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Tendencies of Change in the Chemistry of Precipitation at Three Monitoring Stations 1996-1999

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Abstract

This study compares the results of three stations differing greatly in geography, and tendencies of change in the chemistry of precipitation (open and throughfall) in the years 1996-1999. The mean annual pH is lower than 5.2, and often drops below 4.6. A distinct decline in the concentrations of sulphate ions at all the stations is observed.

Keywords: acid precipitation, throughfall, pH, conductivity, chemical composition.

Introduction

Despite a substantial reduction in recent years in the amount of air-polluting substances discharged by industry in Poland [1, 2], one can still observe acid rain [3-7], whose detrimental effect on geoecosystems, especially woodland, is significant [8-11].

A comparison of the results obtained by various authors is often difficult. This is due to differences in rainwater sampling techniques [12,13], analytical procedures employed [14, 15], and access to results. Still, a comparison of the results of studies carried out at various places seems valuable because it offers the possibility to observe variations in rainwater composition and the temporal pattern of the results, and to define the proportions of natural and man-made contamination.

A significant part of air pollution monitoring is the determination of the composition of throughfall which, depending on the tree species and age, 'stores' particulates falling on rainless days and accumulating on trees (the so-called dry deposition) [16]. Another component of throughfall is those substances that are leached from plant tissues as a result of the aggressive action of precipitation with a low pH [17, 18]. All these processes affect the ultimate chemical composition of water and are responsible for the considerable differences, both qualitative and quantitative, registered in the particular places of observation.

In the present study a comparison is made of the results of three stations greatly differing in geography, and

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tendencies of change in the chemistry of precipitation in the years 1996-1999 are analyzed. The analysis embraces precipitation collected in open terrain henceforth called atmospheric precipitation, and throughfall collected under trees of various species.

Materials and Methods

Rainwater was sampled for four years at three stations in Poland located in climatically different regions:

- station no. 1 - Stara Piła, Rumia forest district, Pomeranian voivodeship,
- station no. 2 - Jeziory, Wielkopolski National Park, Wielkopolska voivodeship, and
- station no. 3 - Chełmowa Góra, Ojców National Park, Małopolska voivodeship.

At station no. 1 the climate is modified by the immediate neighbourhood of the Baltic. The proximity of the sea makes winter mild in terms of temperature, lowers the temperature of summer, and maintains high air humidity throughout the year. Air circulation is longitudinal. The Tri-City agglomeration of Gdańsk, Sopot and Gdynia is some 30 km south of the station. Annual rainfall amounts to 550-600 mm [7].

Wielkopolska voivodeship, where station no. 2 is located, lies in the temperate zone, in an area where maritime and continental influences interpenetrate. Prevailing winds are from the west, mainly westerly and south-westerly quarters. The station is in the Wielkopolski National Park, about 20 km south-west of the Greater Poznań agglomeration. It is the area with the lowest rainfall in Poland, receiving an average of under 550 mm annually [19].

Ojców National Park, where station no. 3 is situated, lies on the Cracow-Częstochowa Upland. It is about 400 km south of station no. 2 and 600 km south of station no. 3. The upland is raised to about 300 m a.s.l. Most winds blowing here come from the west. The diversified relief causes average rainfall to vary. The heaviest rainfall is recorded on north-facing slopes and on tops (about 800 mm), while on valley floors situated in the so-called rain shadow it is lower [3].

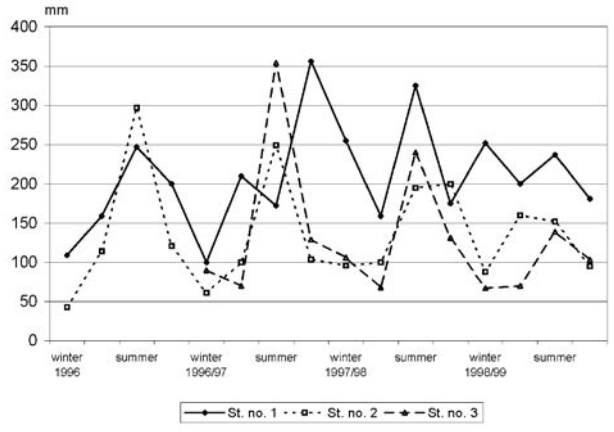

Fig. 1. Seasonal rainfall patterns at stations.

Table 1. Annual rainfall (mm) 1996-1999.

