

## Chemometric analysis of rainwater and throughfall at several sites in Poland

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### Abstract

Precipitation and throughfall samples were collected over a period of 4 years (1 January 1996–31 December 1999) at three different sites in Poland: one on moraine hills, one in the lowlands and one in a mountainous region. The aim of this project was to study the chemical composition of the samples, ionic correlations and fluctuations of selected variables with time in relation to geographical location, type of tree cover and climatic conditions. The samples were characterized by determining the values of pH, electrolytic conductivity and concentrations levels of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$  and  $\text{Mg}^{2+}$ . Statistical analysis revealed significant differences between the results obtained for different sampling site locations and characteristics (region of Poland, open area vs. throughfall) in four cases. The results obtained for precipitation samples were similar to those for throughfall samples only for acidic anions ( $\text{SO}_4^{2-}$  and  $\text{Cl}^-$ ). For open areas, pH fluctuations were observed in 12-month cycles. Differences between the concentration levels of ions in the samples from the three sites could be explained by different amounts of precipitation at these sites. Concentrations of ions in precipitation and throughfall samples followed similar trends, the concentration levels being dependent on the kind of trees in the area, their age, and acidity of the precipitation. Significant differences were found for the concentration factors of the individual ions in throughfall between the sampling sites. Ionic correlations were examined to determine which salts contributed to the observed ion levels.

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### 1. Introduction

Atmospheric precipitation is one of the major factors shaping the living conditions in a given area (Petty and

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Lindberg, 1990; Nikilińska et al., 1995). In Poland, the amount of precipitation increases with increasing elevation above sea level. The amount of precipitation is the greatest in the mountains (more than 1000 mm year<sup>-1</sup>) and in the highlands (more than 600 mm year<sup>-1</sup>). In the lowlands, the amount of precipitation is significantly lower and varies between 450 and 550 mm year<sup>-1</sup>. Total annual precipitation fluctuates significantly from year to year (up to 259% in a given month). Considering the mean annual amount of precipitation, the climate in Poland can be classified as moderately humid. However, only about 68% of the area of Poland has such climate. About 16% of the country has moderately dry climate, while the remaining 16% receives more than 700 mm of precipitation per year.

In Poland, nitrogen oxides and sulfur emissions to the atmosphere are mainly related to automotive transport (50%), followed by power generation (35%), industry (10%) and households (10%). The pollutants may be deposited at various distances from emission sources. Transboundary pollutant transport (as far as 500 km) endangers many ecosystems. Acid rains (Małek, 2001; Walna and Siepak, 1999; Polkowska et al., 1999) cause dying off of forests and destruction of ground cover, acidification of surface waters and soil, and deterioration of building materials (Walna et al., 1998, 2000, 2000a, 2001; Siepak et al., 1999). Monitoring of forest health in Poland indicates a small improvement in the recent years (defoliation factor reduced from 2.77 in 1998 to 2.70 in 1999). However, taking into account the overall percentage of forests with no defoliation (10.4%), Poland places near the bottom on the list of European countries. The share of healthy trees (spruce, fir) continuously decreases; at the same time, pine shoot necrosis and pathogenic fungi are on the rise (Małek, 2001; Walna et al., 2001; Walna and Siepak, 1999; Polkowska et al., 1999; Schulze, 1989; Bredmeier et al., 1995; Zwoździak et al., 1995).

Composition of atmospheric precipitation is determined mostly by the condition of the atmosphere, i.e. the kind and amount of natural and anthropogenic pollutants. Chemical composition of precipitation depends also on its amount and type (rain, snow, hail or fog), wind direction and cloud ceiling. Precipitation transfers pollutants from the atmosphere to water reservoirs and soil. Major pollutants transported in this way include sulfur, nitrogen and carbon compounds, as well as soot and other particulate matter. In industrialized regions, additional pollutants may be involved, including gaseous manufacturing by-products, products of incomplete combustion of coal and other fossil fuels, as well as typical industrial emissions (CO<sub>2</sub>, NH<sub>3</sub>, H<sub>2</sub>S, nitrogen and sulfur oxides, heavy metals, metal oxides). Chemicals dissolved in precipitation are quickly incorporated in the elemental cycles and may cause permanent changes in processes occurring in geosystems

(Schulze, 1989; Bredmeier et al., 1995; Zwoździak et al., 1995). In forest ecosystems, part of atmospheric precipitation does not reach the forest floor directly; it has to penetrate the canopy first. In the process, it undergoes both physical and chemical transformations. Chemical composition of throughfall differs from that of the incidental precipitation because of canopy exchange, as well as dissolution and washing off of aerosols and gaseous pollutants sorbed on the surfaces of leaves, branches and bark. The physicochemical properties of the throughfall are affected by many factors, including the species, age and health of the trees. The contribution of throughfall to the total amount of material deposited on the ground in forests is usually <10%. It was found that in a pine forest, stemflow constituted only about 3% of the total precipitation reaching the ground; on the other hand, throughfall accounted for 83% of the total precipitation. Thus, determination of the chemical composition of throughfall is important when estimating the total deposition onto the forest floor (Chiwa et al., 2003).

Atmospheric pollution may affect the health of forest ecosystems either directly (through contact with plant surfaces resulting in injury to leaves or adversely affecting the physiological functions of the plant), or indirectly (through soil and roots). Indirect effects may persist for dozens of years. Coniferous trees (e.g. spruce) are typically more sensitive to atmospheric pollution than deciduous trees. This is related to the fact that they do not shed the needles, therefore are affected by pollution all year round. In addition, they are exposed to elevated levels of air pollutants generated by the energy sector in winter (SO<sub>2</sub>, NO<sub>x</sub>, particulate matter) when deciduous trees are in dormant state, therefore remain relatively unaffected. As a result, many deciduous trees (e.g. oak, beech) are resistant to air pollution.

The paper presents the results of analysis of precipitation and throughfall samples collected from different tree species (spruce, oak, beech) at three sites located in different parts of Poland: one on moraine hills (Stara Piła forest district—Rumia), another in the lowlands (Wielkopolski National Park—Jeziory) and the last one in a mountainous region (Ojcowski National Park—Ojców). The different forest types at these locations (coniferous, deciduous and/or mixed to a varying extent; old and young trees) are representative of the forests in Poland. The aim of the study was to compare the characteristics of precipitation collected at different sites located throughout Poland, and to identify the similarities and differences between incident precipitation and throughfall. The chemical composition of the samples, ionic correlations and fluctuations of selected variables with time were studied in relation to geographical location, type of tree cover and climatic conditions. The most important factor influencing the possible differences was that two sites were located in

ecologically protected areas (Wielkopolski National Park and Ojcowski National Park), while the third site was located in an unprotected area (Stara Piła forest district). From this point of view, the sites could be classified as ecologically clean or industrially active.

## 2. Experimental

### 2.1. Sampling sites

The study was carried out over a period of 4 years (1996–1999) at three sampling sites located in different parts of Poland. The three locations were characterized by different climates, altitudes, geological structure and plant cover, as well as different pollution sources. Locations of the sampling sites and their more detailed characteristics are described in Table 1 and presented in Fig. 1. The precipitation sampling gauges were located in unobstructed areas, far from tall structures whenever possible. For throughfall samples, the sampling gauges were also located in unobstructed areas, under solitary trees if possible. Once a sampler was set up, it remained at the sampling location for a period of 1 month at a time.

### 2.2. Laboratory analysis

While mostly wet precipitation was collected, the contribution of dry precipitation should not be ignored. A similar approach was used in papers published before (e.g. Reimann et al, 1997; Buijsman et al., 1991; Hansen and Nielsen, 1998). Bulk precipitation was collected continuously over a period of 1 month, transported to the laboratory within the first 3 days of the following month, and analyzed in the laboratory in monthly cycles over a period of 48 months (January 1996–December 1999). It is important to note that no samples were collected in Ojców in 1996. Precipitation samples were transported to the laboratory, where they were analyzed within 96 h of collection (Kot-Wasik et al., 2001). Instrumentation used for the measurements, listed in Table 2, was selected to assure reliable and reproducible results. A detailed description of the experimental methods, their calibration and validation based on a certified reference material (Major Elements in Rain Water No. 409, Commission of the European Communities, Community Bureau Of Reference—BCR) can be found in the following references: Małek (2001), Walna and Siepak (1999), Polkowska et al. (1999), Walna et al. (2000a), Polkowska et al. (2002), Walna et al. (2003).

It was decided to limit the number of chemical components analyzed due to sensitivity of some of them to varying climatic conditions within the collection period. For example, temperature can affect ammonia and  $\text{HCO}_3^-$  concentrations in a sample, which was the

major reason why it was impossible to derive the concentrations of selected chemical components via the condition of electron neutrality. In the case of samples taken in Rumia (Stara Piła forest district), electrical conductivity was not measured during the period from 1997 to 1999. QA/QC was carried out by analysing field samples fortified with analytes of interest. In general, the determined concentrations fell within 10% of the true value, which was considered satisfactory (Polkowska et al., 2002), with the exception of spectrophotometric measurements, in which this value increased to 20%.

### 2.3. Chemometric evaluation

The average values from 12 monthly measurements of each variable, considered to be mean annual values, were subjected to chemometric evaluation. Chemometric analysis techniques typically used in processing of environmental data (Time series (TS) analysis, analysis of variance—ANOVA) were used in the project (Polkowska et al., 2002; Astel et al., 2001, 2001a).

Analysis of variance is a method, which separates individual contributions to the overall variation in a set of experimental data and tests their significance. The sources of variation (one of which is invariably the random measurement error) are each characterized by the sum of squares (SS), i.e. the sum of a number of squared terms representing the variation in question; the number of degrees of freedom (DF), and the mean square, which is the former divided by the latter and can be used to test the significance of the variation contribution by means of the *F*-test. The mean square and the number of degrees of freedom for the overall variation are, respectively, the sums of the mean squares and degrees of freedom of the several contributing sources of variation (Miller, 1991).

