

## Tendencies of changes in the chemical composition of precipitation in the Wielkopolski National Park

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**Abstract:** The results are presented of chemical studies on precipitation based on multi-year observations (1992–2007) carried out in the Wielkopolski National Park (WNP). They are compared with the monitoring data obtained by stations grouped in the European Monitoring and Evaluation Programme (EMEP) network. It was found that over the study period the pH of precipitation tended to grow systematically, thus contributing to a decrease of the annual deposition of ( $H^+$ ) ions. The trend lines of changes in the deposition of hydrogen ions have similar slope coefficients, which indicates similar rate of changes. The year with the lowest pH was 1994, in which the mean annual pH was 3.92. In turn, the acidification level was the lowest in 2006 with pH – 4.80. The deposition of hydrogen ions at all stations often exceeded  $20 \text{ mg}\cdot\text{m}^{-2}\cdot\text{year}^{-1}$ , and at the WNP station it even reached  $70 \text{ mg}\cdot\text{m}^{-2}$  in 1994.

The deposition of acid-forming ions was also analysed. Predominant among them were sulphate ions, but their deposition showed a declining tendency with time. Their maximum values were recorded in precipitation in the WNP –  $707 \text{ mg S}\cdot\text{SO}_4\cdot\text{m}^{-2}$  (2002) and  $260 \text{ mg N}\cdot\text{NO}_3\cdot\text{m}^{-2}$  (2007). It was found that the  $\text{NO}_3/\text{SO}_4$  eq/eq ratio tended to increase, which is indicative of changes in the composition structure of precipitation. This effect resulted from the decrease in  $\text{SO}_2$  emission in the Wielkopolska region and from the increase in  $\text{NO}_x$  emission caused by car traffic in the Park and along its border.

Calcium dominated among the deposited alkaline cations – its share exceeded 50%. The figures recorded for potassium and calcium deposition by lowland EMEP stations were several times lower than those obtained in the WNP and lower than the mean for Poland. Over the last years one can note a stabilisation in the amount of deposited cations.

Key words: *acidification, deposition, pH, throughfall*

### INTRODUCTION

The Wielkopolski National Park (mid-west Poland) is a protected region that needs special care of its woodland, which occupy up to 61% of its area. However, nature in the Park is threatened since it is located close to the Poznań municipality

(25 km away), and to nearby towns of a few thousand inhabitants, especially highly industrialized Luboń of a population of 30 thousand (MICHAŁOWSKI *et al.*, 2003; KOWALSKI, 2004). The development of the transport system with roads both on the Park's edges and those running through is a major source of air pollution (GÓRSKI and PRZYBYŁEK, 2003). The pollution caused by the industrial plants situated a few or a dozen or so kilometres from the forest complex, or pollution carried from distant areas results in elevated amounts of sulphates, chlorides and fluorides (KRYSIK, 2005; WALNA and KURZYCA, 2007). This pollution in the form of dry and wet deposition influences the chemical composition of precipitation (ASTEL *et al.*, 2007; WALNA and SIEPAK, 1999). In the last few years, a major decline in the emission of sulphur compounds has been registered in Poznań, though changes in the emission for the Wielkopolska region as a whole have not been that significant (KRYSIK, 2005; POLKOWSKA *et al.*, 2005; Statistical Data, 2005). The main object of the undertaken research was the impact of changes in the amount and chemical composition of precipitation on the elements of the Park ecosystem over the last few years and the identification of possible protective measures for the WNP woodland. Examples of such an application of climatic studies are publications concerning the growth dynamics of oaks (CZERNIAK *et al.*, 2008; UFNALSKI and SIWECKI, 2002).

The aim of this article is to discuss the results of a chemical study of precipitation in the years 1992–2007. It focused on both, the amount of precipitation and the chemical composition of rainwater collected in open terrain and under tree crowns, including the deposition of acid-forming components. Tendencies of changes were also identified.

## METHODS

### SAMPLING SITE

Observations of precipitation, both in quantitative and qualitative terms, are carried out at the Jeziory Ecological Station of the Adam Mickiewicz University located in the centre of the Wielkopolski National Park (WNP). The site is located at 52°11' N and 16°54' E at an altitude of 82 m a.s.l. The landscape of the Park is a result of numerous geomorphologic processes linked to the movement of a glacier. A substantial part of the Park is covered with poor soils developed from loose or weakly loamy sand where pine forests and mixed pine – oak forests are dominating. Brown soil of higher quality is home to acid oak forests, and oak-hornbeam forests. The sampling place is a forest clearing in a protected area surrounded by extensive patches of woodland; some 200 m away there is a road with light traffic. Rainwater was collected on a daily basis and analysed as soon as possible after the precipitation event. The trees are about 40 years old and 30 cm in diameter.