Stations	1996	1997	1998	1999
1	716	838	914	869
2	576	512	591	495
3	not measured	643	545	544

At all the stations bulk precipitation was collected in an open area and under the trees: at station no. 1, under spruces; at station no. 2, oaks; and at station no. 3, beeches.

Collectors were located at 1.2 m above the ground. All analyses were carried out within 96 hours of sample collection. Measurements of pH were obtained using a CX 315 microcomputer pH-meter, while those of conductivity, a RADELKIS OK-102/1 analogue conductivity meter. Chemical analyses were performed after filtering (0.45μm). Concentrations of K^+ and Na^+ ions were determined using a Carl Zeiss Jena FLAPHO 4 flame spectrophotometer, and those of Mg^{2+} and Ca^{2+} ions with the help of a BUCK Scientific MODEL 210 VGP or Varian 20 atomic absorption spectrophotometer, anions - using ion chromatography (Dionex-100, Dionex-320, Dionex-500), and ammonium - based on the colorimetric technique using MERCK SQ-118 spectrophotometer. The determinations were made in accordance with the Standard Methods [20]. The amount of rainfall was measured using Hellman's collector.

Results and Discussion

Rainfall figures at the research stations differ with the season (Fig.1). All of them have a summer peak, while in winter, or sometimes in spring, rainfalls are lower. Accordingly, the highest rainfall volumes were recorded at stations no. 1 and 3 in 1997 in summer (no. 3, 354 mm) and autumn (no. 1, 356 mm), whereas the lowest figure was recorded in the winter of 1995/96 at station no. 2 (43 mm).

Annual rainfall figures are presented in Table 1. The highest rainfall was recorded at the coastal station - more than 900 mm (1998). The rainfalls at stations 2 and 3 are similar and vary between 500 and 600 mm.

The basic measure of pollution of precipitation is its pH. Presented below are the values of this index recorded both in open terrain and under trees (Table 2). At all the stations the rainwater has a pH of under 5.2, and its annual weighted mean is usually lower than 4.6. The rainfall is the least acidic at station no. 1, but after it has passed through the spruce crown its pH can drop even by unity. At stations no. 2 and 3 the annual pH of precipitation under trees was not much different from that in open terrain; it is a bit higher than the open-terrain pH, which is connected with the tree species (oak and beech). The minimum annual pH, at 3.89 (1998, station no. 2), was recorded under the oak.

Table 2. Mean annual pH values in open field (op.) and throughfall (th.).

Stations	1996	1997	1998	1999
1 op.	5.15	4.81	4.46	4.91
1 th.	3.97	4.15	4.05	4.22
2 op.	4.02	4.18	4.46	4.51
2 th.	4.05	4.51	4.39	4.86
3 op.	not measured	4.44	3.97	4.06
3 th.	not measured	4.85	3.89	4.06

Table 3. Annual rainwater conductivity in open field (op.) and throughfall (th.) [μS/cm].

Stations	1996	1997	1998	1999
1 op.	21	not measured	not measured	not measured
1 th.	49	not measured	not measured	not measured
2 op.	56	62	41	42
2 th.	128	130	78	88
3 op.	not measured	43	59	52
3 th.	not measured	56	71	84

When observing the patterns of change in the pH of precipitation, only station no. 2 can be said to show an upward year-to-year tendency. At the other stations the tendency is hard to identify.

There are wide differences in the electrical conductivity of precipitation under trees and in the open. The values of the former can be several times higher than the latter. Presented below is the monthly pattern of conductivity under trees (Fig. 2).

There is high variability in the mean monthly conductivity figures. It is especially striking at station no. 2, where extreme values of precipitation under trees can exceed 300 μS/cm (May 1996, November 1997). Maximum conductivity values in open (Fig. 3) were recorded at station no. 2 in January 1997 (225 μS/cm), and at station no. 3 in February 1998 (188 μS/cm).

Annual conductivity figures for rainwater from under the trees and from open terrain are listed in Table 3. The lowest mean annual conductivity value was recorded at station no. 1 in 1996. Unfortunately, in the other years this parameter was not measured there. The other mean annual conductivity values recorded in the open are rather similar and indicate a moderate level of pollution of precipitation (40-60 μS/cm) without any characteristic tendency of change.

