

Sulphur Input to the Niepołomice Forest: Changes during 30 Years (Southern Poland)

G. Szarek-Łukaszewska*

W. Szafer Institute of Botany, Polish Academy of Sciences, ul. Lubicz 46, Kraków, Poland

Received: 28 June, 2002

Accepted: 19 September, 2002

Abstract

The Niepołomice Forest, a large forest complex typical of Central European lowlands, is located near an urban-industrial agglomeration in southern Poland. During the past 20 years, SO₂ emissions from industry decreased from 75,000 t yr⁻¹ to 6000 t yr⁻¹. Concentration of SO₂ in the air, and pH, SO₄⁻² concentration in bulk precipitation were measured during the last 11 years and compared with data from the 1970s. The spatial distribution of concentrations and deposition of S were calculated on the basis of 30 bulk precipitation samples in 1999-2000. Mean annual concentration of SO₂ in the air was 8.25 μg m⁻³ in 2000, that is 2.5 times lower than during the period 1967-1978. At the beginning of the 1990s the concentration of SO₂ exceeded the critical level for plants during 3% of the days over the year, and at the end of the 1990s only on single days. In 1999 and 2000 the yearly mean concentration of S-SO₄⁻² in bulk precipitation in the Niepołomice Forest was 1.11 mg l⁻¹, ranging between 0.99 and 1.27 mg l⁻¹ in the forest complex. The yearly mean sulphur deposition (S-SO₄⁻²) was 8.1 kg ha⁻¹, varying from 7.3 to 8.9 kg ha⁻¹. The present concentrations and deposition of S-SO₄⁻² were a quarter those of 1974-1978. The spatial distribution of S deposition pointed to the influx of S compounds to the Niepołomice Forest with air masses from the west. The yearly mean pH of atmospheric precipitation was 4.64 (1999-2000), and was steady within the forest complex. In the Niepołomice Forest, atmospheric precipitation was more acid recently than in the 1970s.

Keywords: SO₂, bulk precipitation, SO₄⁻², forest, Southern Poland

Introduction

Sulphur is an important element in the biogeochemistry of forest ecosystems because of its role as an essential plant nutrient and because of the contribution of sulphur compounds to the cycles of other elements (e.g. H, Al, Ca, Mg) in ecosystems [6]. Despite the low atmospheric content of sulphur compounds, the annual total flux of sulphur through the atmosphere rivals that of the nitrogen cycle [15]. Combustion of fossil fuel, especially coal, releases a large amount of sulphur into the atmosphere. Forest vegetation is an important recipient of airborne sulphur compounds produced by industrial activities because of the reactivity and scavenging efficiency of its

large canopy surface area. The primary forms of airborne pollutant S that are most important to deposition and its effects on the forest system are the oxides SO₂ and SO₄⁻². Both are emitted directly from industrial sources, with SO₂ contributing more than 90% of the total [13].

The high deposition of sulphur from the atmosphere has induced many negative processes in forests. Excessive amounts of sulphur compounds affect the vegetation both directly and indirectly. An important effect of S deposition is extensive acidification, which contributes to nutrient imbalance and destabilization of the forest ecosystem. Forests situated in the neighbourhood of emission sources are most liable to suffer from pollution. An example is the Niepołomice Forest a large forest complex typical of the lowlands of Central Europe. As a result of industrial development, in the 1950s a large

*e-mail: szarek@ib-pan.krakow.pl

urban-industrial agglomeration arose in the vicinity of the forest. In the middle 1970s the effects of pollutant emissions were observed in the forest. At that time the Niepołomice Forest became an object of intense ecological research [e.g., 3]. On the basis of that research the future of the forest was prognosticated. The conclusion was that if pollution would continue to affect the forest to a similar extent, the following 20 years would be crucial for its survival. However, political and economic changes in Poland at the turn of the 1980s/90s led to a considerable decrease in industrial production and, in consequence, emissions of pollutants. In 1998 a program entitled "Natural and anthropogenic effects upon the functioning of forest ecosystems – 50 years of changes in the Niepołomice Forest" was prepared. One of the program objectives was to determine the present input of airborne pollutants and changes in during past decades.