The research was initially limited to basic physico-chemical parameters, but since 2002 it has been expanded to include regular monitoring of the chemical composition of precipitation. Quantitative studies were made using a Hellmann rain gauge and automatically (an Aster station). Samples of bulk precipitation for chemical analyses were collected with the help of one collector 56 cm in diameter placed 1.2 m above the ground in a forest clearing and the similar one under oak trees.

## ANALYTICAL METHODS

pH and electric conductivity were measured on the spot, and the ionic composition was determined with DIONEX 120 chromatograph in the Department of Water and Soil Analysis of the Adam Mickiewicz University in Poznań. Before the transfer, the samples were filtered through a filter with a pore diameter of 0.45 µm and, if necessary, kept in refrigerator, out of light. The reliability of the results was checked against reference material suitable for samples of a low ionic strength – RAIN 95. Analytical details were described in another paper (POLKOWSKA *et al.*, 2005). An essential element of rainfall analysis was the set of meteorological data obtained at the Station through the steady automatic monitoring of a dozen or so parameters. Measurements were registered every 10 minutes. An automatic heating of the collector enabled to gather precipitation in the winter.

## RESULTS AND DISCUSSION

### RAINFALL – ANNUAL AND MONTHLY

Significant differences in the annual rainfall were noted during the study period (Tab. 1). The figures varied from a minimum of 338 mm in 2003 to 656 mm in 2007. The average was 536 mm, nearly equal to the multi-year mean for the area (528 mm) (WOŚ, 1994). The years with below-average precipitation were 1992, 1995, 2003 and 2004. Those with precipitation above the average were 1993, 1994, 2002 and 2007. These measurements show that dry years alternated with those rich in rainfall.

On account of the plants growth regime, the rainfall during the vegetation season (1 Apr.–15 Nov. for oak tree in the Wielkopolska region) was also calculated. The analysis of the data showed that, aside from the year 1992 when the rainfall during the vegetation season was only 204 mm, a period significantly deficient in rainfall was that from 2003 to 2005 when the rainfall did not exceed 300 mm. To describe precipitation variability it is also important to present its structure in the consecutive months. In the 1990s and before the month richest in precipitation was

**Table 1.** Characteristics of rainfall at the Jezioro Ecological Station in the calendar year and in the vegetation season for oak tree in the Wielkopolska region (1. Apr.–15. Nov.)

Year	Total precipitation in vegetation season	Total annual precipitation		% of precipitation in vegetation season	pH in vegetation season	Mean annual pH	Min. pH in vegetation season	Min. annual pH	Conductivity in vegetation season	Mean annual conductivity	Max. conductivity in vegetation season	Max. annual conductivity
	mm	mm	mm									
1992	204	395	395	52	4.62	4.55	3.89	3.89	47	51	151	151
1993	450	623	623	72	4.18	4.26	3.53	3.53	34	40	112	283
1994	379	621	621	61	3.95	3.92	3.50	2.94	27	36	159	159
1995	315	463	463	68	4.28	4.24	3.65	3.65	30	37	88	128
1996	501	576	576	87	4.42	4.31	3.72	3.48	25	29	200	200
1997	426	513	513	83	4.67	4.53	3.87	3.27	31	36	93	353
1998	442	591	591	75	4.74	4.59	3.87	3.70	26	31	90	129
1999	361	495	495	73	4.71	4.65	4.02	3.70	29	33	109	129
2000	379	596	596	64	4.65	4.43	3.67	3.67	33	38	173	232
2001	422	562	562	75	4.52	4.32	3.71	3.39	24	29	75	184
2002	419	639	639	66	4.61	4.32	3.98	3.23	36	31	118	378
2003	236	338	338	70	4.78	4.47	4.08	3.43	36	42	118	294
2004	277	431	431	64	4.57	4.37	3.88	3.38	28	33	87	240
2005	292	523	523	55	4.65	4.42	3.73	3.73	28	34	110	126
2006	433	552	552	79	5.07	4.80	3.90	3.85	22	27	147	147
2007	449	656	656	68	4.70	4.49	3.84	3.58	21	26	137	137

usually July (WOŚ, 1994), e.g. 1993 – 151 mm, 1996 – 185 mm, or 1997 – 171 mm. However, when comparing monthly totals in the recent years (2000–2007), one does not observe the regularity described so far: a fairly even distribution of precipitation over the individual months and a peak in July. In those years the maximum precipitation in July was only noted in 2007 (126 mm). In 2006, exceptionally low precipitation was recorded in June and July (18 mm and 16 mm, respectively) and in September (20 mm), while the maximum precipitation occurred in August (188 mm) (Fig. 1). In 2005, the months with the lowest precipitation in the vegetation season were June (9 mm) and October (6 mm). The situation seemed favourable in 2004 since despite the deficiency of precipitation, its structure was regular.

It is also worth noting that intensive rainfalls of short duration have recently been observed. The automatic measuring system repeatedly recorded more than 5 mm of rain that fell in 10 minutes. Such a violent character of the event, accompanied by a gusty wind, may cause a lot of damage.

