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Original Research

Chemism of Atmospheric Precipitation as a Consequence of Air Pollution: the Case of Poland's Holy Cross Mountains

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Abstract

Physicochemical properties and chemism of atmospheric precipitation, influenced by atmospheric air pollution, are a major element affecting contemporary degradation of the natural environment. It is known that water, apart from its function as a partner in physical reactions, is also the carrier of anthropogenic transformation of the natural environment. Acid rain is all the rain, snow, and mist that contain an unnatural acid. The major sources of acid rain are sulfur dioxide (SO_2) and nitrogen oxides (NO_x) in the atmosphere. Rainwater in equilibrium with carbon dioxide in air is slightly acidic (pH>5.6). However, rainwater is often more acidic due to the natural emissions of SO_2, NO_x, or organic acids. The typical pH values of acid rain resulting from anthropogenic emissions are in the range of 3.5-5.0 [1].

In the literature [2, 3], much discussion is devoted to the problem of acid rain and its adverse influence on forest ecosystems. The combustion of fossil fuels, carbon in particular, has caused a noticeable increase of sulphur emissions to the atmosphere, which has consequently led to higher deposition of sulphur in ecosystems. Atmospheric deposition occurs both in the vicinity of the combustion source and in extensive areas adjacent to industrial and urban centres. As early as the 1970s and 1980s, several attempts were made to Oden [4]. It is known that forest ecosystems are among the most sensitive to atmospheric deposition of acid components. In the more sensitive ecosystems of temperate regions, this accelerated supply of sulphur has caused dramatic changes to chemical composition of soil solutions, and is partly responsible for spreading forest dieback, especially in the mountains [5, 6]. Another consequence of increasing acidification of the soil environment is the increasing mobility and availability of heavy metals [7-9] and an increase of panning of lifegiving elements [10].

Keywords: atmospheric immission, precipitation, acid rain, forest ecosystem, sulphur deposition

Introduction

As research has indicated, the natural environment is subject to continuing transformations and changes due to natural factors and human activity. Understanding the operational mechanisms of the natural environment as well as specification of multi-directional tendencies for their change are of major importance for both theory and practice [11]. The changes that occur in the natural environment are not only of local or regional, but also of global significance. Taking a slow course, they often lead to catastrophic results. An understanding of the operational mechanisms of the natural environment based on thorough knowledge of its past development, recognition of its present state and

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capacity for specifying future tendencies for change is necessary.

Among major elements which determine the cycle of matter in geoecosystems is atmospheric deposition. The air which forms the atmosphere around the earth is an environment into which natural and anthropogenic pollutants are introduced. The pollutants' mobility and extensive spread causes these substances to pass into other environmental components, great distances from their emission sites. Deposition of these components can occur on the dry, wet, and humid ways, causing adverse effect to the environment. Consequently, it is so important to understand the load of substance carried in this way to geoecosystems. Begun in 1994, research in the central part of the Holy Cross Mountains has shown that excess deposition of acidifying components can lead to, for example, deterioration of tree stand well-being, as well as acidification of soil, throughfall, stemflow, and surface waters [12].

Study Area and Experimental Procedures

The study was conducted at the Monitoring Station of Jan Kochanowski University in Kielce, located in the Holy Cross Mountains, at 595 m above sea level, in 2000-08 (Fig. 1). The atmospheric precipitation (wet+dry) was measured at the height of 30 m, i.e. 4 m above tree crowns. For this purpose, in accordance with the integrated monitoring measurement programme requirements, a Hellman rain gauge and a Vaisala rain gauge were used. The measurements were taken in a weekly cycle. Direct field measurements were taken of the physicochemical properties (pH, electrical conductivity) and precipitation height. For the measurement of the physicochemical properties, the Horiba U-10 sensor was used, calibrated each time prior to a measurement series.

For laboratory tests, a water sample was collected to a one-litre Brand polyethylene container. The samples were immediately transported to a laboratory to be stored at 4ºC. Weekly samples were used to make a monthly sample whose chemical composition was determined. The chemical composition was determined with the use of the UV-vis spectrophotometer and MERCK tests; the content of Ca^{++}, Mg^{++}, Na^{+}, K^{+}, NH_4^{+}, SO_4^{--}, Cl^{-}, and NO_3^{-} were determined using a flame photometer. Since 2005, this has been done at the laboratory of the Institute of Environmental Protection in Warszawa, with the use of a Dionex ion chromatograph. The content of SO_4^{2-} ions was analyzed.

