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Results of long–term observations of basic physico–chemical data of atmospheric precipitation in a protected area in Western Poland

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ABSTRACT

The amount, pH, and electrical conductivity of precipitation, based on multi–year observations (1992–2013) carried out in the Wielkopolski National Park (WNP), are summarized. A systematic study of individual precipitation events in open terrain and in throughfall reveals that rainwater is still acidic here. As much as 78% of the precipitation tested had a pH of under 5.1; some very low pH values, even below 3.0, were observed occasionally. However, over the study period the pH of precipitation tended to grow systematically and electrical conductivity kept falling systematically. The mean electrical conductivity showed a slightly elevated level, but episodes with extremely high values (>1 000 μS/cm) could still be observed in throughfall. Studies of throughfall showed it to have a higher pH, but over the entire period its mean annual pH was lower than 5.1. Periods with a precipitation deficit are followed by those with excessive rainfall, which can be regarded as evidence for the instability of the climate. The results obtained were compared against long–term figures recorded at the stations monitoring background air pollution under the European Monitoring and Evaluation Program.

Keywords: *Wielkopolski National Park, pH, electrical conductivity, precipitation amount, tendency*

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1. Introduction

Investigating and assessing the chemical composition of precipitation and atmospheric deposition is essential for understanding how atmospheric pollutants contribute to contemporary environmental concerns, including ecosystem acidification and eutrophication, loss of biodiversity, air pollution, and global climate change.

In 1996, the first global assessment of precipitation chemistry was released as a World Meteorological Organization publication (Whelpdale and Kaiser, 1996). It provided a critical review of worldwide acidic atmospheric deposition. Although data were limited in many regions, the report provided an analysis of the acidic deposition phenomenon and contributed to its understanding. The lowest annual average pH, i.e. the most acidic precipitation, was calculated for the United Kingdom and Poland – about 4.3. Large parts of Central Europe had an annual average higher than 4.5, and in the western and south–western parts of the continent the average pH was higher than 5.0. This first assessment formed a basis for additional national and international initiatives designed to understand and reduce the adverse effects of acidic deposition. At a global scale, precipitation pH and H^+ wet deposition figures were published by Rodhe et al. (2002), who applied a chemical transport model to predict the geographical distribution of pH and the wet deposition of H^+. These authors estimated that the lowest pH values occurred in Europe, China, and Eastern North America.

Over the last ten years the interest in these issues in East–Central Europe has declined considerably. Generally, inquiry has tended to evolve towards model research or global recapitulations (e.g. Bouwman et al., 2002; Erisman et al., 2005; Westling et al., 2005; Torseth et al., 2012; Vet et al., 2014). It seems, however, that the complex nature of atmospheric precipitation may be understood better when the research accommodates not only the results of stations monitoring background air pollution under the European EMEP network (Co–operative Program for Monitoring and Evaluation of the Long–Range Transmission of Air Pollutants in Europe) on which models are usually built, but also changes in the composition of precipitation near large urban agglomerations or near emission sources.

This paper seeks to present and discuss the results of a long–term study of atmospheric precipitation conducted in an area which, although part of a national park, also experiences strong human impact. Apart from the rainfall amount, changes in its pH and electrical conductivity (EC) are described. While studies of the quality of precipitation provide information about its acidity, its EC is usually ignored. Even if the numerical value of this parameter does not provide exact information about the nature of pollution, together with pH it can supply crucial information, and in the case of multi–year measurements, also about the tendency of change over a longer time perspective. To illustrate the different natures of the processes, the results obtained were compared against long–term figures recorded at places free from direct human impact.

2. Experiments

2.1. Site description

The research was carried out at the Jeziory Ecological Station of Adam Mickiewicz University, situated in the Wielkopolski National Park (WNP) in West–Central Poland (52°15'56" N, 16°48'06" E). The sampling location is a forest clearing (80 m x 50 m) in a protected area surrounded by extensive patches of woodland; some 200 m away there is a road with moderate traffic, at an altitude of 82 m a.s.l. (Google Maps, 2014). The Wielkopolska Region, where the Jeziory Station is located, lies in the temperate zone, its climate being transitional between the continental and maritime types. Its characteristic feature is great fluctuations in the pattern of seasons in successive years. The mean multi–year values of parameters significant for the spread of pollution are as follows: temperature, 8.3 °C, mean relative humidity, 79%; mean wind velocity, 3.5 m/s, precipitation, 517 mm (Lorenc, 2005). The macro–scale air advection over the sampling site originates in the western quadrant (NW, W and SW), particularly in the middle layers of the troposphere (2 500–5 000 m a.s.l.). In the lower troposphere, in turn, air flow is frequently from the north, carrying short–distance transport from local emitters and from the Poznan agglomeration (Kolendowicz et al., 2011).