#### THE pH OF PRECIPITATION

The most important parameter describing possible negative effects that precipitation may have on vegetation and soil is pH of the rainwater. Table 1 shows weighted mean annual pH values for the years 1992–2007. The mean annual pH varied from a minimum of 3.92 in 1994 to a maximum of 4.80 in 2006. On average, the pH for this period was 4.4. An analysis of the 16 years of observations indicated a slightly increasing tendency (Fig. 2) but it wasn't statistically significant ( $r = 0.4124$  at  $p = 0.1125$ ). The use of a polynomial function gave better approximation. However, it was difficult to find an adequate justification for such a form.

Also worth noting were the extremely low pH values of precipitation, even below pH 3.0 (1994). The minimum pH varied from 2.94 to 3.89, or 3.5 on average. The Table 1 also shows weighted annual means of precipitation pH for the vegetation season. Because lower pH of precipitation in winter is a well-known regularity, mean pH in the vegetation season (4.6) was higher than the annual mean. The minimum pH in the vegetation season was usually lower than 4.0, with the lowest, 3.50, recorded also in 1994. Unfortunately, such a low pH in the growing season may cause damage to the outer layer of a leaf and let the rain inside the plant tissue, which can trigger some adverse physiological processes (ASHENDEN, 2002).

The structure of precipitation is presented in Table 2. It rests on the division of all the precipitation events in a year into groups according to their pH range (JANSEN *et al.*, 1988). Exceptional precipitation was that occurring between 1994 and 1996, 2000 and 2002, and 2004 and 2005, since the proportion of episodes with a pH lower than 4.6 was near or over 60%. A record year for rain acidity was 1994, when 91% of the precipitation had pH below 4.6.

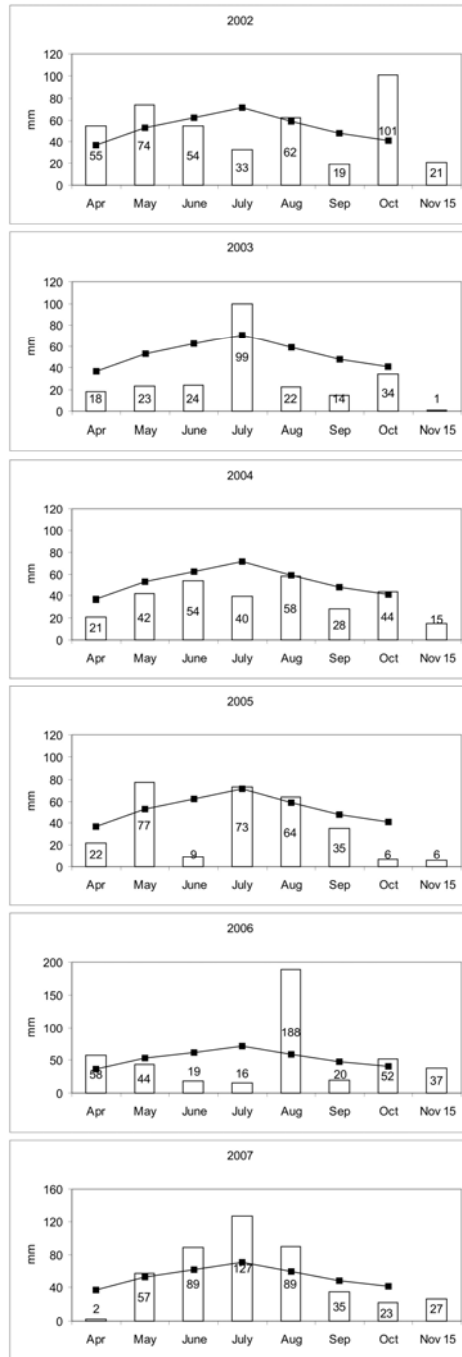


Fig. 1. Monthly sums of precipitation in the vegetation seasons (2002–2007) against the multi-year mean

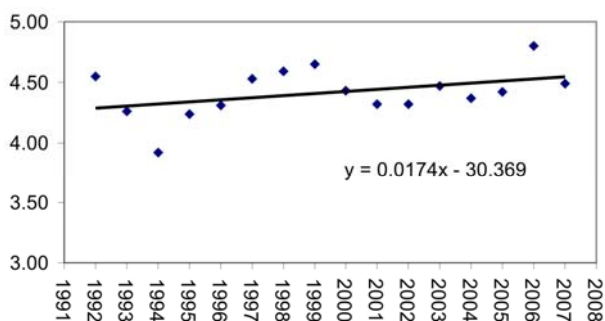


Fig. 2. Tendency of changes in the pH of precipitation – annual weighed mean, 1992–2007

In periods of no precipitation, the surface of plants gathers deposits and dust which, when it rains, partly dissolve and get into the ground. The amount of deposits and dust depends, among others, on time intervals between the rainfalls, the size of leaves, and the wind force. The amount of rainfall that reaches the ground depends on tree species, their age, habitat, and other factors. Therefore, any comparison of pH and composition of the throughfall with data from another place is difficult. However, the obtained figures are important since they expand our quantitative and qualitative knowledge of dry deposition, so hard to collect and analyse. In the period under study (1992–2007), rainfall was collected under oaks (ca. 40 years old). The mean annual pH of the throughfall varied from 3.8 in 1994 to 4.8 in 1999 and 2007 being 4.6 on average. The minimum figures noted in subsequent consecutive years were close to 4.0 or lower. The lowest pH recorded was 2.93 in 1994. The increasing trend of the annual average of throughfall pH over the study period was statistically significant as the correlation coefficient equalled  $r = 0.6516$  at  $p = 0.0062$  (Fig. 3).