The SO_2 immissions volume was analyzed by a Horiba APSA 350E analyzer. The measurements were taken over an automated cycle. The obtained data were averaged to 30-minute values, and then to average daily values, with the reservation that the value be calculated from a minimum of 36 correct 30-minute results. To draw backward trajectories, the HYSPLIT model was applied.

Statistical and Graphic Processing

In order to identify trends, correlations and levels of statistical significance of the parameters under determination, the collected data were statistically processed with the Statistica v. 6.0 and Origin v. 6.0 software. Spearman's non-parametric rank correlation test and Pearson's correlation coefficient were applied.

Results and Discussion

The presence of local- and remote-origin pollution in atmospheric air is the reason for acid rains in the central part of the Holy Cross Mountains [13, 14].

The studied physicochemical properties (pH, SEC) have shown that average weighted pH values for bulk precipitation over the multi-year period of 2000-08 amounted to pH 4.73, ranging from pH 4.35 in 2008 to pH 5.30 in 2004 and 2007 (Fig. 2). The analysis of data pertaining to the frequency of precipitation with specific pH levels was

Fig. 1. Location of the monitoring station in the Holy Cross Mountains.

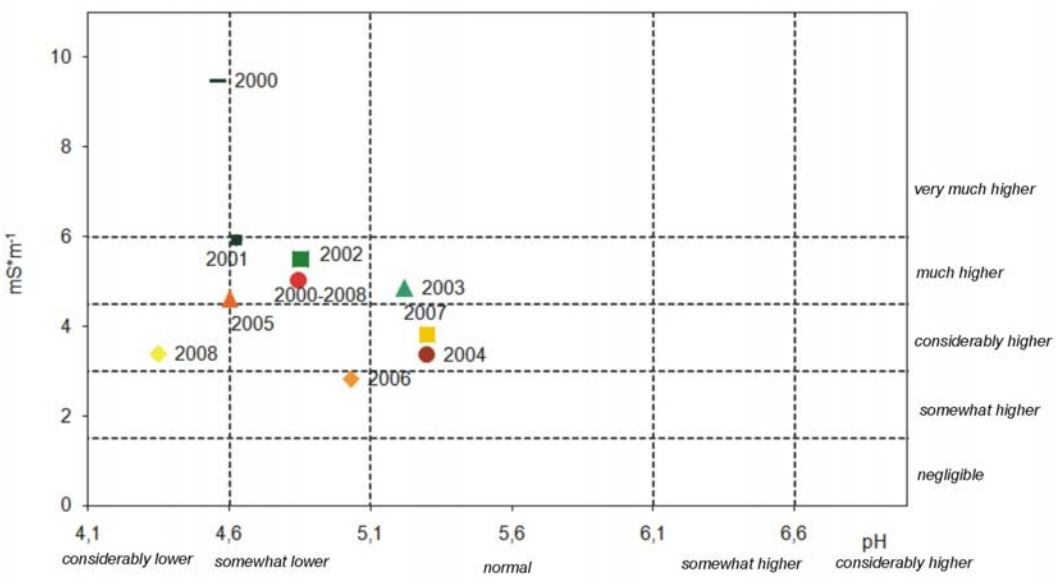

Fig. 2. Assessment of pH and electrolytic conductivity of atmospheric precipitation in 2000-08.

performed based on the assessment by Jansen et al. [15]. The obtained nine-year average pH value enable the classification of atmospheric precipitation in the Holy Cross Mountains as precipitation with somewhat lower pH levels.

Over the nine measurement years, 379 weekly data were obtained. In 168 cases, precipitation with pH levels below 5.1, ranging from 5.1 to 6.1, and 43 cases of the pH range exceeding 6.1, were recorded. Among all the classes as distinguished by Jansen et al. [15], the highest share belonged to precipitation whose pH ranged from 5.1 to 6.1 (44.3%) and from 4.6 to 5.1 (24.8%). The lowest frequency was found in precipitation whose pH>7.1 with the share of 0.8% (three cases). The conducted annual analysis of pH-specific precipitation frequency has shown that the years 2000-01 and 2008 were characterized by the highest share of precipitation with pH levels below 5.1. In 2000, the percentage of precipitation with pH<5.1 amounted to 65.4%, 68.4% in 2001, and 66.7% in 2008. The years 2002, 2003, 2005, and 2007 were characterized by the highest percentage of precipitation classified as normal (pH 5.1-6.1) (Fig. 3).