TS are sequences of interdependent random variables (observations) describing a phenomenon at successive points in time. The purpose of TS analysis is:

- to perform statistical analysis of the relations between successive observations;
- to predict (forecast) future values of the TS;
- to detect the mechanisms that govern the changes in the observed phenomenon in time; in other words, to determine the nature of the phenomenon represented by the sequence of observations.

In this research, we concentrated on finding periodical relations in the distribution of variables. The tool most commonly used for this purpose is Fourier analysis, which examines the harmonic structure of the TS. The purpose of the analysis is to break down a TS containing periodical components into a number of basic functions (sine and cosine). This kind of analysis allows the

Table 1  
Detailed characteristics of the sampling sites (Polkowska et al., 1999; Walna et al, 2003, 2000a; Walna and Siepak, 1999)

Site no.	Sampling site location	Geographic coordinates	Elevation (m a.s.l.)	Prevailing forest type	Site description	Sampling	Potential pollution sources
No. 1	Stara Piła—Rumia	N 54°34'E 18°21'	122	Spruce	The sampling site consisted of two sub-stations located within the Stara Piła forest district in Rumia, 10 km west of a large urban agglomeration (Gdynia, Sopot, Gdańsk). One sub-station was located in a forest clearing, the other inside the forest.	Precipitation gauges in the forest sub-station were placed within a 30 m square. They consisted of 2 or 51 polyethylene bottles wrapped in aluminum foil and equipped with funnels of 15.5 or 20.3 cm diameter. To prevent large solid particles from entering the gauges in the forest substation, a smaller funnel covered with polyethylene screen (mesh size 2 × 2 mm in summer and 4 × 4 mm in winter) was placed inside each bigger funnel. During the periods of heavy snowfall, the bottle—funnel assemblies were replaced with 51 polyethylene buckets, 21 cm in diameter. The gauges were placed on stands at various distances from the ground: 0.5 m (forest site), 0.65 m (forest site in winter) or 1.5 m (forest clearing)	<ul style="list-style-type: none"> <li>● urban agglomeration including Rumia, Gdynia, Sopot and Gdańsk</li> <li>● transportation routes (railway, highways)</li> <li>● industry, including oil refinery, fertilizer plant and fish processing plants</li> <li>● shipyards and shipping industry (e.g. sulphur)</li> </ul>
No. 2	Jeziory	N 52° 11'E 16° 54'	82	Oak	Sampling sites were located within the Ecological Station Jeziory and in the nearby forest, 15 km south of a large urban agglomeration (Poznań); within the Wielkopolski National Park	Incident precipitation and throughfall were collected using plastic funnels of 56 cm diameter and 47 cm height. Tall sidewalls (24 cm) prevented precipitation from sputtering; small diameter funnel outlet (1.5 cm) was tightly fitted into polyethylene bottles collecting the samples. The gauges were located on steel stands, 1.5 m from the ground.	<ul style="list-style-type: none"> <li>● urbanization of the regions adjacent to the park</li> <li>● transportation routes around and inside the park</li> <li>● industry, including potato processing plant and phosphorus fertilizer plant</li> </ul>

No. 3	Ojców	N 50° 12'E 19°49'	430	Beech	<p>Sampling sites in the Ojcowski National Park were located in a nature reserve, on a permanent experimental ground on the northern side of Chełmowska Góra (470.6 m above sea level) sloping to Sąspowska Valley. The area of the site is variegated, with elevation differences reaching 145.1 m. It is located 30 km north of two large urban agglomerations (Kraków and Katowice), 20 km from the city of Olkusz.</p>	<p>The large surface area of the gauge (2500 cm<sup>2</sup>) made it possible to analyze precipitation even when its amount was very small (&lt; 1 mm). The sampling ground was divided into 450 20-m<sup>2</sup>. Sixteen precipitation gauges were located at each sampling location. The gauges were made of dederon, which is permeable to precipitation and dries quickly. The surface area of the gauge was 1697 cm<sup>2</sup>. Incident precipitation was collected in a clearing using four opaque plastic gauges placed 1.2 m above ground. The gauges were located at a distance of 120–150 m from the centre of the permanent experimental ground, 40 m from the tree line. Snow samples were collected using 8 plastic containers with 130 cm<sup>2</sup> openings, distributed evenly over each of the three sampling sites.</p>	<ul style="list-style-type: none"> <li>● Olkusz–Bukowna industrialized area</li> <li>● mining of zinc and lead ores</li> <li>● urban agglomeration including Olkusz, Katowice and Kraków</li> <li>● low emissions originating from the village of Ojców and the city of Skąła</li> <li>● burning of coal and other materials for household heating in winter</li> </ul>
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detection of cycles of various lengths in the TS, which initially appear to be random noise. Specific procedures for the introduction of mathematical formulae describing Fourier analysis can be found in the literature on statistics and data analysis (e.g. Ott, 1984; Johnson, 1984). In this study, a commercial statistics software package, Statistica 5.0 for Windows (StatSoft Inc., Tulsa, USA), was applied for chemometric data mining.

### 3. Results and discussion

Measurements within the project were carried out at three forest sites in Poland: Rumia (Stara Piła forest district), Jeziory (Wielkopolski National Park) and Ojców (Ojcowski National Park). In total, 264 samples were analyzed, and over 2300 individual measurement results were obtained. The results are summarized in Table 3.



Fig. 1. Locations of the sampling sites.

#### 3.1. Ionic composition

Mean annual pH of the precipitation at all three sites was nearly always lower than 5, often reaching values lower than 4.6 (classified as very acidic). The highest pH values were recorded at the Stara Piła site. They ranged from 4.46 (1998) to 5.15 (1996). At the Jeziory and Ojców sites, the precipitation was significantly more acidic, the pH values ranging from 3.90 (1996, Ojców) to 4.51 (1999, Jeziory). At both sites (Ojców in particular), the low pH of the precipitation was most likely related to industrial emissions from large industrial regions nearby and/or to long-range transboundary pollutant transport aided by the prevailing wind direction. The pH of the throughfall depended on the type of tree cover. At the Stara Piła site, pH of the throughfall collected under spruce trees was significantly lower (as much as by 1 unit) than pH of incident precipitation. On the other hand, the pH values of precipitation and throughfall collected under oak trees in Jeziory and beech trees in Ojców either did not differ significantly, or were slightly higher for throughfall. In general, throughfall pH tended to increase over the period examined at all three sites.

Both the pH and the conductivity of throughfall and stemfall may be affected by a number of factors, including forest type (coniferous vs. deciduous), canopy density, tree age, amount of precipitation and/or wind direction. Higher pH values of throughfall from deciduous trees compared to incident precipitation were observed before at the Jeziory station (Walna and Siepak, 1999). On the other hand, stemfall pH of 3.6 was found for a pine forest at a different location. The pH of throughfall from a mixed fir-beech tree forest (Św. Krzyż site, Poland) ranged from 4.38 to 4.77, while mean monthly pH of stemfall was 3.44 and 3.47 for fir and beech trees, respectively. Stemfall from a mixed

Table 2  
Analytical techniques and instrumentation used in the study

Analyte or physico-chemical parameter	Technique	Instrument
pH	Potentiometry	<ul style="list-style-type: none"> <li>● Field pH-meter with combination electrode (Orion, Poland)</li> <li>● Microprocessor-controlled CX 315 pH-meter (calibrated using "pure water" buffer set for pH determination in low ionic strength solutions) (Poland)</li> </ul>
Electrolytic conductivity	Conductometry	<ul style="list-style-type: none"> <li>● CC 311 conductometer (Elmetron, Poland)</li> <li>● OK—102/1 conductometer (Radelkis, Hungary)</li> </ul>
Na <sup>+</sup> , K <sup>+</sup> Ca <sup>2+</sup> , Mg <sup>2+</sup>	Flame photometry Atomic absorption spectroscopy	<ul style="list-style-type: none"> <li>● FLAPHO 4 spectrophotometer (Carl Zeiss Jena, Germany)</li> <li>● BUCK Scientific Model 210 VGP (USA)</li> <li>● Varian model 20 (USA)</li> </ul>
SO <sub>4</sub> <sup>2-</sup> , Cl <sup>-</sup> , NO <sub>3</sub> <sup>-</sup>	Ion chromatography	<ul style="list-style-type: none"> <li>● Dionex model 320 (USA)</li> <li>● Dionex model 500 (USA)</li> <li>● Dionex model 100 (USA)</li> </ul>

Table 3  
Mean annual concentrations of ions in precipitation samples collected between 1 January 1996, and 31 December 1999 ( $\text{mg l}^{-1}$ )