The present work was part of this research, addressing sulphur deposition from the atmosphere to the Niepołomice Forest and its temporal and spatial variability.

Site Description

Niepołomice Forest is situated in the southern, most industrialized part of Poland. The forest border is 10–35 km to the east of the urban-industrial Kraków agglomeration (Fig. 1). In 1954 a steelwork was built at the eastern periphery of the city. General characteristics of the Niepołomice Forest are given in Table 1.

Table 1. General characteristics of the Niepołomice Forest.

Location	49°59' - 50°07'N 20°13' - 20°28'E
Area	110 km ²
Bedrock	Pleistocene fluvioglacial sands underlain by or intercalated with sediments, fertile alluvia of the Vistula River, cohesive, very fine sands and heavy loams with sand or sandy-loam intercalations in bottom layer
Soil	grey brown (lessive) podzolic soils, brown, podzolized, gleyed soils, old warp soil
Wind	mainly from western quadrants
Precipitation (annually)	700 mm
Air temperature	+8.2°C (VII +18°C, I and II -3°C)
Vegetation period	218 days
Forest (vegetation)	coniferous, mixed deciduous forest
Main tree species	<i>Pinus sylvestris</i> , <i>Quercus robur</i>

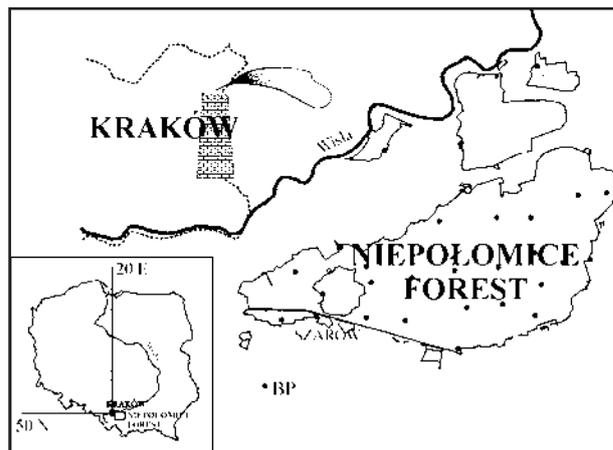


Fig. 1. Location of the Niepołomice Forest and bulk precipitation (BP) collectors in the forest complex.

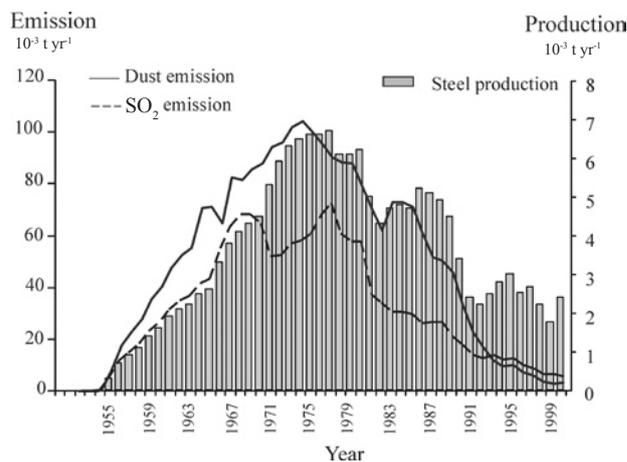


Fig. 2. Steel production, dust and SO₂ emissions from the steelwork from 1954 to 2000.



Fig. 3. Emissions of dusts and gases from the province of Kraków during 1978 - 1998 (GUS 1977 - 1999).

Materials and Methods

Data on emissions of SO₂ and dusts by the steelwork during 1950–2001 were obtained from the Department of Environmental Protection of the steelworks, and data on emissions for the whole region of Kraków for 1976–1998 from statistical year books [4]. Daily concentrations of SO₂ in the air, measured continuously in Szarów (south-western edge of the Niepołomice Forest) (Fig. 1) in 1989–2000, were obtained from the Provincial Inspectorate of Environmental Protection in Kraków [17].

