	Average	Min.-Max	Median	V (%)	Average
	Half year											
Winter	0.56-2.87	0.84	57	0.99	0.191-32	0.51	49	0.51	0.005-0.016	0.009	38	0.009
Summer	0.32-1.52	0.82	34	0.86	0.22-0.45	0.34	24	0.34	0.003-0.016	0.009	39	0.009
	Season of year											
Autumn	0.18-1.56	0.50	58	0.59	0.10-0.64	0.28	53	0.32	0.003-0.013	0.008	55	0.008
Winter	0.34-2.90	0.64	81	0.75	0.11-1.39	0.34	71	0.41	0.003-0.016	0.007	57	0.007
Spring	0.82-2.91	1.18	42	1.40	0.34-1.19	0.64	35	0.67	0.005-0.021	0.009	48	0.010
Summer	0.40-2.71	0.83	58	0.95	0.17-0.45	0.30	30	0.30	0.004-0.018	0.008	40	0.009

V – coefficient of variation; Min.-Max – the lowest and the highest monthly concentration.

Table 6
 Variation in the monthly and total annual loads of mineral nitrogen forms [$\text{mg} \cdot \text{dm}^{-3}$] in precipitation water in the vicinity of Olisztyn in the years 1993–2008

Year	N-NH ₄				N-NO ₃				N mineral			
	Monthly loads			Sum total	Monthly loads			Sum total	Monthly loads			Sum total
	Min.-Max	Median	V (%)		Min.-Max	Median	V (%)		Min.-Max	Median	V (%)	
1993	0.07–0.83	0.44	5	5.10	0.04–0.54	0.15	6	2.29	0.11–1.33	0.57	5	7.44
1994	0.09–0.93	0.36	5	5.27	0.04–0.39	0.13	6	2.06	0.12–1.31	0.50	5	7.39
1995	0.10–1.66	0.44	7	7.25	0.01–0.54	0.15	7	2.45	0.12–2.21	0.57	7	9.74
1996	0.10–0.94	0.40	4	5.49	0.05–0.44	0.15	5	2.13	0.15–1.38	0.59	5	7.65
1997	0.01–1.69	0.33	9	5.67	0.01–0.49	0.15	7	2.26	0.03–2.20	0.47	8	7.99
1998	0.11–0.48	0.30	4	3.54	0.03–0.37	0.14	5	1.87	0.14–0.86	0.47	4	5.45
1999	0.05–1.15	0.31	7	4.76	0.06–0.53	0.16	6	2.33	0.12–1.55	0.47	6	7.14
2000	0.01–0.92	0.21	7	3.73	0.01–0.33	0.12	6	1.86	0.02–1.17	0.36	6	5.62
2001	0.01–0.83	0.19	8	3.48	0.01–0.33	0.15	6	1.83	0.05–1.17	0.34	7	5.34
2002	0.08–1.04	0.30	7	4.14	0.04–0.54	0.13	7	2.76	0.17–1.57	0.47	6	6.98
2003	0.01–0.81	0.29	7	4.53	0.01–0.34	0.16	6	1.99	0.03–1.08	0.50	6	6.57
2004	0.06–0.96	0.39	6	5.22	0.00–0.67	0.11	9	2.10	0.14–1.64	0.51	6	7.39
2005	0.02–5.20	0.24	18	8.09	0.03–0.31	0.10	6	1.42	0.05–5.32	0.37	15	9.57
2006	0.03–1.35	0.28	8	5.42	0.01–1.13	0.11	11	2.78	0.04–1.82	0.39	8	8.28
2007	0.06–1.04	0.36	6	5.51	0.08–0.83	0.24	6	3.88	0.26–1.89	0.58	6	9.47
2008	0.08–1.29	0.41	7	5.59	0.07–0.32	0.20	3	2.33	0.16–1.44	0.70	5	7.99
Average				5.17				2.27				7.50

Table 6 contd.

Year	N-NH ₄				N-NO ₃				N mineral			
	Monthly loads			Sum total	Monthly loads			Sum total	Monthly loads			Sum total
	Min.-Max	Median	V (%)		Min.-Max	Median	V (%)		Min.-Max	Median	V (%)	
	Half year											
Winter	1.13-1.45	1.71	28	1.86	0.51-1.68	0.91	31	0.96	1.94-4.42	2.62	25	2.84
Summer	1.45-6.36	3.14	37	3.31	0.60-2.20	1.27	37	1.31	2.41-7.40	4.68	29	4.65
	Season of year											
Autumn	0.16-1.78	0.68	61	0.78	0.13-1.19	0.36	70	0.41	0.34-2.41	1.18	55	1.20
Winter	0.17-1.73	0.55	58	0.73	0.14-0.92	0.32	59	0.38	0.39-2.56	0.89	55	1.12
Spring	1.23-2.05	1.59	16	1.61	0.47-1.50	0.76	30	0.79	1.82-3.34	2.32	19	2.41
Summer	0.82-5.90	1.90	61	2.06	0.32-1.37	0.59	47	0.69	1.21-6.24	2.73	48	2.77

V – coefficient of variation; Min.-Max – the lowest and the highest monthly loads.