A measure of the amount and composition of dry deposition gathered on leaves could be the electric conductivity of the throughfall. The average figures varied from  $77 \mu\text{S}\cdot\text{cm}^{-1}$  (in 1997, 1998 and 2007) to  $149 \mu\text{S}\cdot\text{cm}^{-1}$  (1992). The figures in each year were two to four times higher than the conductivity of rainfall in open terrain. The mutual relations and tendencies of changes are shown in Fig. 4. For conductivity in open terrain, the decreasing trend was statistically significant as the correlation coefficient equalled  $r = -0.6002$  at  $p = 0.0140$ , while for the throughfall conductivity the correlation coefficient equalled  $r = -0.2682$  at  $p = 0.3152$ . It should be noted that the conductivity of throughfall varied much more than the conductivity of rainfall in the open area, which can be observed when comparing the maximum figures of electric conductivity in the subsequent consecutive years. These figures exceeded  $1000 \mu\text{S}\cdot\text{cm}^{-1}$  (1370 in 1996 and 1,470 in 2000). The tendency of changes in the electric conductivity of precipitation, both in the open and in throughfall, is downward, which is indicative of declining pollution of the rainwater.

**Table 2.** Structure of the acidity of precipitation at the Jezziory Ecological Station according to Jansen's classification (%)

Type	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007
Above normal pH > 6.5	5	0	0	3	0	3	0	2	0	1	0	4	0	0	5	2
Slightly above normal pH 6.1–6.5	0	0	0	0	2	5	2	2	0	0	1	5	2	0	3	3
Normal pH 5.1–6.1	29	30	5	10	4	20	18	10	11	13	12	17	16	14	32	16
Slightly acidic pH 4.6–5.1	28	18	4	20	27	23	32	47	30	21	23	30	21	15	26	33
Considerably acidic pH 4.1–4.6	30	26	29	41	32	36	42	32	38	41	47	24	37	44	27	33
Highly acidic pH < 4.1	8	26	62	26	35	13	6	7	21	24	17	20	24	26	7	13



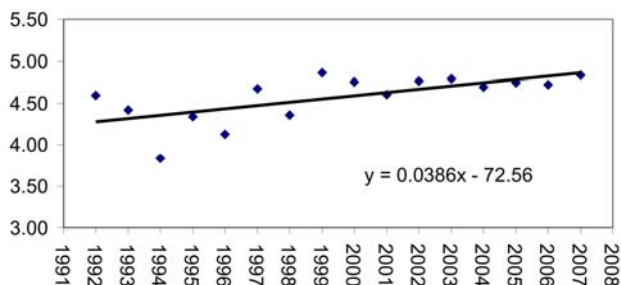


Fig. 3. Tendency of changes in the pH of throughfall, 1992–2007

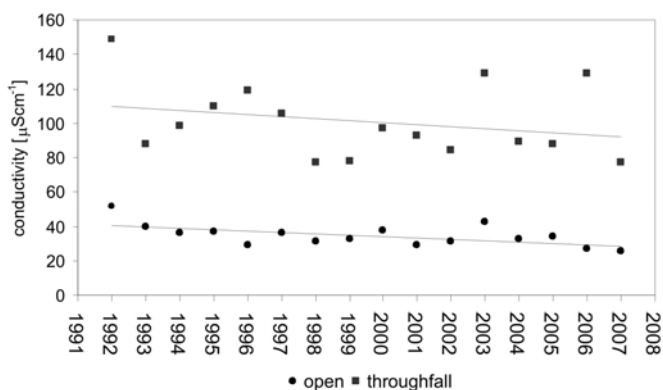


Fig. 4. Tendency of changes in the annual conductivity of precipitation in open terrain and in throughfall, 1992–2007

#### THE CHEMICAL COMPOSITION OF PRECIPITATION – DEPOSITION OF POLLUTION

The effect that the components of precipitation exert on vegetation can be estimated by analysing either the concentration or deposition per unit area ( $\text{m}^2$ , ha) in a given time interval (month, year) calculated on the basis of the concentration and the amount of rainfall. Both methods describe precipitation, though each in a slightly different way. Therefore, the discussion below will concern changes in the concentrations and/or the deposition.