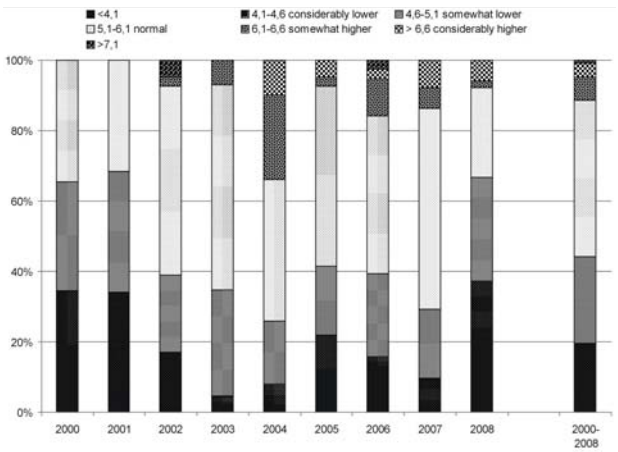

Fig. 3. Frequency of pH-specific precipitation in 2000-08.

The seasonal pH analysis shows that the lowest values were recorded in winter months. The reason for acidity growth in this period is the increased emission of acidic components into the air related to the heating season. Highest pH values were noted in spring and summer months. The results obtained in the Holy Cross Mountains are typical of extensive areas in Poland [16] and Europe [17-19].

The value of electrical conductivity (SEC) indicates the content of substances dissolved in water. In the multi-year period, conductivity values in bulk precipitation ranged from 2.82 (2006) to 9.48 $mS \cdot m^{-1}$ (2000), with the average weighted amounting to 5.02 $mS \cdot m^{-1}$. In the research period, according to the classification of Jansen et al. [15], conductivity values lowered considerably, from the much higher in 2000 to the somewhat higher in 2006 (Fig. 2).

This tendency clearly points to an improvement in atmospheric air quality and a decrease in the quantity of components deposited in the Holy Cross Mountains. Seasonal dynamics of electrolytic conductivity, inversely proportional to the pH value, has also been noted. Maximum conductivities were noted at minimum pHs, and vice versa. Minimum conductivity values were noted in warmer months (May to September), higher in the colder months (November to March).

The reduced volumes of $S\text{-}SO_2$ emissions to atmospheric air in Poland have been reflected in the decreasing concentrations of this gas in the Holy Cross Mountains as well (Fig. 4) and $S\text{-}SO_4$ loads delivered to the substratum with bulk precipitation.

Thanks to this, descruse of conductivity values described above occurs. As the research of Aikawa and Hiraki [20] show, concentrations of SO_4^{2-} in rain water influence conductivity. The correlation factor obtained by these authors, which amounts to 0.80 strong correlation of conductivity and concentration of SO_4^{2-}.

Table 1. Total SO_2 emission in the professional power industry in Poland in 1995-2008 [21, 22].

Source	1995	2000	2002	2003	2004	2005	2006	2007	2008
	Gg								
Professional power industry	1223	805	706	722	704	673	717	664	448

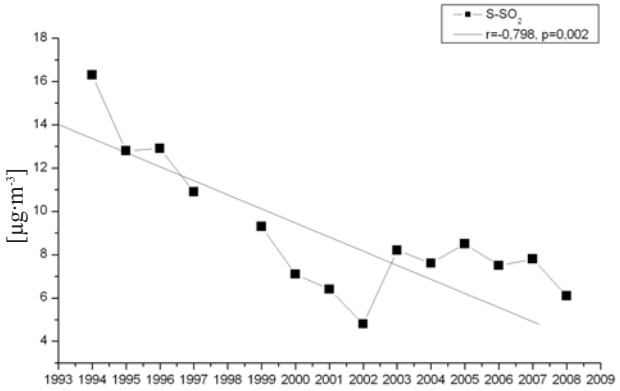

Fig. 4. Changing $S-SO_2$ concentrations in atmospheric air in the central part of the Holy Cross Mountains.

As has been demonstrated by studies into $S-SO_2$ immissions volume conducted over the years 1994-2008, there occurs a statistically significant downward trend in the concentrations of this gas. The obtained result r, which amounted to -0.798, indicates a very high correlation. This trend results on the one hand from the economic crisis, and on the other from pro-environmental investment projects implemented at company level. The date contained in the statistical yearbook of the Polish Statistical Office in 1995-2008 clearly shows the decrease of SO_2 emissions amounting to, for example in the professional power industry, more than 60%. These years can be divided into two periods. The first one comprising the years 1995-2002, when the emission decreased from 1,223 to 706 Gg, and in 2003-08 it underwent fluctuations and in the year 2008 it amounted to 448 Gg (Table 1).