Site	Sample type	Year	pH	Electric conductivity ( $\mu\text{S}$ )	$V$ (mm)	$\text{SO}_4^{2-}$ ( $\text{mg l}^{-1}$ )	$\text{NO}_3^-$ ( $\text{mg l}^{-1}$ )	$\text{Cl}^-$ ( $\text{mg l}^{-1}$ )	$\text{Ca}^{2+}$ ( $\text{mg l}^{-1}$ )	$\text{K}^+$ ( $\text{mg l}^{-1}$ )	$\text{Na}^+$ ( $\text{mg l}^{-1}$ )	$\text{Mg}^{2+}$ ( $\text{mg l}^{-1}$ )
<i>Rumia-Stara Piła forest district</i>												
	P	1996	5.61	21.17	716	4.84	10.18	1.50	2.88	0.44	0.42	0.20
		1997	4.97	—	838	7.81	2.96	1.58	2.55	0.34	0.48	0.24
		1998	4.75	—	914	1.99	1.73	1.18	2.14	0.30	0.39	0.18
		1999	5.22	—	870	1.49	3.28	1.38	2.32	0.37	0.45	0.21
	T	1996	4.23	49.08	429	18.78	20.32	5.47	4.10	3.04	1.30	0.70
		1997	4.64	—	419	24.12	14.05	8.95	3.54	3.11	1.37	0.85
		1998	4.67	—	523	15.11	6.57	6.23	3.01	2.95	1.19	0.60
		1999	5.02	—	529	11.32	7.98	5.83	2.98	2.93	1.21	0.58
<i>Jeziory-Wielkopolski National Park</i>												
	P	1996	4.14	56.33	576	6.10	1.60	3.10	1.98	0.29	0.55	0.24
		1997	4.49	61.98	513	6.40	0.64	3.40	1.23	0.30	0.66	0.24
		1998	4.57	41.22	591	4.60	0.58	2.00	1.38	0.67	1.14	0.38
		1999	4.56	42.18	495	5.00	0.60	5.00	1.07	1.90	0.40	0.22
	T	1996	4.33	128.22	—	6.70	4.60	3.50	3.60	0.60	2.00	1.50
		1997	4.70	130.47	—	14.90	1.10	3.97	2.50	2.20	2.31	1.42
		1998	4.74	77.59	—	16.00	0.82	2.15	2.90	3.40	2.15	1.70
		1999	5.20	88.37	—	6.00	0.80	6.00	1.30	3.50	1.50	1.22
<i>Ojców-Ojcowski National Park</i>												
	P	1996	—	—	—	—	—	—	—	—	—	—
		1997	4.56	43.33	643	4.46	1.83	0.84	0.83	1.13	0.19	0.13
		1998	4.28	59.25	545	4.23	0.98	0.86	1.43	0.99	0.25	0.32
		1999	4.76	52.54	379	4.04	3.16	0.33	1.59	2.68	0.57	0.24
	T	1996	—	—	—	—	—	—	—	—	—	—
		1997	5.08	56.68	435	10.06	5.34	3.03	3.26	2.77	0.35	0.60
		1998	4.39	59.25	393	6.50	3.79	1.11	3.62	2.37	0.03	0.49
		1999	4.93	84.71	379	10.66	16.14	3.19	5.03	6.87	0.80	0.91

P—precipitation, T—throughfall.

pine-spruce forest in Wigry (Poland) was also highly acidic (pH of 3.71 and 3.39 for pine and spruce, respectively). The lower pH of stemfall was most likely related to the long contact time between water and the rough tree bark characterized by highly developed surface, which facilitated the dissolution of organic acids and acidic aerosols from dry precipitation.

Other factors also affect throughfall and stemfall pH. As the age of a tree increases, its capacity to neutralize precipitation decreases. The neutralizing capacity of coniferous forests is generally lower compared to deciduous forests, since the former usually grow on acidic soils (Mazurek and Zwoliński, 2000). In a study by Zimka and Stachurski (1996), the biggest pH changes in throughfall were observed in mature spruce forests (roughly 3-fold increase in the load of  $H^+$  ions, resulting in lowering of pH to 3.7). In a young spruce forest, the changes were less significant, and they were practically non-existent in a beech forest (ibid). In a Norwegian study of different types of forests, throughfall pH was found to be 6.0 for birch and alder, 5.8 for willow and 5.5 for spruce (Hongve et al., 2000).

Acid rains adversely affect both above- and underground parts of trees. They may wash out significant amounts of Ca, Mg and K compounds from needles, leaves and/or tree bark, resulting in a deficit of these nutrients. For example, in the case of fir tree needles, the deficit of basic cations leads to the formation of free organic and mineral acids, which may disturb photosynthetic processes and cause damage to cell walls.

Conductivities of the samples collected between 1996 and 1999 at the Jeziory and Ojców sites fell within the range 41–130  $\mu S cm^{-1}$ , which puts them in the elevated-to high-conductivity category. Precipitation collected in Stara Piła in 1996 had much lower conductivity—21  $\mu S cm^{-1}$ , falling within the slightly elevated category. In the case of throughfall, the result was 62  $\mu S cm^{-1}$ . In general, the electric conductivity of the throughfall was approximately 30–50  $\mu S cm^{-1}$  higher than that of the precipitation samples.

The concentration of sulfate ions in the precipitation and throughfall decreased markedly over the period of the study at all three sites (by as much 74% at the Stara Piła site and 22% at the Jeziory site). At the Stara Piła site, acidity was mainly related to both sulfate and nitrate ions. This was not the case at the Jeziory site, where sulfate ions prevailed. At the Ojców site, the sulfate:nitrate ratio (in  $meq l^{-1}$ ) was 3:1. The highest concentrations of chloride ions were recorded at the Jeziory site, while the lowest at the Ojców site.

Chemical composition of the throughfall was significantly modified compared to the precipitation, both in terms of pH and the ionic composition. The largest concentration increase was observed for  $SO_4^{2-}$ ,  $Cl^-$  and  $K^+$  at the Stara Piła site;  $NO_3^-$  at the Ojców site; and  $Mg^{2+}$  at the Jeziory site.

### 3.2. Ionic correlations

Correlation coefficients between the different components of precipitation and throughfall were calculated for all events. The results, in the form of correlation matrices for ion pairs, are presented in Table 4.

Most of the correlation coefficients for samples collected in open areas were greater than 0.5. Very strong correlations between ions in precipitation (correlation coefficients greater than 0.95) were found in 4 cases for the Stara Piła site, 3 cases for the Jeziory site and 9 cases for the Ojców site. In throughfall, correlation coefficients for ion pairs were also greater than 0.5 in most cases. Very strong correlations were found in 7 cases for the Stara Piła site, 13 cases for the Ojców site, and only 2 cases for the Jeziory site.

Overall, the large number of correlated ion pairs points to co-occurrence of certain pollutants at all forest sites examined within this study. Nitrate, sulfate and chloride ions were correlated most probably because their precursors,  $SO_2$ ,  $NO_x$  and  $Cl_2$ , are often co-emitted (especially during combustion of fossil fuels), and because they behave similarly in precipitation. In the case of precipitation, the  $SO_4^{2-}$ – $NO_3^-$ – $Cl^-$  correlation was the strongest for samples collected at the Ojców site. For throughfall samples, this correlation was observed at all three sites.

In the case of the cations,  $Ca^{2+}$ ,  $Mg^{2+}$  and  $K^+$  may have been correlated because they occur in similar salts in soil, water, etc. (Saxena et al., 1996; Tanner, 1999; Jacob et al., 1985; Asman et al., 1981). For incident precipitation, only  $Ca^{2+}$  and  $K^+$  ions were correlated at all sites. On the other hand, all possible correlations between  $Ca^{2+}$ ,  $Na^+$ ,  $Mg^{2+}$  and  $K^+$  ions were observed for throughfall at the Stara Piła and Ojców sites.

In incident precipitation samples from all sites, the strongest correlations were observed between  $SO_4^{2-}$  anions and  $Mg^{2+}$  cations, as well as  $Cl^-$  anions and  $Na^+/K^+$  cations. The same was true for throughfall samples, but additional correlations occurred between  $SO_4^{2-}$  anions and  $Na^+$  cations, as well as  $NO_3^-$  anions and  $Ca^{2+}/K^+$  cations. The correlations between  $Ca^{2+}$ ,  $Na^+$ ,  $Mg^{2+}$  cations and  $Cl^-$  anions;  $Ca^{2+}$ ,  $Na^+$ ,  $Mg^{2+}$ ,  $K^+$  cations and  $NO_3^-$  anions; as well as  $Ca^{2+}$ ,  $Na^+$ ,  $Mg^{2+}$ ,  $K^+$  cations and  $SO_4^{2-}$  anions; were most likely related to reactions of atmospheric acids ( $H_2SO_4$ ,  $HNO_3$  and  $HCl$ ) with alkaline species present in the atmosphere. Similar data can be found in the literature (Saxena et al., 1996; Ruijgrok and Romer, 1993; Lin et al., 1999). Strong positive correlation between  $Na^+$  and  $Cl^-$  in both bulk deposition and throughfall was found in Denmark (oak wood), 75 km from the North Sea. The authors suggested that the correlation was the strongest at the coastal heath showing the dominance of sea salts in atmospheric deposition (Hansen and Nielsen, 1998).

Table 4  
Ion pair correlations (white background represents precipitation, bold represents throughfall)