When considering the impact of precipitation on woodland, the above-mentioned results of pH measurement should be supplemented by annual figures of hydrogen ion deposition calculated as the sum of the products of total rainfall and hydrogen ion concentrations obtained from successive pH measurements (Fig. 5). The figures varied from  $8\text{--}11 \text{ mg}\cdot\text{m}^{-2}$  to over  $70 \text{ mg}\cdot\text{m}^{-2}$ , which corresponds to  $0.1\text{--}0.7 \text{ kg}\cdot\text{ha}^{-1}$ . When analysing the pattern of change in the deposition of hydrogen ions, a certain periodicity and simultaneous downward tendency can be observed.

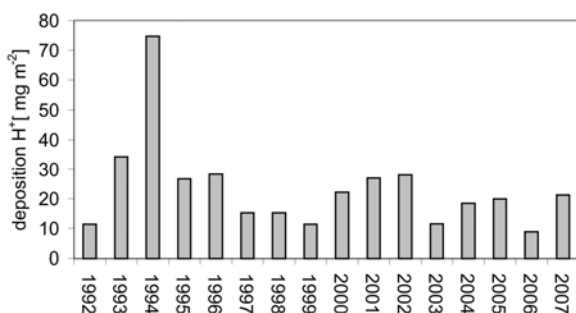


Fig. 5. Deposition ( $\text{mg}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ ) of hydrogen ions with precipitation, 1992–2007

The presented significant acidity of precipitation is due to sulphur oxides and chlorides of industrial origin as well as transport-related nitrogen oxides in the air. A small role is also played by fluorides, typical of the area under study due to phosphate fertiliser factory located close to the Park and to other regional and supra-regional emitters of this type of pollution. The diagramme (Fig. 6) presents the bulk deposition of these compounds in the years 2002–2007. The deposition of sulphates, unlike the other pollutants, decreased considerably from 2,122 to 1,418  $\text{mg}\cdot\text{m}^{-2}$ , while that of nitrates increased to 1,153  $\text{mg}\cdot\text{m}^{-2}$ . Therefore, the structure of deposited compounds was found to change. It is illustrated by the sulphates to nitrate ratio of deposition, which changed from 3 to 1.5. This is a result of recently lower emission of  $\text{SO}_2$  in the Wielkopolska region and increasing  $\text{NO}_x$  emission caused by car traffic in the Park, on the road from Poznań to Wrocław running along its border, and on the nearby A2 highway. The above-presented changes are reflected in decreasing average concentration of sulphates, from 3.6  $\text{mg}\cdot\text{dm}^{-3}$  in 2002 to 2.2  $\text{mg}\cdot\text{dm}^{-3}$  in 2007, and in increasing average concentration of nitrates, from 1.4 to 1.8  $\text{mg}\cdot\text{dm}^{-3}$ , respectively. The level of chlorides seems to be quite stable at 0.6  $\text{mg}\cdot\text{dm}^{-3}$ . However, attention should be paid to extreme concentrations of acid-forming compounds noted during the year. For example, in 2003 maximum

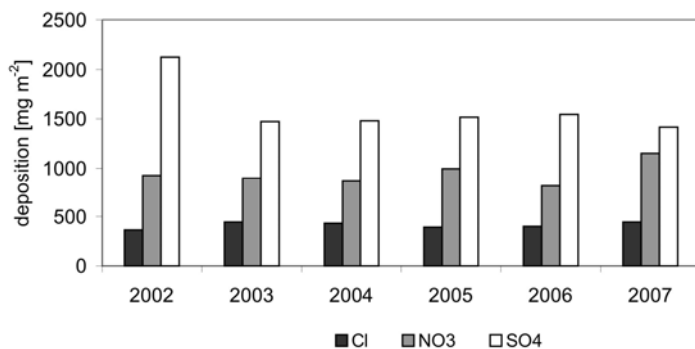


Fig. 6. Deposition ( $\text{mg}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ ) of acid-forming ions (chlorides, nitrates and sulphates), 2002–2007

concentrations in a single precipitation event were  $45.1 \text{ mg}\cdot\text{dm}^{-3}$  for sulphates,  $37.2 \text{ mg}\cdot\text{dm}^{-3}$  for nitrates, and  $2.5 \text{ mg}\cdot\text{dm}^{-3}$  for chlorides. These figures exceed even a dozen times the mean concentration observed in this area. High levels of sulphates were also recorded in the next years:  $40.1 \text{ mg}\cdot\text{dm}^{-3}$  in 2004,  $20.5 \text{ mg}\cdot\text{dm}^{-3}$  in 2005,  $19.8 \text{ mg}\cdot\text{dm}^{-3}$  in 2006 and  $13.6 \text{ mg}\cdot\text{dm}^{-3}$  in 2007. Still, a strong downward tendency in such extremely high concentrations is readily visible.