It is estimated that in Europe, depending on the region, the decrease of the volume of sulphur deposited in the last two decades, from the end of the 70s, amounts to from 70 to 90% [23]. In eastern German states in 1992-95, a 70% decrease in $S-SO_2$ immissions volume was noted [24].

Research has also clearly demonstrated a decrease in $S-SO_4$ deposition volume, which is in accordance with other research carried in this part of Europe [19, 25]. A linear regression chart indicates another statistically significant trend at the significance level of $p<0.001$, and the obtained result r indicates average correlation. The highest load was noted in 2001 (30.87 kg $S-SO_4$ $ha^{-1}\cdot a^{-1}$), and the lowest in 2004 (3.49 kg $S-SO_4$ $ha^{-1}\cdot a^{-1}$). Maximum values of sulphate load were noted in winter months. Higher values in winter months tend to be lower in warmer periods, with minimums between May and September, resulting from lower industrial emissions (Fig. 5).

The conducted analysis of the correlation between $S-SO_2$ concentration volumes and direction of air mass inflow has shown that increasing concentrations are observed when air masses flow into the Holy Cross Mountain area from SW (Fig. 6). This is suggested by analyses of backward trajectories charted with the HYSPLIT model. It is an effect of pollution emitted from industrial centres of Poland and the Czech Republic which cumulate in the air [26]. In the case of air mass inflow from N, a visible drop in the observed $S-SO_2$ concentrations in atmospheric air occurs. The northern air mass inflow routes do not contain any significant emission sources. Relation of air mass inflow with the use of this model and pH volume of rain water was found by Lekouch et al. [27].

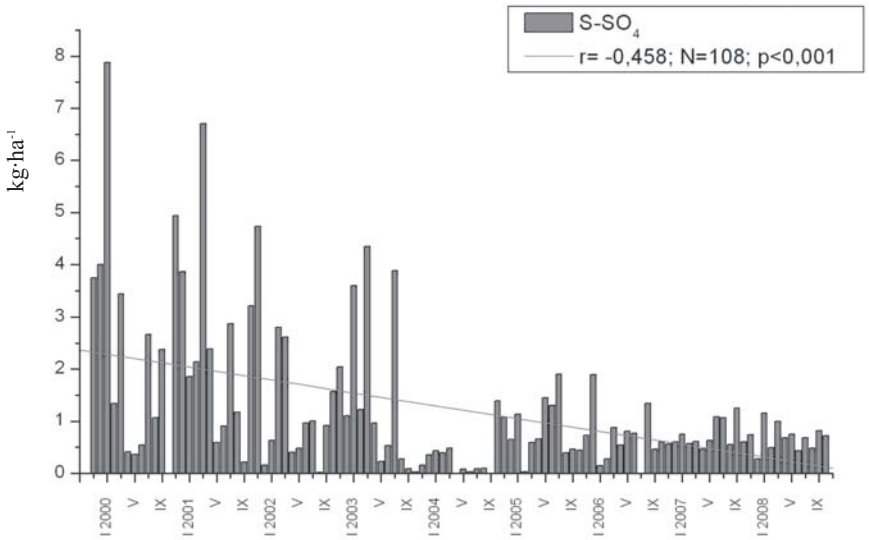

Fig. 5. Monthly deposition of $S-SO_4$ load in 2000-08.

Based on the studies by Smith et al. [5] and Smith and Fowler [28] conducted in Great Britain, it has been noted that 50% of the sulphur present in the atmosphere reaches ecosystems with atmospheric precipitation. Research carried out in Japan [29] show a clear relationship between acidity and the Mount of SO_4^{2-} in rain and the presence of sulphur in the air.

The average weighted pH value of atmospheric precipitation, despite the considerable drop in the sulphur load with atmospheric precipitation, continues at a level markedly different from the value characteristic of unpolluted precipitation. These are values characteristic of extensive areas in Poland and Europe [16, 19]. Of major importance in the shaping of atmospheric precipitation chemism are distant emission sources.