	pH	<i>V</i> (mm)	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	Ca <sup>2+</sup>	K <sup>+</sup>	Na <sup>+</sup>	Mg <sup>2+</sup>	
<i>Rumia–Stara Piła forest district</i>										
pH	1.00	<b>0.71</b>	<b>-0.56</b>	<b>-0.84</b>	<b>0.10</b>	<b>-0.89</b>	<b>-0.55</b>	<b>-0.46</b>	<b>-0.41</b>	
<i>V</i> (mm)	-0.90	1.00	<b>-0.91</b>	<b>-0.87</b>	<b>-0.49</b>	<b>-0.87</b>	<b>-0.96</b>	<b>-0.95</b>	<b>-0.90</b>	
SO <sub>4</sub> <sup>2-</sup>	0.10	-0.45	1.00	<b>0.60</b>	<b>0.76</b>	<b>0.62</b>	<b>0.98</b>	<b>0.92</b>	<b>0.97</b>	
NO <sub>3</sub> <sup>-</sup>	0.93	-0.97	0.23	1.00	<b>0.02</b>	<b>0.99</b>	<b>0.70</b>	<b>0.72</b>	<b>0.58</b>	
Cl <sup>-</sup>	0.52	-0.66	0.83	0.46	1.00	<b>0.00</b>	<b>0.72</b>	<b>0.70</b>	<b>0.82</b>	
Ca <sup>2+</sup>	0.84	-0.98	0.60	0.90	0.79	1.00	<b>0.70</b>	<b>0.69</b>	<b>0.57</b>	
K <sup>+</sup>	1.00	-0.93	0.17	0.94	0.56	0.87	1.00	<b>0.98</b>	<b>0.99</b>	
Na <sup>+</sup>	0.09	-0.11	0.62	-0.11	0.80	0.27	0.11	1.00	<b>0.97</b>	
Mg <sup>2+</sup>	0.07	-0.17	0.76	-0.07	0.85	0.34	0.10	0.98	1.00	
	pH	Electric conductivity	<i>V</i> (mm)	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	Ca <sup>2+</sup>	K <sup>+</sup>	Na <sup>+</sup>	Mg <sup>2+</sup>
<i>Jeziory-Wielkopolski National Park</i>										
pH	1.00	<b>-0.63</b>	—	<b>-0.12</b>	<b>-0.80</b>	<b>0.66</b>	<b>-0.97</b>	<b>0.87</b>	<b>-0.65</b>	<b>-0.59</b>
Electric conductivity	-0.54	1.00	—	<b>-0.13</b>	<b>0.60</b>	<b>0.04</b>	<b>0.44</b>	<b>-0.84</b>	<b>0.43</b>	<b>-0.17</b>
<i>V</i> (mm)	-0.38	-0.14	1.00	—	—	—	—	—	—	—
SO <sub>4</sub> <sup>2-</sup>	-0.59	0.99	-0.22	1.00	<b>-0.50</b>	<b>-0.68</b>	<b>0.22</b>	<b>0.30</b>	<b>0.80</b>	<b>0.66</b>
NO <sub>3</sub> <sup>-</sup>	-0.99	0.42	0.43	0.49	1.00	<b>-0.18</b>	<b>0.72</b>	<b>-0.93</b>	<b>0.07</b>	<b>0.13</b>
Cl <sup>-</sup>	0.13	-0.05	-0.88	0.09	-0.13	1.00	<b>-0.79</b>	<b>0.20</b>	<b>-0.77</b>	<b>-0.99</b>
Ca <sup>2+</sup>	-0.93	0.35	0.70	0.37	0.94	-0.46	1.00	<b>-0.74</b>	<b>0.65</b>	<b>0.75</b>
K <sup>+</sup>	0.52	-0.71	-0.57	-0.60	-0.46	0.74	-0.63	1.00	<b>-0.32</b>	<b>-0.11</b>
Na <sup>+</sup>	0.33	-0.29	0.71	-0.45	-0.31	-0.88	0.03	-0.40	1.00	<b>0.69</b>
Mg <sup>2+</sup>	0.35	-0.49	0.73	-0.62	-0.30	-0.82	0.02	-0.23	0.97	1.00
<i>Ojców-Ojcowski National Park</i>										
pH	1.00	<b>0.23</b>	<b>0.47</b>	<b>0.94</b>	<b>0.42</b>	<b>0.96</b>	<b>0.12</b>	<b>0.39</b>	<b>0.68</b>	<b>0.53</b>
Electric conductivity	-0.50	1.00	<b>-0.75</b>	<b>0.54</b>	<b>0.98</b>	<b>0.49</b>	<b>0.99</b>	<b>0.99</b>	<b>0.87</b>	<b>0.95</b>
<i>V</i> (mm)	-0.54	-0.45	1.00	<b>0.15</b>	<b>-0.61</b>	<b>0.21</b>	<b>-0.82</b>	<b>-0.63</b>	<b>-0.33</b>	<b>-0.50</b>
SO <sub>4</sub> <sup>2-</sup>	-0.36	-0.63	0.98	1.00	<b>0.70</b>	<b>1.00</b>	<b>0.44</b>	<b>0.67</b>	<b>0.88</b>	<b>0.79</b>
NO <sub>3</sub> <sup>-</sup>	0.98	-0.30	-0.72	-0.55	1.00	<b>0.65</b>	<b>0.95</b>	<b>1.00</b>	<b>0.95</b>	<b>0.99</b>
Cl <sup>-</sup>	-0.83	-0.06	0.92	0.82	-0.93	1.00	<b>0.39</b>	<b>0.63</b>	<b>0.85</b>	<b>0.75</b>
Ca <sup>2+</sup>	0.09	0.81	-0.89	-0.96	0.31	-0.63	1.00	<b>0.96</b>	<b>0.81</b>	<b>0.90</b>
K <sup>+</sup>	0.86	0.02	-0.90	-0.79	0.95	-1.00	0.60	1.00	<b>0.94</b>	<b>0.99</b>
Na <sup>+</sup>	0.73	0.23	-0.97	-0.90	0.86	-0.99	0.75	0.98	1.00	<b>0.98</b>
Mg <sup>2+</sup>	-0.49	1.00	-0.46	-0.64	-0.29	-0.08	0.82	0.03	0.24	1.00

3.3. Statistical analysis

Table 5 presents statistical descriptors of the chemical composition of the precipitation samples (minimum, maximum and mean value; standard deviation, median and variance). For all variables, the skewness factors ranged from -2 to +2, indicating that in all cases the data distribution approached Gaussian distribution. Consequently, no additional transformations were required for chemometric analysis of the data. Multi-dimensional analysis of variance and Fourier analysis of TS were used for further processing of data (Nascu et al., 1999; Brueggemann and Rolle, 1998; Walker et al., 2000; Ukonmaanaho et al., 1998; Miller, 1991). The data were divided into three categories with regard to the sampling site (Stara Piła, Jeziory, Ojców) and into two more categories with regard to the sample type

(precipitation or throughfall). ANOVA analysis showed that the division into the chosen categories was statistically significant at a significance level of  $\alpha = 0.05$  for five variables (pH, Cl<sup>-</sup>, Ca<sup>2+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>). Figs. 2A and B present the distribution of mean monthly pH values in precipitation and throughfall at the three sites in the 1997–1999 period. Acidity of the precipitation at the Stara Piła and Ojców sites was related to nitrate and chloride ions; at the Jeziory site, the acidity was related to nitrate and sulfate ions (see correlations in Table 4). Similar trends were presented in a paper by Raben et al. (2000), who studied changes in pH for a mixed spruce, oak and pine forest in Germany over the period from 1994 to 1998.

The results indicate that there were statistically significant differences between the pH values in precipitation and throughfall. Table 6 presents examples of

Table 5  
Statistical descriptors of the chemical composition of precipitation and throughfall at the three sampling sites

	<i>N</i>	Mean	Median	Minimum	Maximum	Variance	Standard deviation	Skewness factor
<i>Rumia-Stara Pila forest district (precipitation)</i>								
pH	4	5.14	5.10	4.75	5.61	0.14	0.37	0.57
<i>V</i> (mm)	4	834.50	854.00	716.00	914.00	7211.67	84.92	−1.22
SO <sub>4</sub> <sup>2−</sup>	4	4.03	3.42	1.49	7.81	8.52	2.92	0.79
NO <sub>3</sub> <sup>−</sup>	4	4.54	3.12	1.73	10.18	14.60	3.82	1.81
Cl <sup>−</sup>	4	1.41	1.44	1.18	1.58	0.03	0.17	−0.83
Ca <sup>2+</sup>	4	2.47	2.44	2.14	2.88	0.10	0.32	0.57
K <sup>+</sup>	4	0.36	0.36	0.30	0.44	0.00	0.06	0.68
Na <sup>+</sup>	4	0.44	0.44	0.39	0.48	0.00	0.04	0.00
Mg <sup>2+</sup>	4	0.21	0.21	0.18	0.24	0.00	0.03	0.56
<i>Rumia-Stara Pila forest district (throughfall)</i>								
pH	4	4.64	4.66	4.23	5.02	0.10	0.32	−0.28
<i>V</i> (mm)	4	475.00	476.00	419.00	529.00	3490.67	59.08	−0.02
SO <sub>4</sub> <sup>2−</sup>	4	17.33	16.95	11.32	24.12	29.75	5.45	0.36
NO <sub>3</sub> <sup>−</sup>	4	12.23	11.02	6.57	20.32	39.62	6.29	0.74
Cl <sup>−</sup>	4	6.62	6.03	5.47	8.95	2.51	1.58	1.77
Ca <sup>2+</sup>	4	3.41	3.28	2.98	4.10	0.28	0.53	0.87
K <sup>+</sup>	4	3.01	3.00	2.93	3.11	0.01	0.08	0.52
Na <sup>+</sup>	4	1.27	1.26	1.19	1.37	0.01	0.08	0.52
Mg <sup>2+</sup>	4	0.68	0.65	0.58	0.85	0.02	0.12	1.09
<i>Jeziory-Wielkopolski National Park (precipitation)</i>								
pH	4	4.44	4.53	4.14	4.57	0.04	0.20	−1.83
Electric conductivity	4	50.43	49.26	41.22	61.98	107.03	10.35	0.24
<i>V</i> (mm)	4	543.75	544.50	495.00	591.00	2198.25	46.89	−0.04
SO <sub>4</sub> <sup>2−</sup>	4	5.53	5.55	4.60	6.40	0.74	0.86	−0.08
NO <sub>3</sub> <sup>−</sup>	4	0.86	0.62	0.58	1.60	0.25	0.50	1.99
Cl <sup>−</sup>	4	3.38	3.25	2.00	5.00	1.54	1.24	0.59
Ca <sup>2+</sup>	4	1.42	1.31	1.07	1.98	0.16	0.40	1.41
K <sup>+</sup>	4	0.79	0.49	0.29	1.90	0.58	0.76	1.70
Na <sup>+</sup>	4	0.69	0.61	0.40	1.14	0.10	0.32	1.35
Mg <sup>2+</sup>	4	0.27	0.24	0.22	0.38	0.01	0.07	1.90
<i>Jeziory-Wielkopolski National Park (throughfall)</i>								
pH	4	4.74	4.72	4.33	5.20	0.13	0.36	0.38
Electric conductivity	4	106.16	108.30	77.59	130.47	736.78	27.14	−0.13
SO <sub>4</sub> <sup>2−</sup>	4	10.90	10.80	6.00	16.00	27.89	5.28	0.02
NO <sub>3</sub> <sup>−</sup>	4	1.83	0.96	0.80	4.60	3.43	1.85	1.97
Cl <sup>−</sup>	4	3.91	3.74	2.15	6.00	2.55	1.60	0.61
Ca <sup>2+</sup>	4	2.58	2.70	1.30	3.60	0.93	0.96	−0.72
K <sup>+</sup>	4	2.43	2.80	0.60	3.50	1.83	1.35	−1.06
Na <sup>+</sup>	4	1.99	2.08	1.50	2.31	0.12	0.35	−1.25
Mg <sup>2+</sup>	4	1.46	1.46	1.22	1.70	0.04	0.20	0.00
<i>Ojców-Ojcowski National Park (precipitation)</i>								
pH	3	4.53	4.56	4.28	4.76	0.06	0.24	−0.49
Electric conductivity	3	51.71	52.54	43.33	59.25	63.88	7.99	−0.46
<i>V</i> (mm)	3	522.33	545.00	379.00	643.00	17809.33	133.45	−0.74
SO <sub>4</sub> <sup>2−</sup>	3	4.24	4.23	4.04	4.46	0.04	0.21	0.32
NO <sub>3</sub> <sup>−</sup>	3	1.99	1.83	0.98	3.16	1.21	1.10	0.64
Cl <sup>−</sup>	3	0.68	0.84	0.33	0.86	0.09	0.30	−1.73
Ca <sup>2+</sup>	3	1.28	1.43	0.83	1.59	0.16	0.40	−1.46
K <sup>+</sup>	3	1.60	1.13	0.99	2.68	0.88	0.94	1.69
Na <sup>+</sup>	3	0.34	0.25	0.19	0.57	0.04	0.20	1.58
Mg <sup>2+</sup>	3	0.23	0.24	0.13	0.32	0.01	0.09	−0.52