An annual bulk deposition of fluoride ions is presented in Fig. 7. They are especially dangerous on account of their specific character. The deposition related to rainfall collected in the open area has stabilised over the last few years. However, owing to the high reactivity of these ions, it is crucial to analyse their concentration in each rainfall event.

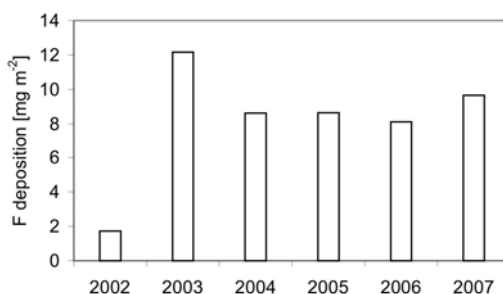


Fig. 7. Deposition ( $\text{mg}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ ) of fluoride ions (bulk), 2002–2007

To illustrate mutual relationships between the concentrations of fluorides in open-terrain precipitation and in throughfall, the pattern of their variability in 2007 is presented in Fig. 8. The diagramme shows that the fluoride levels under trees were from several to more than ten times higher. This indicates significant fallout of fluorides in the form of dust. The annual deposition of fluorides under trees in 2007 was  $18 \text{ mg}\cdot\text{m}^{-2}$ , twice that in the open area. The diagramme reveals also periodicity in the occurrence of fluoride pollution – a decreased concentration in the summer season. This regularity also holds for the throughfall.

The totals of acid-forming substances falling on the Wielkopolski National Park in the recent years were:  $70 \text{ meq}\cdot\text{m}^{-2}$  in 2002,  $58 \text{ meq}\cdot\text{m}^{-2}$  in 2003, the same in 2004, 2005 and 2006, and  $61 \text{ meq}\cdot\text{m}^{-2}$  in 2007. The predominant ions were sulphates, which accounted for 63% in 2002, while nitrate ions contributed in 22% and chloride ions – in 15%. In the subsequent years the percentages of sulphates decreased while those of nitrates increased to 25% and chlorides to 20%. The deposition of cations (Ca, Mg, Na, K) showed stabilisation over the recent years and remained at  $40 \text{ meq}\cdot\text{m}^{-2}$ . The predominant ion was calcium (56%), while magnesium contributed in 12%, potassium in 16%, and sodium in 16% to the total deposition. The amounts of  $\text{N-NH}_4^+$  in the precipitation amounted on average to

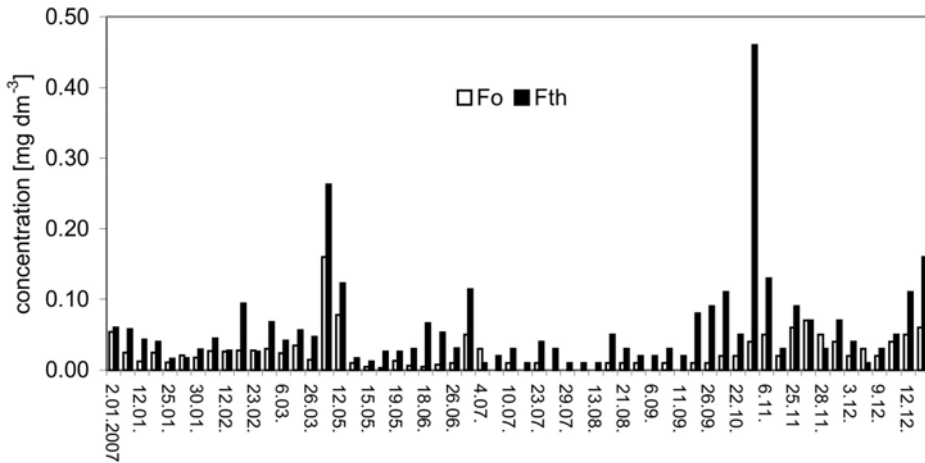


Fig. 8. Concentration of fluoride ions in open-terrain precipitation (Fo) and in throughfall (Fth), 2007

$399 \text{ mg} \cdot \text{m}^{-2} \cdot \text{year}^{-1}$  in the years 2002–2006. It was similar to the country mean ( $427 \text{ mg} \cdot \text{m}^{-2} \cdot \text{year}^{-1}$ ) but higher than at the station abroad (WALNA and KURZYCA, 2007).

## COMPARISONS

Observations and results of research on precipitation are often compared to obtain information about the level of environmental pollution or tendencies of change. However, results should be compared with caution (KURZYCA *et al.*, 2008). The reasons are as follows. Most significant differences between the results were observed when precipitation samples were obtained in different collecting procedures, both in terms of the mode and frequency of sampling. The differences in the concentrations of particular ions between the corresponding wet-only and bulk precipitation samples could reach 100%. On the other hand, equalisation of samples and results led to differences in the results reaching 20%. Significant differences were also observed among samples undergoing different procedures imposed by the method and time of storage prior to physico-chemical analysis. The type of sample vessel did not affect obtained result, but the type of sampler was important (even the collecting surface was observed to have an influence). The concentrations of analytes in a sample were also found to be changing during the storage time, with pH changing by even 1.6 units, which corresponded to more than a 15-fold difference in the concentration of  $\text{H}^+$ .