On passing through the tree crown, precipitation water is enriched with substances washed from the leaf surface and those leached from its tissue. This can be observed by comparing both conductivity and chemical composition of precipitation under trees and in the open. The diagrams below show the composition of anions and cations in precipitation at the three stations.

Figs. 4a and 4b present the chemistry of rainfall at station no. 1. Despite the nearness of the sea, the calcium cation predominates at this station (2.14-2.88 mg/L). Other cations recorded include ammonium (0.74-1.89 mg/L), sodium (0.39-0.48 mg/L), and potassium (0.30-0.44 mg/L). Potassium content in throughfall is strikingly high in comparison with atmospheric precipitation (2.93-3.11 mg/L). As to the anion composition of open-terrain precipitation at station no. 1, contrary to expectations it is not chloride ions that predominate (1.18-1.80 mg/L), but sulphate (1.49-7.81 mg/L) and nitrate ions (1.73-10.18 mg/L). The level of phosphate ions is very low, merely 0.1-0.2 mg/L. Anion concentrations in throughfall can be several times higher: sulphates, 11.31-24.12 mg/L; nitrates, 6.57-24.12 mg/L, chlorides, 5.47-8.95 mg/L and phosphates, 0.42-0.53 mg/L.

A similar comparison of the ionic composition of precipitation for station no. 2 is presented in Figs. 5a and 5b.

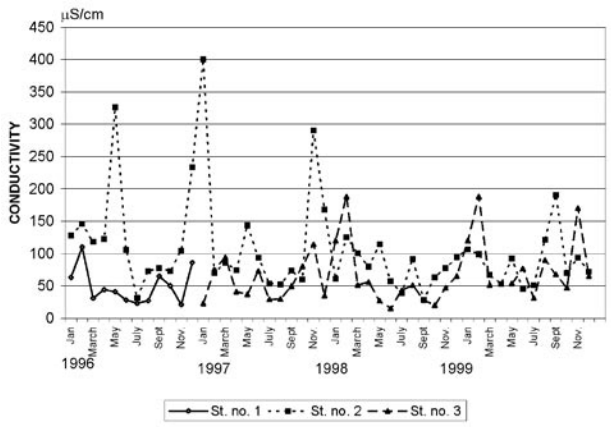

Fig. 2. Monthly pattern of conductivity under tree.

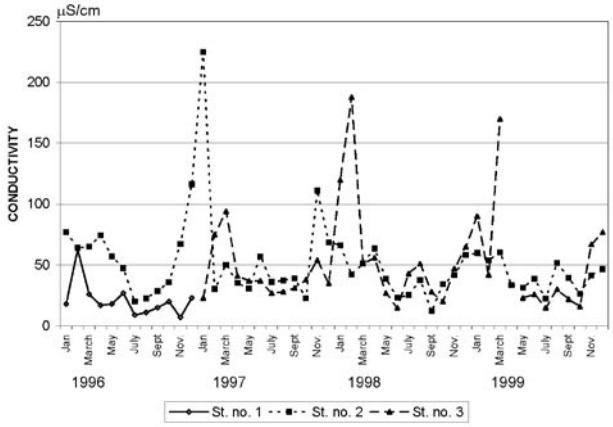

Fig. 3. Monthly pattern of conductivity in open area.

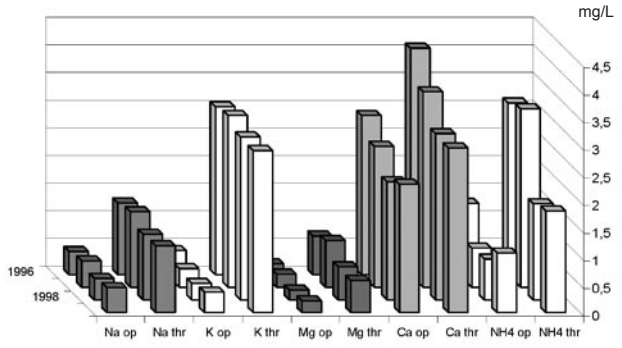

Fig. 4a. Concentrations of NH_4^+, Na^+, Mg^{2+}, Ca^{2+}, and K^+ in precipitation collected in the open and under trees (spruce), station no 1.