With regard to the amount of atmospheric precipitation, the experimental period was divided into very dry, dry, normal and wet years. The highest load of total mineral nitrogen and nitrogen forms was noted in wet years ($8.87 \text{ kg} \cdot \text{ha}^{-1}$ on average), while the lowest load of total mineral nitrogen ($7.13 \text{ kg} \cdot \text{ha}^{-1}$ on average) as well as N-NH_4 ($4.80 \text{ kg} \cdot \text{ha}^{-1}$ on average) – in years with normal precipitation. The lowest deposition levels of N-NO_3 ($1.76 \text{ kg} \cdot \text{ha}^{-1}$ on average) and N-NO_2 ($0.03 \text{ kg} \cdot \text{ha}^{-1}$ on average) was observed in dry and very dry years, respectively. As regards the loads of total mineral nitrogen and its main component, N-NH_4 , the years of the studied period may be listed in order of decreasing values, as follows: wet > very dry > dry > normal. This confirms the observation that the amount of atmospheric deposition of mineral nitrogen was determined primarily by the concentrations and loads of N-NH_4 , which were on average twofold higher than those of N-NO_3 .

The proportions of mineral nitrogen forms in precipitation water varied widely, both within (seasonal variation) and between the analyzed years. In the normal year 2002 and in the wet year 2007, the levels of N-NH_4 and N-NO_3 were similar, but in the dry year 2005 the contribution of N-NH_4 was six-fold higher. Particularly high disproportions between the share of N-NH_4 and N-NO_3 were noted in 2005, when the amount of N-NH_4 was 11-fold higher in the summer half-year, and 19-fold higher over summer months. The periodic variation ($V = 25 \%$ in the winter half-years, $V = 29 \%$ in the summer half-years) and seasonal variation ($V = 19 \%$ in the spring, $V = 55 \%$ in the fall and winter) in mineral nitrogen loads was affected mostly by precipitation amounts and the concentrations of nitrogen forms in precipitation water (Table 6). As the amount of precipitation was higher in the summer half-years than in the winter half-years, the atmospheric deposition of mineral nitrogen compounds was also substantially higher (by 64 %) in the summer half-years, and the predominant compound was N-NH_4 whose share was by 78 % higher in this period.

Mineral nitrogen loads were twofold higher in the summer and spring than in the fall and winter. The highest loads of N-NH_4 and N-NO_2 were reported in the summer, and of N-NO_3 – in the spring. It is highly desirable that the major part of the annual mineral nitrogen load is deposited in the summer half-year, i.e. during the growing season, as it supports the bioaccumulation of nitrogen by plants and the sorption of ammonium ions in the soil. On the other hand, the fact that the summer load of nitrogen, in particular N-NH_4 , is larger than the spring load is less beneficial because the nutrient requirements of field crops and grassland vegetation are lower in the summer. The important role of vegetation cover in reducing atmospheric pollution is reflected by a significant decrease in the nutrient outflow in the summer half-year. The pollutant adsorption capacity of vegetation, in particular in forest areas, is reduced in wet years [10].

Conclusions

1. In the vicinity of Olsztyn, the 1993–2008 period was dominated by years with average precipitation levels (9 years), three years were found to be wet, three years were dry and one year was very dry. The majority of the annual precipitation (77 % on average) occurred in the summer half-year. Summer was the wettest season (37 % of the

total annual precipitation on average), followed by the spring and fall (23 % each), and winter was the driest season (17 %).

2. The pH of precipitation water ranged from acid (pH = 3.8) to slightly basic (pH = 8.12). The average pH determined for the years 1993–2008 was 5.6. Rainfall was usually slightly acidic (72 %) to acidic (21 %), with a low proportion of slightly basic (5 %) and neutral (approx. 2 %) samples.

3. The amount of nitrogen atmospheric deposition was determined by precipitation levels and the concentrations of mineral nitrogen compounds in precipitation. N-NH₄ dominated in precipitation water with respect to both concentrations (0.92 mg · dm⁻³ on average) and loads (5.17 kg · ha⁻¹ on average). The concentrations and loads of N-NH₄ were twofold higher than those of N-NO₃, while N-NO₂ was present in low quantities (annual deposition below 0.01 kg · ha⁻¹).