To avoid the above-mentioned mistakes, annual observations were made based on identical method of precipitation collection and analysis. The research was carried out in the Wielkopolski National Park and in the centre of Poznań city, 25 km north-west of the Park. Obtained results were compared and their annual

patterns turned out to be highly similar. The similarity concerned all the analysed ions. Concentrations were usually lower in the Park while extreme figures were recorded on the same day, sometimes with a one-day shift (Figs 9, 10). Such observations show that the main impact on the composition of precipitation in the Wielkopolski National Park was not only the large industrial emitters in Luboń, but also some sources in the city and farther away from the Poznań metropolitan area (WALNA *et al.*, 2004).

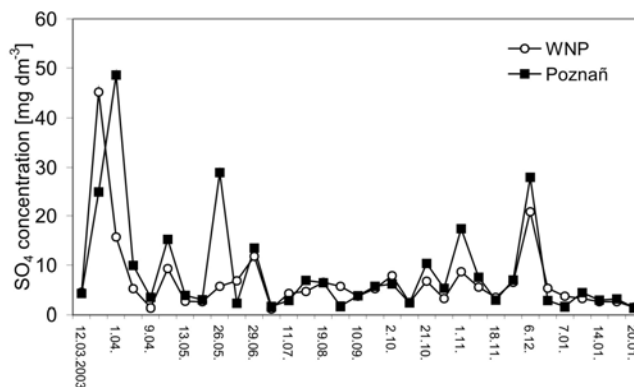


Fig. 9. Comparison of sulphate concentrations in precipitation collected at the Ecological Station (Wielkopolski National Park) and in the Poznań city centre (2003)

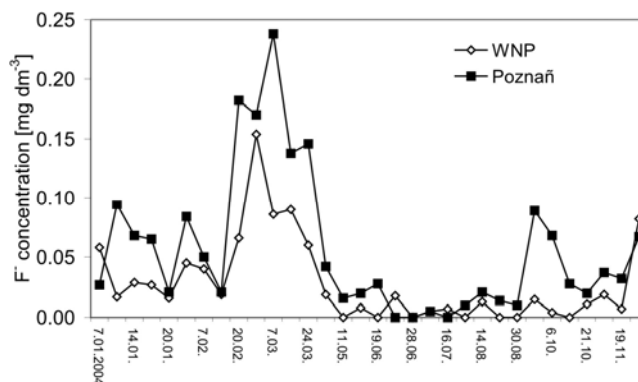


Fig. 10. Comparison of fluoride concentrations in precipitation collected at the Ecological Station (Wielkopolski National Park) and in the Poznań city centre (2004)

A comparison of the quantities of acid-forming substances deposited together with precipitation at different monitoring stations, including those from the EMEP programme, may be burdened with the errors mentioned earlier. However, such a comparison offers an insight into how the proximity of the sea (PL0004 – Łeba)

can change the composition of the deposited substances resulting from the elevated levels of chloride ions, or how the location in the mountains (PL0003 – Śnieżka, SK0002 – Chopok) boosts the deposition of all the components because rainfall there is twice as intensive as in the lowlands (Fig. 11). Detailed information on the location of the stations can be found in other publications and EMEP materials (MSC-W Report 2005; WALNA and KURZYCA, 2007). The results obtained in the Wielkopolski National Park exceed the figures in the corresponding lowland stations probably because of closer proximity to pollution sources. Also interesting is a comparison of the mean annual pH values at the selected stations shown in Fig. 12. Here, too, the impact of employed methodology on obtained results should be considered. The pH figure for the Station in the Wielkopolski National Park is the lowest.

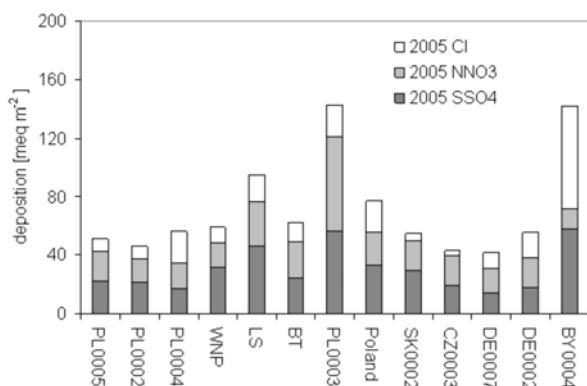


Fig. 11. Comparison of the deposition of acid-forming ions at Polish stations and neighbouring foreign stations in 2003: PL0005 – Jarczew, PL0002 – Diabla Góra, PL0004 – Łeba, WNP – Jeziory Ecological Station, LS – Lower Silesia, BT – 'Black Triangle', PL0003 – Śnieżka, SK – Chopok, CZ0003 – Košetice, DE0007 – Neuglobsow, DE0002 – Langenbrugge, BY0004 – Vysokoe; locations in the map – see WALNA and KURZYCA (2007)