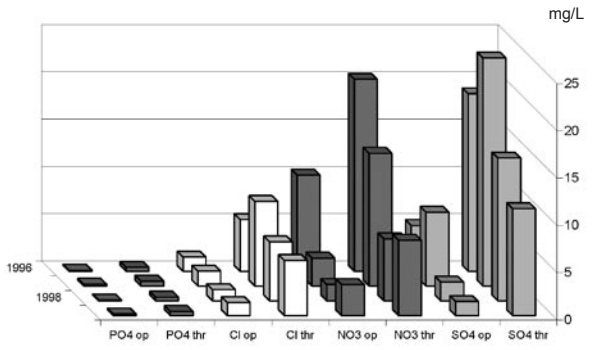

Fig. 4b. Concentrations of SO_4^{2-}, Cl^-, NO_3^-, PO_4^{3-} in precipitation collected in the open and under trees (spruce), station no 1.

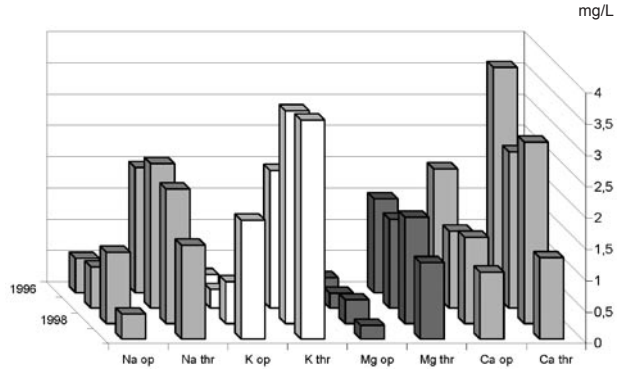

Fig. 5a. Concentrations of Na^+, Mg^{2+}, Ca^{2+}, and K^+ in precipitation collected in the open and under trees (oak), station no 2.

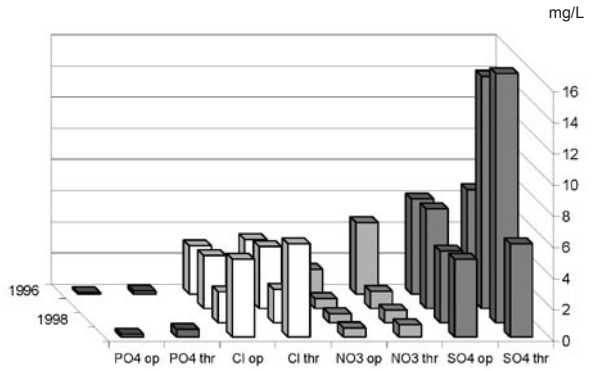

Fig. 5b. Concentrations of SO_4^{2-}, Cl^-, NO_3^-, PO_4^{3-} in precipitation collected in the open and under trees (oak), station no 2.

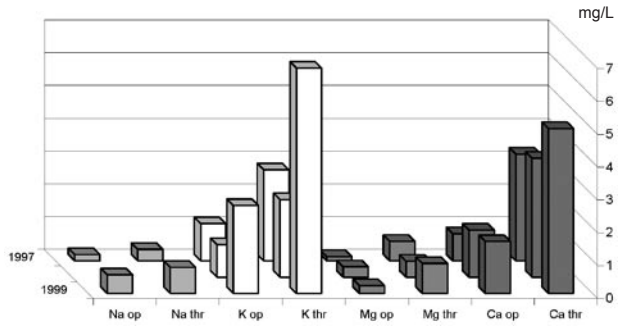

Fig. 6a. Concentrations of Na^+, Mg^{2+}, Ca^{2+}, and K^+ in precipitation collected in the open and under trees (beech), station no 3.

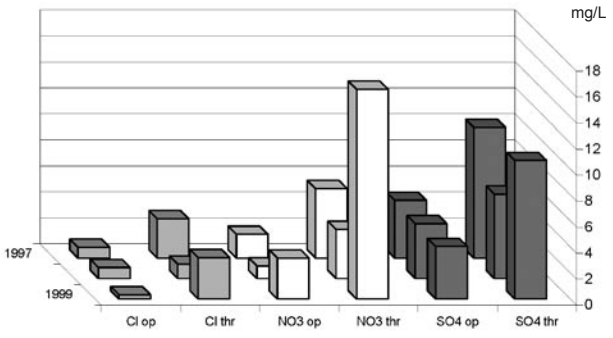

Fig. 6b. Concentrations of SO_4^{2-}, Cl^-, NO_3^-, in precipitation collected in the open and under trees (beech), station no 3.