Table 5. (continued)

	N	Mean	Median	Minimum	Maximum	Variance	Standard deviation	Skewness factor
<i>Ojców-Ojcowski National Park (throughfall)</i>								
pH	3	4.80	4.93	4.39	5.08	0.13	0.36	−1.41
Electric conductivity	3	66.88	59.25	56.68	84.71	240.08	15.49	1.68
V (mm)	3	402.33	393.00	379.00	435.00	849.33	29.14	1.29
SO <sub>4</sub> <sup>2−</sup>	3	9.07	10.06	6.50	10.66	5.05	2.25	−1.59
NO <sub>3</sub> <sup>−</sup>	3	8.42	5.34	3.79	16.14	45.25	6.73	1.63
Cl <sup>−</sup>	3	2.44	3.03	1.11	3.19	1.34	1.16	−1.69
Ca <sup>2+</sup>	3	3.97	3.63	3.26	5.03	0.88	0.94	1.43
K <sup>+</sup>	3	4.00	2.77	2.37	6.87	6.21	2.49	1.68
Na <sup>+</sup>	3	0.39	0.35	0.03	0.80	0.15	0.39	0.49
Mg <sup>2+</sup>	3	0.67	0.60	0.49	0.92	0.05	0.22	1.28

numerical results of ANOVA analysis obtained for precipitation samples, while Fig. 3 illustrates the relationships found. The calculated *F* value of 3.908 was greater than the critical value of 3.63 (*p* < 0.05), therefore the null hypothesis that mean pH values at the three sites were similar in both types of samples had to be rejected and the alternative hypothesis that the differences were statistically significant had to be accepted. The mean pH of precipitation at the Stara Piła site was much higher (pH = 5.14) than at the two remaining sites, Jeziory and Ojców (pH = 4.44 and 4.53, respectively). This was most likely related to the west- and south-west wind-driven inflow of acidic industrial emissions containing sulfur and nitrogen oxides over the latter two sites.

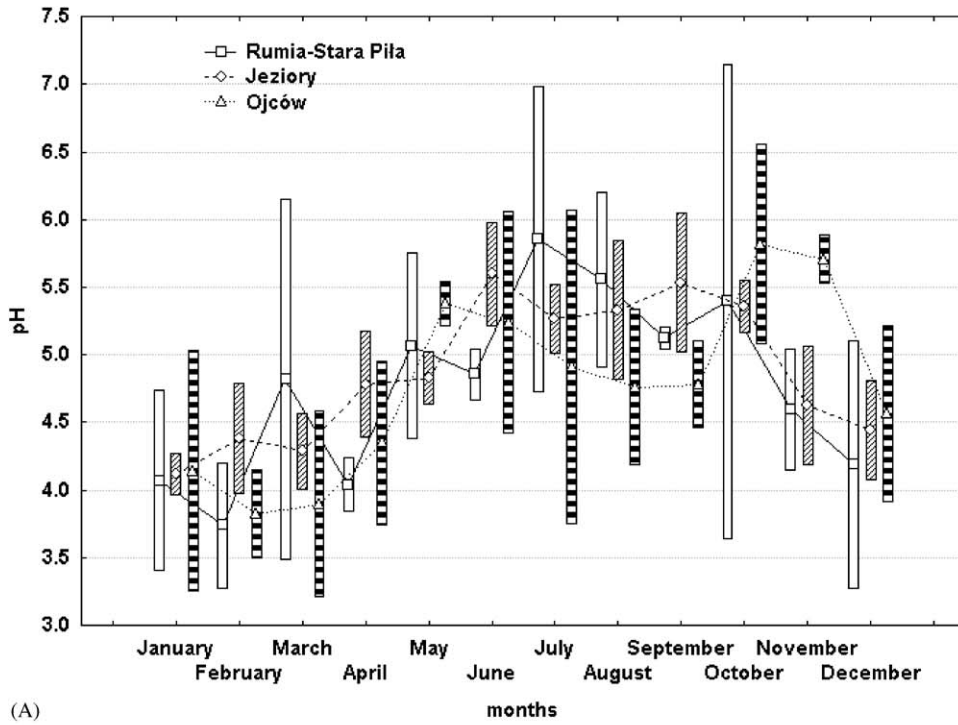
Analysis of variance showed also that categorization of the data sets was statistically important for clarifying the differences between the concentration levels of the Cl<sup>−</sup>, Ca<sup>2+</sup>, Na<sup>+</sup> and Mg<sup>2+</sup> ions at the three sites. The results indicate that the levels of Cl<sup>−</sup> in throughfall in Rumia—Stara Piła ( $\overline{\text{Cl}^-} = 6.62 \text{ mg l}^{-1}$ ) were significantly higher than in Jeziory ( $\overline{\text{Cl}^-} = 3.91 \text{ mg l}^{-1}$ ) and Ojców ( $\overline{\text{Cl}^-} = 2.44 \text{ mg l}^{-1}$ ); in addition, these levels were higher than the levels determined for incident precipitation collected in Stara Piła ( $\text{Cl} = 1.41 \text{ mg l}^{-1}$ ). This observation could most likely be explained by the constant presence of salts (mostly NaCl) from sea salt aerosols in the coastal air. These salts tend to deposit on leaf surfaces and are washed off with precipitation to form the throughfall.

The considerable share of the Na<sup>+</sup> ions in the rainfall could be explained by the proximity of the Baltic Sea. ANOVA showed that mean concentrations of Na<sup>+</sup> ions in throughfall from Stara Piła ( $\overline{\text{Na}^+} = 1.27 \text{ mg l}^{-1}$ ) and Jeziory ( $\overline{\text{Na}^+} = 1.99 \text{ mg l}^{-1}$ ) were significantly higher than the concentrations for Ojców ( $\overline{\text{Na}^+} = 0.39 \text{ mg l}^{-1}$ ). It is well known (Plaisance et al., 1997) that these ions are found in the form of NaCl in rainwater; they are thought to represent sea salt aerosols. Table 6 shows an

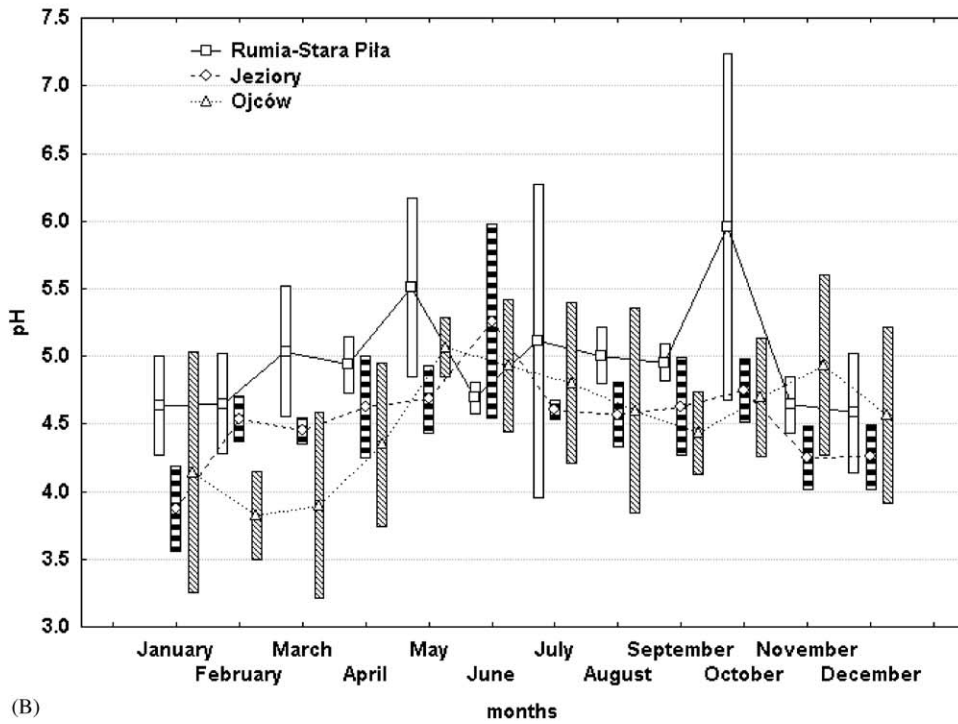
example of the numerical results of ANOVA analysis for Cl<sup>−</sup> ions. In addition, Fig. 4 presents the distribution of mean values and 95% confidence intervals for the three sampling sites and the two categories of rainfall. Based on the results of ANOVA analysis, it was assumed that the concentrations of Cl<sup>−</sup> ions in throughfall decreased with increasing distance from the Baltic Sea. At the same time, it was observed that a decrease in the concentration of Cl<sup>−</sup> in throughfall was accompanied by an increase in the concentrations of Mg<sup>2+</sup> and Ca<sup>2+</sup>. ANOVA showed that for the Jeziory site, the mean value of Mg<sup>2+</sup> concentration was higher in throughfall ( $\overline{\text{Mg}^{2+}} = 1.46 \text{ mg l}^{-1}$ ), while for the Ojców site the concentration of Ca<sup>2+</sup> was higher ( $\overline{\text{Ca}^{2+}} = 3.97 \text{ mg l}^{-1}$ ). This might have been related to the presence of calcium ions (from weathering of the calcite rocks) in the air.