The Park is a valuable fragment of nature from the national perspective; it is also an element of the European Ecological Network Natura 2000. It measures 7 584 ha, and 14 840 ha together with its buffer zone. The research on the chemical composition of precipitation started at the Station in 1992; it indicates that the WNP receives a substantial influx of strong acids from atmospheric sources (Walna et al., 2003; Walna et al., 2004; Walna et al., 2007). A particular threat to nature in the Park is air pollution, caused mainly by the vicinity of Poznan, a city of 700 thousand inhabitants, 25 km north of the Park, as well as of a number of neighboring towns with populations of just under 10 thousand. Poznan is among the cities posing a high environmental threat through emitting air pollutants, although since 2005 one can observe a rapid decline in its SO_2 levels, while NO_X levels remain fairly constant (see the Supporting Material, SM, Figure S1) (GUS, 2013; Pulyk, 2013).

In a wider, regional perspective (the Wielkopolska region), the scale and structure of gas emissions are largely determined by the power–industry sector (70% of emissions). When analyzing the sum total of emissions from plants known as particularly burdensome, one can note a systematic drop in SO_2 levels, with a stepwise reduction to one–fifth of those over the years 2008–2009, while the NO_X level only decreased by 35% between 1992 and 2011 (GUS, 2013). Another significant contributor to the pollution of precipitation is a large chemical plant, situated 10 km north of the collection site. It has been manufacturing phosphate fertilizers, hydrofluoric acid, and sulfuric acid for years. Its effect on the acidity and fluoride content of precipitation was described, among others, in Kolendowicz et al. (2011), Walna et al. (2007) and Walna et al. (2013).

Gaseous pollutants also come from distant sources. During the several decades, Europe has experienced large reductions in emissions. Those of sulfur dioxide were reported to drop by 65% between 1990 and 2009 (EMEP/CEIP, 2011). The economic recovery in Eastern Europe led to increased NO_X levels from road traffic in this area after 2000 (Vestreng et al., 2009), but on the other hand, NO_X emissions from traffic in Western Europe decreased by 31%, and most of this reduction occurred in the first decade of the century (Torseth et al., 2012). In Poland (GUS, 2013), one can observe a significant drop in SO_2 levels, from 2 820 thousand tonnes in 1992, to 910 thousand tonnes in 2011. But NO_X emission was much slower to change in that period: from 1 130 thousand tonnes to just over 800 thousand tonnes, and since 2000 it has remained at roughly the same level.

2.2. Methods

The precipitation research was conducted between 1 January 1992 and 31 January 2013. Because the sampling extended over a long period, care was taken for protocols to always be the same and for the collectors and bottles to be of the same types. Bulk precipitation, which is defined as atmospheric deposition collected in an open funnel in a location not affected by the vegetation canopy, was gathered by means of funnel–shaped plastic collectors with a diameter of 56 cm and a height of 47 cm. A 24–cm–high edge prevents the splattering of samples, while a small outlet 1.5 cm in diameter adheres directly to a polyethylene container (5 L) collecting rainwater. The apparatus is supported on a steel stand 1.5 m high. The considerable dimensions of the rain gauge (2 461 cm^2) allow an analysis of even minimum precipitation (<1 mm). Field samples were collected and analyzed immediately after each rainfall event. The program of the research on atmospheric precipitation in open terrain was enriched by studies of throughfall collected under the crown of deciduous trees. For this purpose, similar rain gauges were set up among nearby oak trees. The trees are about 40 years old and 30 cm in diameter.

Efforts were made to collect all precipitation that fell at that time, but for technical reasons, or due to contamination by birds, the percentage of total rainfall analyzed was 92–97%. The number of precipitation samples in the calendar year ranged from 49 (2011) to 93 (2008), 65 on average. The number of throughfall samples was smaller (58 on average) than of those collected in open terrain.

Quantitative studies were made using a manually operated Hellmann rain gauge and an automatic TPG 962 as part of an ASTER station (10 min intervals, 0.1 mm sensitivity), equipped with automatic heating in winter when air temperature falls below 1 °C. Additionally, the amount of precipitation was calculated by dividing the volume of rainwater caught in a collector by its area.

Immediately after a precipitation event, measurements were made in a nearby laboratory of the pH of rainwater [an Elmetron CP 315 pH–meter with a low ionic strength buffer in compliance with ISO (2008)] and its specific electrical conductivity [an Elmetron CC 311 conductivity meter in compliance with ISO (1985)]. Both determinations were performed on unfiltered samples.

A statistical analysis of the results was made. The normality of the distribution was checked by the Kolmogorow–Smirnov and Lilliefors tests. For statistical trend analysis, nonparametric Mann Kendall–tau tests were applied to examine the significance of trends for all pH values, electrical conductivity, and amount of precipitation. This test is recommended by the WMO for this kind of data, and is suitable because it is not particularly sensitive to missing data or outliers, and requires no assumption of normality (Gilbert, 1987; Hunova et al., 2014). The slope of the trend was calculated using the nonparametric Sen's method. A simple linear regression model was used for slope estimates for annual means. The significance of differences was estimated using Mann–Whitney tests.

The annual volume–weighted mean of the pH values was calculated from mean volume–weighted H^+ concentrations. The annual average electrical conductivity was calculated as volume–weighted values.

3. Results and Discussion

3.1. Precipitation amount

Monthly rainfall. In spite of substantial differences in the monthly precipitation totals in the individual years, their means over the years 1992–2013 were similar to mean monthly figures obtained in