Cation concentrations in open-terrain precipitation look as follows: sodium, 0.40-1.12 mg/L; potassium, 0.30-1.90 mg/L; magnesium, 0.22-0.38 mg/L; and calcium, 1.07-1.98 mg/L. The respective anion concentrations: phosphates, 0.1-0.2 mg/L; chlorides, 2.0-5.0 mg/L; nitrates, 0.58-1.6 mg/L; and sulphates, 4.6-6.4 mg/L. In the composition of throughfall, the concentrations of all the ions were several times higher.

The data for station no. 3 only embrace the years 1997-1999 (Fig. 6a and b). Cation concentrations in atmospheric precipitation recorded in those years are as follows: sodium, 0.19-0.57 mg/L; potassium, 0.99-2.68 mg/L; magnesium, 0.13-0.32 mg/L; and calcium, 0.83-1.59 mg/L. Respective anion concentrations: chlorides, 0.33-0.86 mg/L; nitrates, 0.97-3.16 mg/L; and sulphates, 4.04-4.46 mg/L.

A comparison of the results of chemical and physicochemical studies with those obtained at other measuring stations in Europe is difficult for methodological or analytical reasons [12-15]. Other difficulties include the fact that the results are often presented in the form of histograms showing the distribution of a given parameter, or that deposition rather than concentration values are given, and arithmetic means cannot be compared with weighted means.

Electric conductivity as a summary measure of rainfall pollution can rarely be found in publications. In Poland precipitation observations carried out at Storkowo [21] and Łeba [1] supplies figures much smaller than those recorded at the stations described above - about 20 μS/cm. Equally low values (23 μS/cm) are reported for observations carried out in northern Italy [22]. High values (67 μS/cm) are given by Verhoeven for Germany [23]. More popular is information about pH and nitrate and sulphate ions associated with this parameter. The data presented in our paper are similar to those given in the literature for acidic precipitation in Central Europe, for which pH equals 4.3 [24]. Somewhat higher figures are reported for Lithuania [25], 4.7 in the years 1994-1999, and similar ones for Saxony, 4.3 [26].

The amounts of strong-acid anions reported for Central Europe [24] are equal to 3.4 mg/L for SO_4, 1.8 mg/L for NO_3, and 0.5 mg/L for Cl. The data published for Sweden [27] are lower: 1.8 mg/L and 2.2 mg/L, and for Lithuania, 2.28 mg/L and 2.79 mg/L, respectively. The Polish monitoring stations mentioned earlier report values close to 2 mg/L; they showed a downward tendency over the years 1994-1996. By comparison, the data given in our paper indicate a much lower content of nitrates, especially at station 2, and high concentrations of sulphates at stations 2 and 3 indicative of the dominant effect of pollution coming from the burning of fuels rather than from traffic-related pollution.

Conclusions

• At all the research stations the mean annual pH is lower than 5.2, and often drops below 4.6, a value characteristic of very acid precipitation.

• It is only at station no. 2 (Jeziory), situated in the middle of the Wielkopolski National Park, that the pH of rainwater tended to grow over the study period.

• One can state that at stations no. 2 (Jeziory) and 3 (Ojców) it is largely sulphate ions which contribute to rain acidity.

• When comparing the chemical compositions of atmospheric precipitation in the years 1996-1999, one can observe a distinct decline in the concentrations of sulphate ions at all the stations. The drop is most readily visible at station no. 1 (Rumia), situated near the Baltic Sea.

• The concentrations of nitrate ions at stations no. 1 (Rumia) and 2 (Jeziory) show a downward tendency.

• Man-made sources of pollution can be shown to have a big impact on precipitation at station no. 2 (Jeziory); the concentration of chloride ions is much higher there than at the seaside station no. 1 (Rumia), where most of them are probably of natural origin.

• The location of station no. 2 (Jeziory) in the Wielkopolski National Park is likely to have greatly reduced the inflow of transport-related pollution, as evidenced by an exceptionally low concentration of nitrates.

• The passage of rainwater through tree crowns modifies its composition considerably, both in terms of pH and ionic content. The biggest increase in the concentration is observed in the case of sulphates (station no. 1) as well as potassium and magnesium (station no. 2).

• Plans are made to seek correlation between the pollution of precipitation (concentrations of particular ions) and inflow directions of air masses in order to identify the most serious pollution sources.

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