In the case of the SO<sub>4</sub><sup>2−</sup>, NO<sub>3</sub><sup>−</sup> and K<sup>+</sup> ions, the subdivision into the different categories turned out to be insignificant for the average concentrations of these ions. The differences between the values of these parameters were insignificant between the three sampling sites.

To identify any other possible differences between the samples collected at the three sites located in different parts of Poland, the data sets were further examined by TS analysis. In order to examine the structure of a given TS, the data were subjected to Fourier spectrographic analysis, using the Hamming criteria to assess the spectral concentration. This procedure was presented before (Sharaf et al., 1986). Calculations performed for the pH data sets confirmed that there were no periodic trends for the precipitation samples, independently of the sampling site (Stara Piła, Jeziory or Ojców). Fourier analysis did not reveal any periodic cycles in the TS. On the other hand, 12-month cycles were detected in selected throughfall samples. The effect was very pronounced at the Stara Piła and the Jeziory sites. At the Ojców site, cycles of different periods seemed to have been superimposed on the 12-month cycles. Fig. 5A presents an example of a Fourier analysis periodogram



(A)



(B)

Fig. 2. Distribution of mean monthly pH values of precipitation for the 1997–1999 period at the three sampling sites (2A—incident precipitation, 2B—throughfall).

for Jeziory, while Fig. 5B shows a similar periodogram for Ojców. Distinct 12-month cycles were discovered in the TS structure of the throughfall pH. Identification of the period cycle ( $T = 12$  months) in the variation of the pH values in the case of throughfall samples allowed for seasonal decomposition of the smoothed data. Fig. 6 illustrates seasonal decomposition of mean pH values of precipitation (Fig. 6A) and throughfall (Fig. 6B), including sampling location. One of the findings was that during certain months (May–September), mean pH value of the throughfall was significantly higher than the pH during the November–April period. The results of the analysis suggested two clearly distinct periods during a year: the winter season (November–April) and the summer season (May–September). During the summer

months, an increase in the pH value could be observed at the Stara Piła and Jeziory sites, (pH = 5.3), while during the winter months, the average pH value was lower (pH = 4.4 for Stara Piła and pH = 4.5 for Jeziory). At the Ojców site, the pH value during the summer and winter periods was rather stable and oscillated between 5.0 and 5.1. Precipitation acidity at the Stara Piła and Jeziory sites in winter was most likely elevated due to an increase in the emission of “household” pollutants (e.g. sulfur oxides from domestic combustion of fossil fuels) in winter.

The  $\text{Cl}^-/\text{Na}^+$  ratio calculated for both kinds of precipitation ranged from 0.37 to 23. In throughfall samples, this ratio was 2–3 times higher than in precipitation. The only exception was the Jeziory site, where this ratio was 2–3 times smaller. In fact, the  $\text{Cl}^-/\text{Na}^+$  ratios in throughfall samples from the Jeziory site (1.37) and in precipitation samples from the Rumia-Stara Piła and Ojców sites (2.09 and 1.80, respectively) were close to the value characteristic of NaCl (1.54).

The  $\text{NO}_3^-/\text{Na}^+$  ratio varied within a wide range, from 0.14 to 46. Only at the Jeziory site, the value of this ratio (0.44) was close to that of  $\text{NaNO}_3$ . The  $\text{SO}_4^{2-}/\text{Na}^+$  ratio ranged from 1.58 to 103 and was generally much higher than that for  $\text{Na}_2\text{SO}_4$  (or for sea salt in the case of the Rumia-Stara Piła site).

Selected ionic ratios ( $\text{Cl}^-/\text{Na}^+$ ,  $\text{NO}_3^-/\text{Na}^+$ ,  $\text{SO}_4^{2-}/\text{Na}^+$ ,  $\text{K}^+/\text{Na}^+$ ,  $\text{Mg}^{2+}/\text{Na}^+$ ,  $\text{Ca}^{2+}/\text{Na}^+$ ) were subjected to

Table 6

An example of double classification analysis of variance for mean values of  $\text{Cl}^-$  in throughfall and precipitation samples collected at the three sites

Effect	SS	DF	MS	$F_{\text{obtained}}$	$F_{\text{critical}}$
<b>Category 1: sampling site</b>	<b>23.00</b>	<b>2</b>	<b>11.50</b>	8.10	3.63
Category 2: sample type	33.81	1	33.81	23.81	4.49
Intergroup	23.23	2	11.61	8.18	3.63
Intragroup	22.72	16	1.42		
Total	102.76	21	4.89		

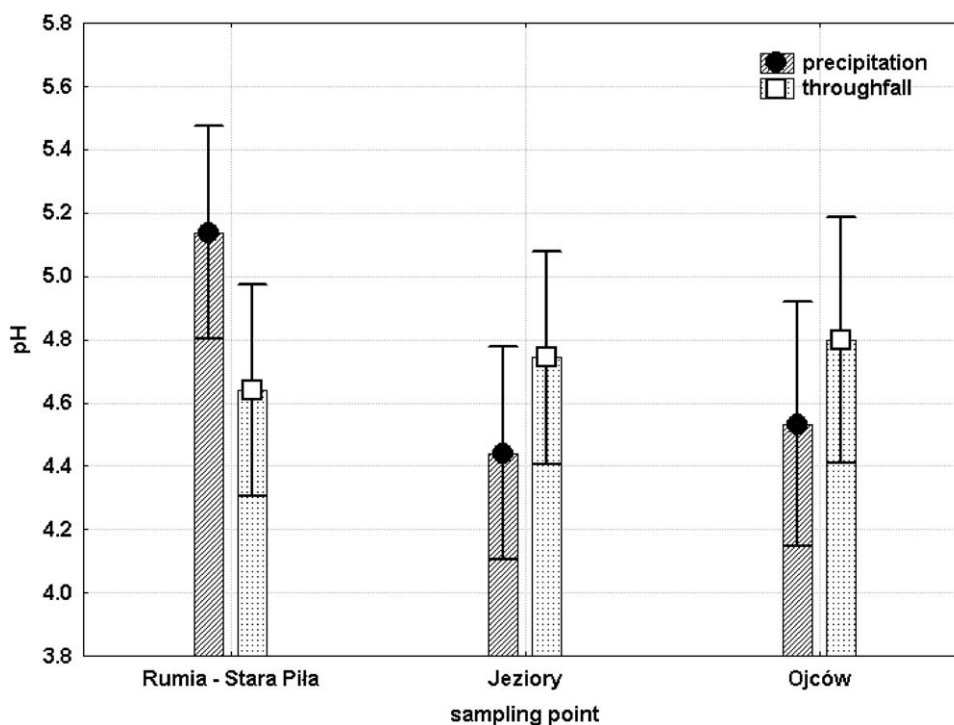


Fig. 3. Average pH values of incident precipitation and throughfall collected at the three sampling sites.

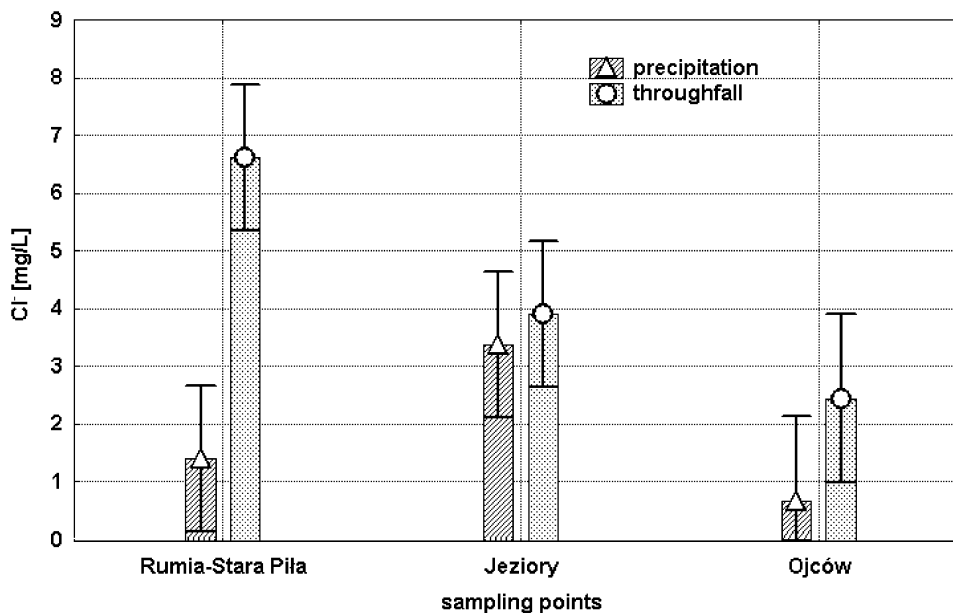


Fig. 4. Mean concentrations of  $\text{Cl}^-$  ions ( $\text{mg l}^{-1}$ ) (including 95% confidence intervals) in incident precipitation and throughfall collected at the three sampling sites.

statistical evaluation using univariate ANOVA. The results indicated that there were no statistically significant differences between throughfall and precipitation samples collected at all sites. The scatter of the results overlapped, with no extreme values. Thus, the hypothesis that the sites differed with respect to the occurrence and concentration of these ions had to be rejected.