Conclusions

The hitherto conducted research into atmospheric air and precipitation quality has shown that the elevation of the Holy Cross Mountains above the surrounding areas causes their exposure to pollutant immissions of both local and remote origin from the dominant S, SW, and W wind directions. An analysis of data obtained in the Holy Cross Mountains has demonstrated that total yearly sulphur loads delivered to the substratum with atmospheric precipitation in 2000-08 have dropped. These results are confirmed by the above-discussed classification of precipitation on account of reaction and electrolytic conductivity. Hence, it may be stated that the investigated geosystem has shown a positive change trend toward

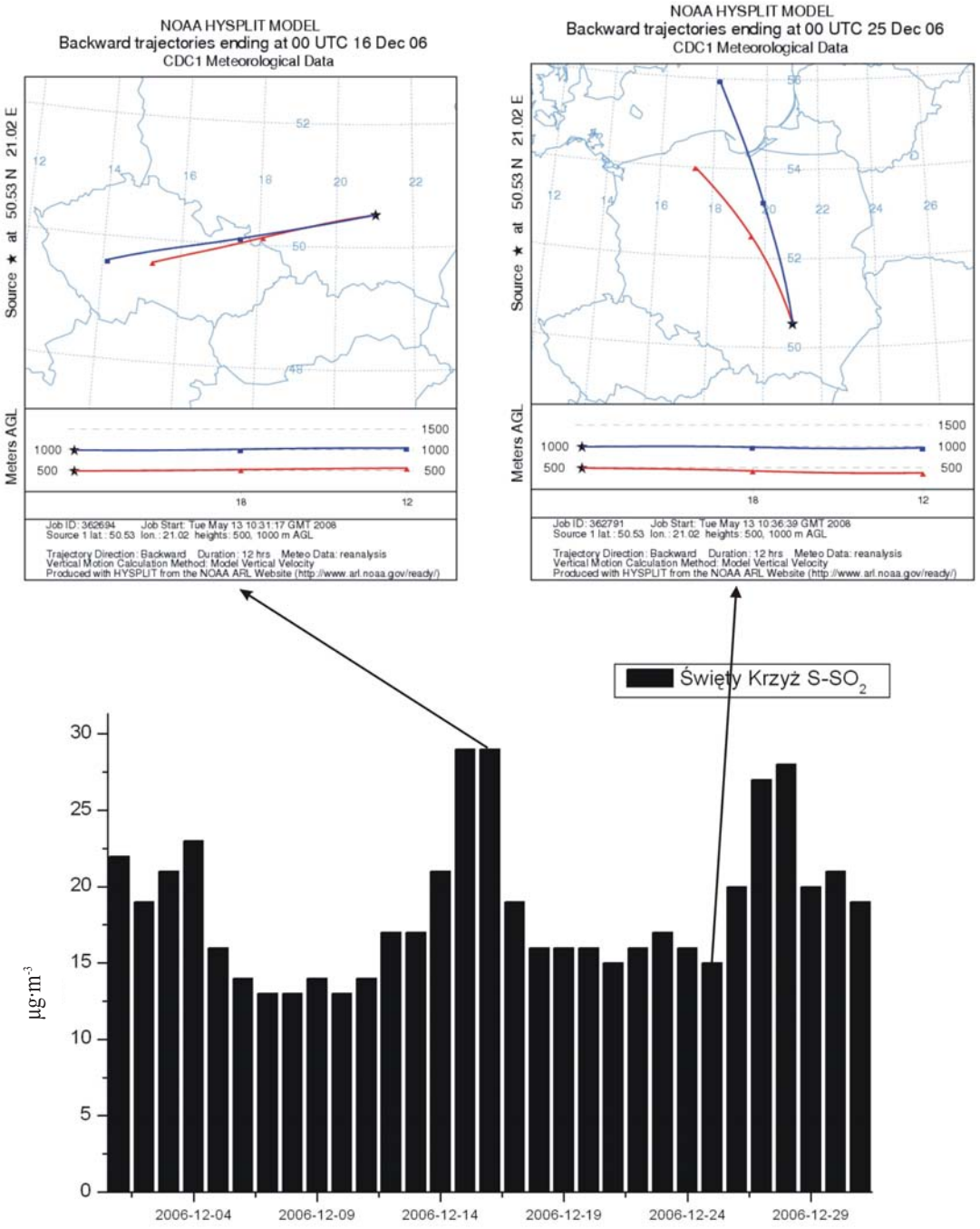

Fig. 6. Correlation between immission volume and air mass inflow direction. Backward trajectories were drawn with the HYSPLIT model.

"normalization" of the precipitation in terms of pH values and electrolytic conductivity. The multi-year monitoring of the chemism of atmospheric precipitation enables a statement that the present state of the natural environment in the Holy Cross Mountains depends, to a large extent, on the S-SO_4 deposition volume. Its impact on vegetation, soil, and water is longitudinal, synergic, or antagonistic, which leads to changes in soil acidity and matter cycle, the result of which is the accelerated dieback of old-growth fir-tree forests.

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