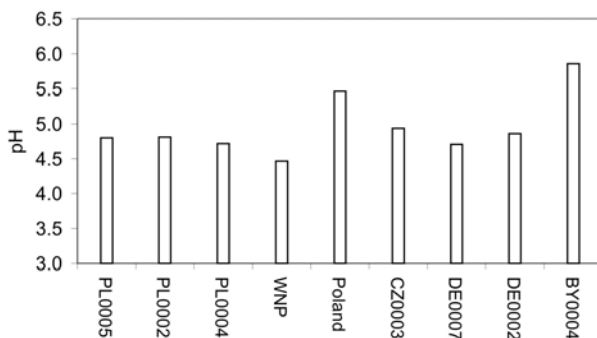


Fig. 12. Comparison of rainfall pH at various monitoring stations (2003) (descriptions as in Fig. 11) Locations in the map – see WALNA and KURZYCA (2007)

## SUMMARY

1. The quantitative observations of precipitation show major differences in the annual rainfall. In two years the rainfall was below 400 mm. However, mean annual precipitation in the study period (1992–2007) was similar to the multi-year average.

2. The most unfavourable period was 2003–2005 when the rainfall in the vegetation season was less than 300 mm.

3. The analysis of monthly rainfall sums indicates periods of several months with low precipitation and months when the precipitation was considerably higher than the average.

4. Episodes of quite intensive rainfalls were observed.

5. Precipitation both in the open area and under the trees had low mean annual pH, and the pH of individual events was often lower than 4.0. However, in the period under study, pH of open-terrain precipitation and throughfall tended to increase slightly.

6. Precipitation pollution expressed as the means of electric conductivity showed declining tendency. Still, there were rainfall episodes of extremely high pollution. An exceptional accumulation of dust pollution was observed in the throughfall.

7. Several years long study revealed higher deposition of acid-forming compounds in the Park than in the lowland monitoring stations. Their structure in the Wielkopolski National Park changes – the deposition of sulphates decreases and the deposition of nitrates increases. The reason is a lower emission of SO<sub>2</sub> in the Wielkopolska region and an increasing emission of NO<sub>x</sub> caused by car traffic.

8. The presence of fluorides in precipitation, especially in throughfall, should be noted.

9. The Wielkopolski National Park is under unfavourable influence of air pollution intensified by periodic deficits of precipitation causing hard conditions for the forest vegetation.

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## STRESZCZENIE

### **Kierunki zmian składu chemicznego opadów atmosferycznych w Wielkopolskim Parku Narodowym**

Słowa kluczowe: *depozycja, opad podkoronowy, pH, zakwaszenie*

Przedstawiono wyniki badań chemicznych opadów atmosferycznych, opartych na wieloletnich obserwacjach (1992–2007), prowadzonych w Wielkopolskim Parku Narodowym (WPN) i porównano z rezultatami badań monitoringowych stacji, będących w europejskiej sieci EMEP. Stwierdzono, że w tym czasie pH opadów ulegało systematycznemu podwyższeniu powodując obniżenie rocznej depozycji jonów  $[H^+]$ . Linie trendu zmian depozycji jonów wodorowych charakteryzują się zbliżonym współczynnikiem nachylenia, co wskazuje na podobne tempo zmian. Rokiem o najniższym pH był 1994 r., w którym średnie roczne pH osiągnęło wartość 3,92. Natomiast rokiem o najmniejszym zakwaszeniu okazał się 2006 r. – pH



4,80. Depozycja jonów wodorowych we wszystkich stacjach monitoringu EMEP w Polsce często przekraczała wartość  $20 \text{ mg}\cdot\text{m}^{-2}\cdot\text{rok}^{-1}$ , a w WPN osiągnęła w 1994 r. wartość  $70 \text{ mg}\cdot\text{m}^{-2}$ .

Przeanalizowano depozycję jonów kwasotwórczych. Wśród nich dominowała depozycja jonów siarczanowych, wykazując wartości malejące w kolejnych latach. Wartości maksymalne wyniosły –  $707 \text{ mg S}\cdot\text{m}^{-2}$  (2002) i  $260 \text{ mg N-NO}_3\cdot\text{m}^{-2}$  (2007). Stwierdzono wzrastający współczynnik  $\text{NO}_3/\text{SO}_4 \text{ eq/eq}$ , wskazujący na zmiany w strukturze składu anionów. Wśród deponowanych kationów alkalicznych najwyższe wartości przyjmuje wapń stanowiąc ponad 50%. Stacje nizinne EMEP charakteryzują się wartościami depozycji potasu i wapnia kilkukrotnie niższymi niż uzyskane w WPN oraz niższymi niż średnie dla Polski. W ostatnich latach obserwuje się stabilizację ilości deponowanych kationów.

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