#### 3.4. Throughfall/precipitation relationships

Fig. 7 presents the concentration factors of selected ions in throughfall (thr) as compared to precipitation (pr) for samples collected at the three sites between 1996 and 1999 (Walna et al., 2003). The lines connecting the data points for the sum of cations and the sum of anions were added for visualisation purposes only and do not represent mathematical relationships. The values of the concentration factors ranged from 0.77 to 7.6 for the anions, and 0.07 to 14.3 for the cations. One notable exception was observed for the anions: the throughfall/precipitation ratio for  $\text{NO}_3^-$  determined in 1997 in Ojców was over 45. At the Rumia-Stara Piła and the Jezioro sites, the concentration factors remained relatively constant, with little scatter. Statistical analysis indicated that there were no significant differences between the concentration factors for  $\text{Cl}^-$  at the three sites. In the case of  $\text{NO}_3^-$  ions, significant differences were found between the Jezioro and the Ojców sites, while for the  $\text{SO}_4^{2-}$  ions there were significant differences between the

values found for the Rumia-Stara Piła site and those for the Jezioro and the Ojców sites. The throughfall/precipitation ratio for the sum of cations remained relatively constant at the three sampling sites, varying between 2.09 and 3.47; for the sum of anions, the variability was a little higher, ranging from 1.21 to 5.70.

In a similar study carried out in Spain, (oak forest), the largest throughfall/precipitation enrichment factors (17.4) were observed for  $\text{K}^+$  (Rodrigo et al., 2003). In other studies, the concentration factors for spruce forests ranged from 4.7 to 21.4 (Whelan et al., 1998; Hansen et al., 1994), while for mixed forests the concentration factors were 37.5 (spruce, fir, larch) and 20 (spruce, fir, larch, beech, birch) (Balestrini et al., 1998). Increased concentrations of ions in the throughfall were related to canopy exchange and dissolution of dry deposition components. The phenomenon was particularly clear in the case of spruce needles, whose area is significantly larger than the area of leaves on deciduous trees (Walna and Siepak, 1996).

Composition of cations in throughfall generally followed the same pattern as in incident precipitation. Individual ion concentrations varied depending on the type of forest, age of trees and acidity of precipitation. Cation concentrations in throughfall samples from this study followed the same sequence, independently of the sampling site and forest type (Stara Piła–spruce; Jezioro–oak; Ojców–beech):  $\text{Ca}^{2+} > \text{K}^+ > \text{Na}^+ > \text{Mg}^{2+}$ . A similar sequence was observed for oak forest in Spain (Rodrigo et al., 2003). Different sequences were

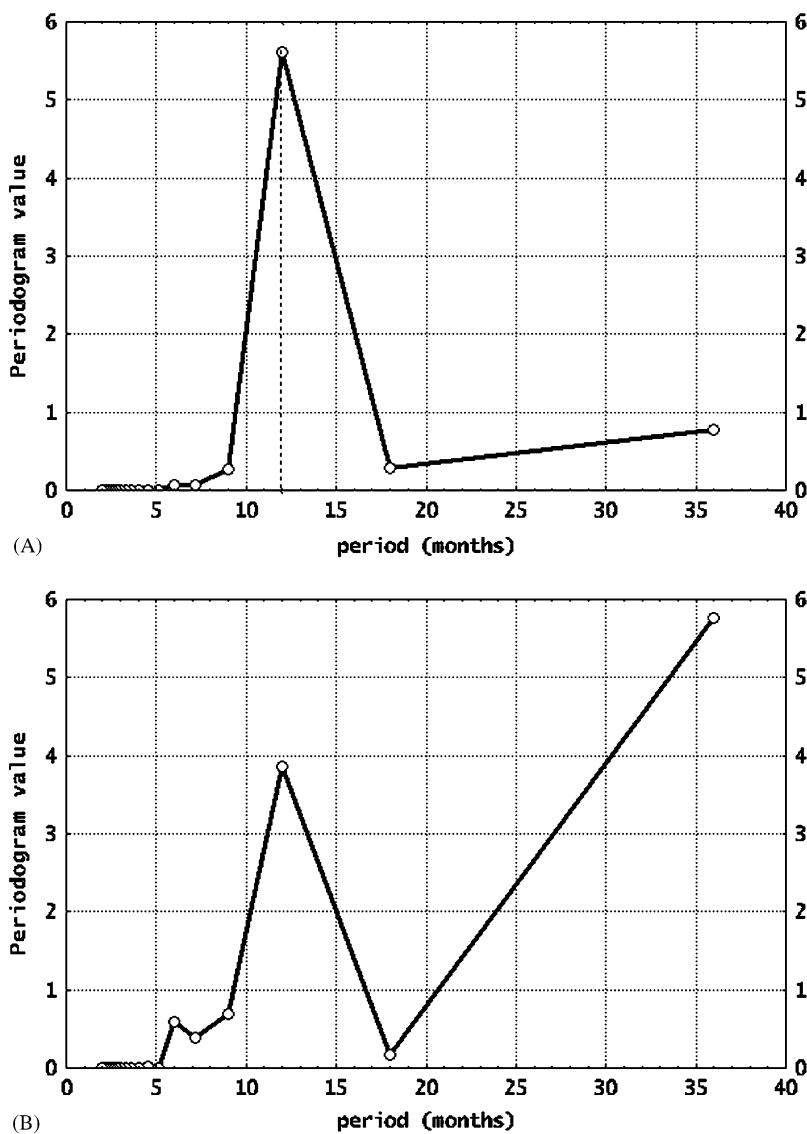


Fig. 5. Examples of Fourier analysis periodograms obtained for precipitation samples collected at Jeziory (5A) and Ojców (5B).

observed in northern Italy for beech forests ( $K^+ > Mg^{2+} > Ca^{2+} > Na^+$ ) and spruce forests ( $K^+ > Ca^{2+} > Mg^{2+} > Na^+$ ) (Bini and Bresolin, 1998). Yet another sequence was observed in Denmark ( $Na^+ > K^+ > Mg^{2+} > Ca^{2+}$ , spruce) and in Holland ( $K^+ > Na^+ > Ca^{2+} \gg Mg^{2+}$ , spruce) (Hansen et al., 1994). In the Amazon Basin (non-flooded forest), the ionic sequence was:  $Mg^{2+} > K^+ > Na^+ > Ca^{2+}$  (Forti and Moreira-Nordemann, 1991).

The ionic sequence for anions in incident precipitation collected at the Stara Piła site was  $NO_3^- > SO_4^{2-} > Cl^-$ . The sequence for throughfall collected under spruce trees was somewhat different:  $SO_4^{2-} > NO_3^- > Cl^-$ . Similar anionic sequences were observed for incident

precipitation and throughfall collected at the Ojców site, as well as for throughfall collected in Holland (Hansen et al., 1994). The sequence at the Jeziory site was different ( $SO_4^{2-} > Cl^- > NO_3^-$ ) for both incident precipitation and for throughfall. Yet another sequence,  $Cl^- > SO_4^{2-} > NO_3^-$ , was observed for precipitation and throughfall in Spain (Rodrigo et al., 2003), and for throughfall in Denmark (Hansen et al., 1994).

#### 4. Conclusions

Precipitation and throughfall samples were collected over a period of 4 years (1 January 1996–31 December