4. In the vicinity of Olsztyn, the input of mineral nitrogen via precipitation per ha per year ranged from 5.34 to 9.74 kg, including 5.17 kg · ha⁻¹ N-NH₄, 2.27 kg · ha⁻¹ N-NO₃ and 0.05 kg · ha⁻¹ N-NO₂ on average. The highest mineral nitrogen load was noted in wet years (8.87 kg · ha⁻¹ on average), while the lowest – in years with normal precipitation (4.80 kg · ha⁻¹ on average).

5. Most nitrogen was deposited from the atmosphere in precipitation over the growing season, which supported its accumulation in plants and soil, thus reducing groundwater and surface water pollution.

References

- [1] Biernacka E. and Macioszczyk A.: *Post. Nauk Roln.*, 2005, **3**, 61–73.
- [2] Miczyński J., Wojkowski J. and Jurkiewicz T.: *Pieniny Przyroda i Człowiek*, 1998, **6**, 137–141.
- [3] Pawlik-Dobrowolski J., Lempicka A. and Rossa L.: *Kształowanie się obiegu materii w systemach stawów o funkcji gospodarczej i ekologicznej*, Pawlik-Dobrowolski (ed.). Wyd. IMUZ Falenty, 2003, 20–33.
- [4] Woroniecki T.K. and Rumaszczyk E.: *Wiad. Melior. Łąk.*, 2008, **3(418)**, 131–133.
- [5] Sapek A., Nawalany P. and Barszczewski J.: *Woda Środow. Obszar. Wiej.*, 2003, **3** zes. spec. (6), 67–77.
- [6] Koc J., Solarzski K. and Koc-Jurczyk J.: *Zesz. Probl. Post. Nauk Roln.*, 2008, **528**, 223–229.
- [7] Solarzski J. and Solarzski K.: *Zesz. Probl. Post. Nauk Roln.*, 1996, **443**, 91–95.
- [8] Kondracki J.: *Geografia regionalna Polski*. WN PWN Warszawa 2000, 103–118.
- [9] Kaczorowska Z.: *Prace Geograficzne, IGiPZ PAN*, 1962, **33**, 7–17.
- [10] Szymczyk S. and Glińska-Lewczuk K.: *Nawozy i Nawożenie*, 2004, **2(19)**, 41–49.

SEZONOWA ZMIENNOŚĆ STĘŻEŃ I ŁADUNKÓW MINERALNYCH ZWIĄZKÓW AZOTU W OPADACH ATMOSFERYCZNYCH W OKOLICACH OLSZTYNA

Katedra Melioracji i Kształowania Środowiska
Uniwersytet Warmińsko-Mazurski w Olsztynie

Abstrakt: Badania prowadzono w latach hydrologicznych 1993–2008 w stacji meteorologicznej w Tomaszowie koło Olsztyna. Obejmowały one: pomiary dobowych ilości opadów atmosferycznych, pobrania wód po każdym opadzie atmosferycznym, pH, EC oraz stężeń i ładunków mineralnych związków azotu: N-NO₂, N-NO₃, N-NH₄. Badania wykazały, że w latach 1993–2008 w okolicach Olsztyna dominowały lata o przeciętnych ilościach opadów atmosferycznych, a także wystąpiły 3 lata wilgotne, 3 suche oraz 1 rok

bardzo suchy. Przeważająca część (średnio 77 %) opadu rocznego występowała w półroczu letnim. Spośród pór roku najwilgotniejsze było lato (średnio 37 % opadu rocznego), a najsuchsza była zima z ilością opadów na poziomie 17 % sumy rocznej. Wody opadowe miały odczyn pH 3,8 do pH 8,12), średnio pH 5,6. Wśród nich dominował odczyn słabo kwaśny (72 %) i kwaśny (21 %). Ładunek azotu wnoszonego wraz z opadami zależał od ich ilości i stężenia w nich mineralnych związków azotu. Pod względem stężenia i wielkości ładunku dominował N-NH₄, a N-NO₂ występował w marginalnych ilościach. Na 1 ha w okolicach Olsztyna wraz z opadami atmosferycznymi rocznie trafiało od 5,34 do 9,74 kg azotu mineralnego, w tym średnio: 5,17 kg · ha⁻¹ N-NH₄, 2,27 kg · ha⁻¹ N-NO₃ i 0,05 kg · ha⁻¹ N-NO₂. Największy ładunek azotu mineralnego wystąpił w latach wilgotnych (średnio 8,87 kg · ha⁻¹), a najmniejszy (średnio 4,80 kg · ha⁻¹) w latach normalnych. Przeważająca część depozycji atmosferycznej azotu występowała w okresie wegetacji, co umożliwiało jego akumulację w roślinach i glebie, a w efekcie ograniczało zanieczyszczenie nim wód gruntowych i powierzchniowych.

Słowa kluczowe: wody opadowe, azot, depozycja atmosferyczna