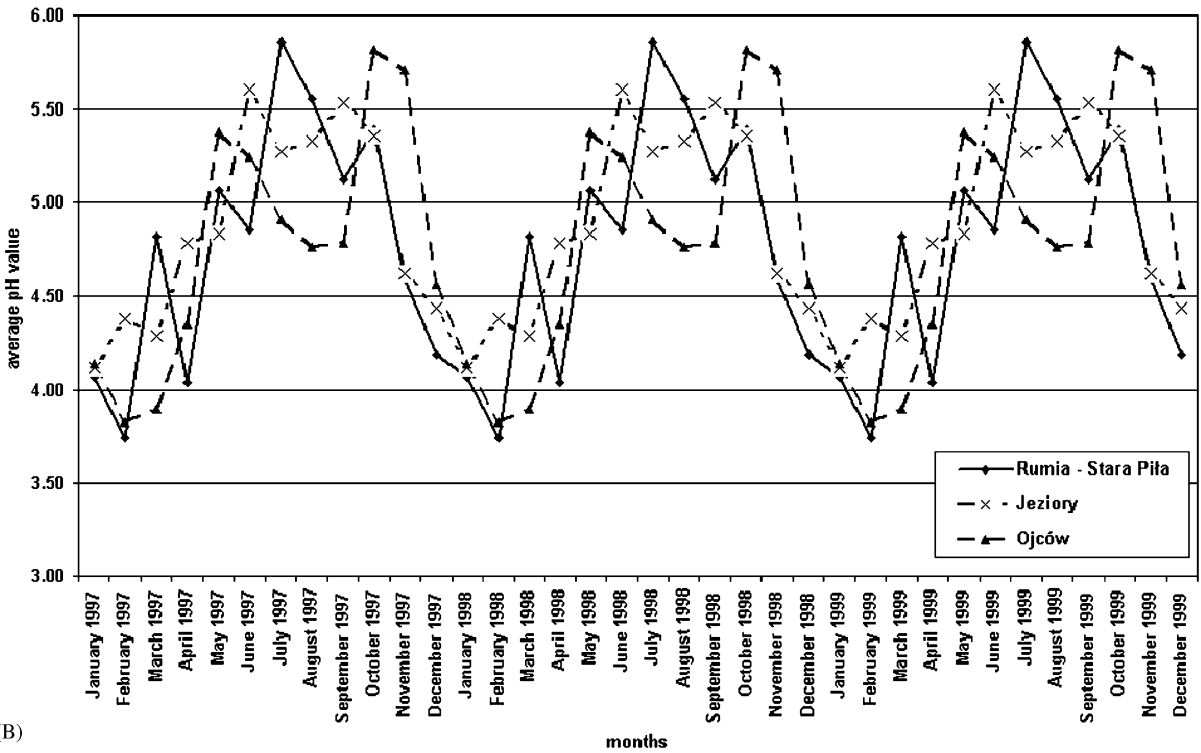
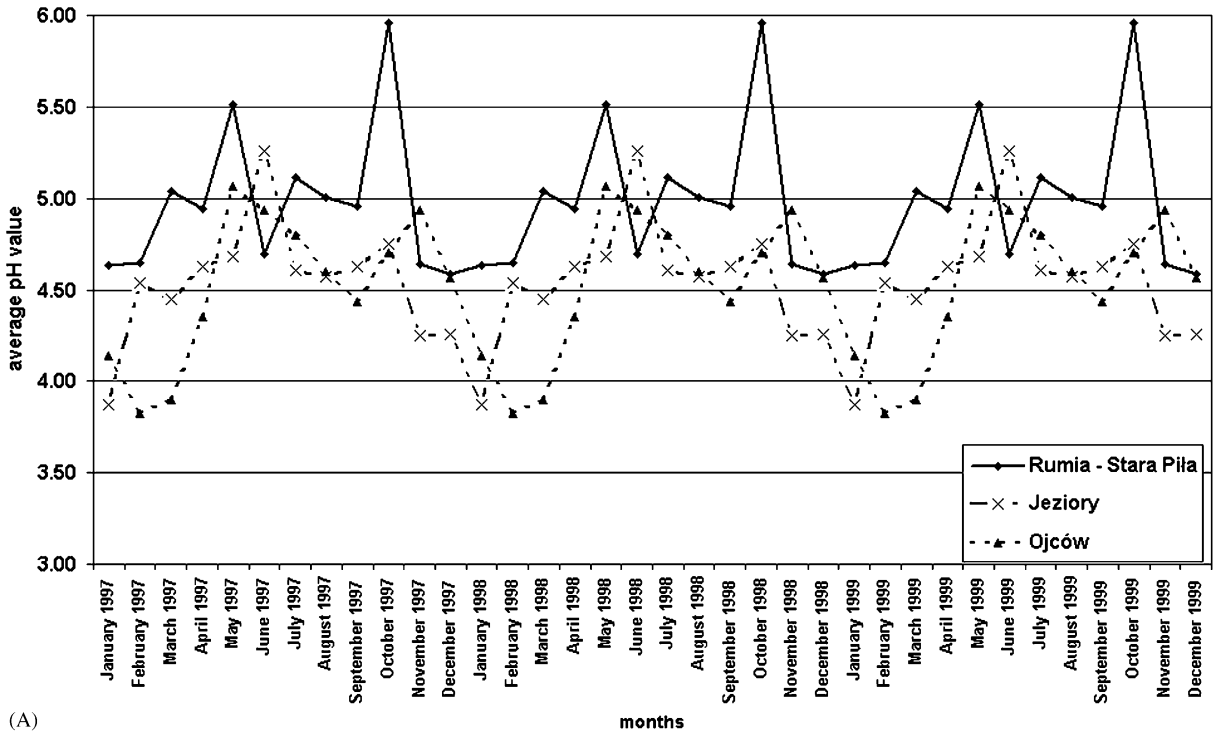


Fig. 6. Seasonal decomposition of mean pH values of incident precipitation (6A) and throughfall (6B), including sampling location.

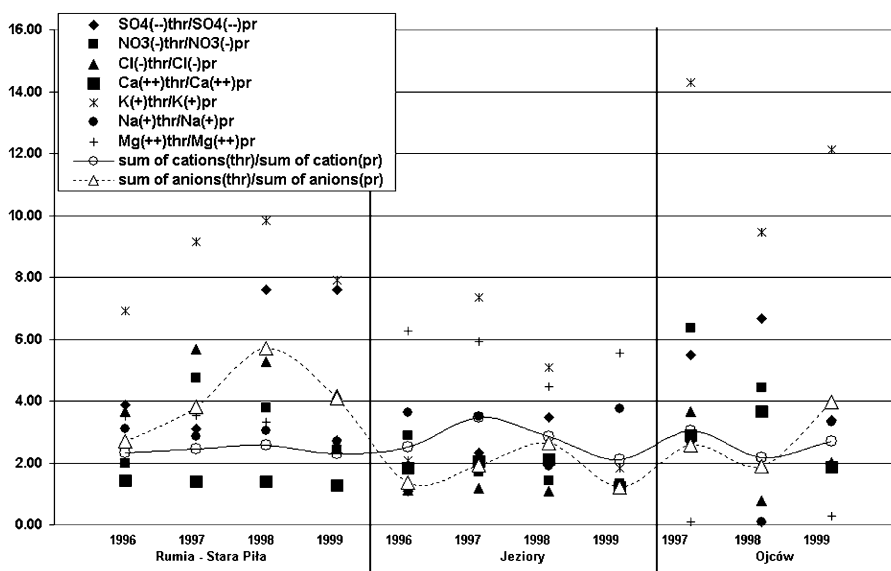


Fig. 7. Throughfall/incident precipitation concentration factors for  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$  and  $\text{Mg}^{2+}$  ions, the sum of cations and the sum of anions, for samples collected at the three sites between 1996 and 1999.

1999) at three sites of very different characteristics in Poland (Stara Piła—moraine hills; Jeziory at Wielkopolski National Park area—lowlands; Ojców at Ojcowski National Park area—mountainous region). Both National Parks involved in the study belong to the most polluted protected areas in Poland. The Wielkopolski National Park is located close to a large urban agglomeration (Poznań); in addition, it is exposed to long-range pollutant transport from a German industrial region owing to the prevailing western and south-western winds. The Ojcowski National Park is located close to Cracow urban agglomeration and exposed to winds from the Silesia industrial region. The Stara Piła site is located next to the Gdańsk-Sopot-Gdynia Tricity, close to the Gulf of Gdańsk on the Baltic Sea.

A representative body of data was collected for 9 parameters (pH, electrolytic conductivity, and concentration levels of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$  and  $\text{Mg}^{2+}$  ions). ANOVA and TS analysis were applied to study the chemical composition of the samples, ionic correlations, and fluctuations of selected variables with time in relation to geographical location, type of tree cover and climatic conditions. Strong correlations between ions (correlation coefficients greater than 0.95) were found in 4, 3 and 9 cases for precipitation collected at the Stara Piła, Jeziory and Ojców sites, respectively.

In the case of throughfall, strong correlations between ions were found in 7 cases for the Stara Piła site, 13 cases for the Ojców site, and only 2 cases for the Jeziory site. For incident precipitation, the  $\text{SO}_4^{2-}$ – $\text{NO}_3^-$ – $\text{Cl}^-$  correlation was the strongest for samples collected at the Ojców site. In incident precipitation samples from all sites, the

strongest correlations were observed between  $\text{SO}_4^{2-}$ –anions and  $\text{Mg}^{2+}$  cations, as well as  $\text{Cl}^-$  anions and  $\text{Na}^+$ / $\text{K}^+$  cations. The same was true for throughfall samples, but additional correlations occurred between  $\text{SO}_4^{2-}$  anions and  $\text{Na}^+$  cations, as well as  $\text{NO}_3^-$  anions and  $\text{Ca}^{2+}$ / $\text{K}^+$  cations. Analysis of the correlations between co-occurring ions confirmed the significance of the relationship between chemical composition of precipitation and chemical substances emitted into the atmosphere. Statistical analysis of eight of the parameters analyzed (conductivity being the exception) was performed, with categorization into three categories with regard to the sampling site and two categories with regard to the sample type. The results showed that for five variables (pH,  $\text{Cl}^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ) there were significant differences between the results obtained for different sampling site locations and characteristics (region of Poland, open area vs. throughfall).

TS analysis indicated no periodic trends in the pH of incident precipitation samples, independently of the sampling site (Stara Piła, Jeziory or Ojców). On the other hand, 12-month cycles were detected in selected throughfall samples from the Stara Piła and Jeziory sites. At the Ojców site, cycles of different periods seem to have been superimposed on the 12-month cycles. For the Stara Piła and Jeziory sites, TS analysis results suggested the occurrence of two clearly distinct periods during a year: the winter season (November–April) and the summer season (May–September). During the summer months, an increase in the pH could be observed at the Stara Piła and Jeziory sites, (pH = 5.3), while during the winter months, the average

pH value was lower (pH = 4.4 for Stara Piła and pH = 4.5 for Jeziory).

Analysis of variance performed for selected ionic ratios ( $\text{Cl}^-/\text{Na}^+$ ,  $\text{NO}_3^-/\text{Na}^+$ ,  $\text{SO}_4^{2-}/\text{Na}^+$ ,  $\text{K}^+/\text{Na}^+$ ,  $\text{Mg}^{2+}/\text{Na}^+$ ,  $\text{Ca}^{2+}/\text{Na}^+$ ) found no statistically significant differences between throughfall and precipitation samples collected at all three sites.

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