In the Niepołomice Forest, bulk precipitation (BP) was collected at 30 stations regularly distributed in open areas in the forest (Fig. 1). The rain collectors were plastic funnels (15 cm in diameter), covered with fine mesh, connected to plastic 2 l containers covered with aluminium foil against the light. The snow collectors were 5 l containers (25.8 cm in diameter). The collectors were placed 2 m above the ground. From January 1999 to December 2000, water fluxes were measured at 2-week intervals. The collectors were replaced after each sampling. The volume and pH of each sample were measured, and concentrations of SO₄⁻² were determined by ionic chromatography (Dionex 100). Using the same method, ion concentrations were determined in bulk precipitation, collected every month from 1993 to 1998 at the station in Szarów.

The deposition of S-SO₂ to the forest was estimated from measured SO₂ concentration in the atmosphere and the deposition velocity of SO₂ to the forest. The deposition velocity (Vd) of SO₂ to the forest ranges from 0.2 to 2 cm/s. In this paper Vd=0.008 cm/s was accepted after Grodziński et al. [3]. The deposition of S-SO₄⁻² was calculated by multiplying ion concentration by water flux in a given time. Statistical analyses used the 2-weeks or monthly mean concentration of SO₂ in the air, and the 2-week concentrations, monthly weighted mean concentration and mean deposition of SO₄⁻² and H⁺, with regression analysis and test of randomness. Statistical analysis employed the Statgraphics package. Spatial interpolation of data employed the Surfer package.

Results and Discussion

SO₂ in Air

In 1954 the steelwork in Kraków started to produce steel, and as production rose emission of pollutants increased (Fig. 2). In 20 years it reached a very high level, 75,000 t SO₂ per year and 100,000 t dust per year. During the next 20 years, emissions decreased to the present level of 6000 t SO₂ and 3000 t dust per year. Emissions from other sources in the Kraków region also decreased from the late 1970s to 1990s (Fig. 3). In the 1990s dust emissions continued to decrease as disused works were closed and modern technologies were installed in existing works, but gas emissions remained unchanged. Dusts emitted by

industrial sources neutralized acid compounds originating from gas emissions in the atmosphere. Thus the reduction in dust emissions did not improve the situation of the Niepołomice Forest because the precipitation was more acidic.

The mean annual concentration of SO₂ in the air was 8.25 µg m⁻³ in 2000, lower than during 1967–1978 (20 µg m⁻³) [7]. Concentrations of SO₂ for the Niepołomice Forest were lower than those in the neighbouring agglomeration of Kraków (24 µg m⁻³ in the end 1990s) [17] and higher than in some areas situated far from industrial centres and towns in Denmark (from 12 to 22 µg m⁻³ in the 1970s and 2.6 SO₂ µg m⁻³ in the 1990s) [5].

SO₂ concentrations showed cyclic variability over the year (Fig. 4) (test of randomness p<0.01). The highest were noted in the cold half of the year (October–March); the mean concentration was 32.40 µg m⁻³ in 1989 and 12.06 µg m⁻³ in 2000. Concentrations in the warm half (April–September) were much lower, 8.80 and 4.65 µg m⁻³, respectively. Grodziński et al. [3] found seasonal differences in ambient SO₂ in the Niepołomice Forest in the 1970s but the concentrations were higher, 36.35 µg m⁻³ average in the cold half of the year and 11.98 µg m⁻³ in the warm half in the 1970s.

High concentrations of pollutants in the air in the cold, season are connected with intense combustion of coal, which is an important fuel and in the past was the main one. The degree of air pollution depends not only on the amount of emissions but also on meteorological factors. Winds in the Niepołomice Forest area blow mainly from the west. In winter, a fairly constant balance of air masses causes SO₂ to be steadily propagated in the same wind direction [7]. Seasonal variability of daily SO₂ concentrations in the air, with the highest concentrations in winter months, is characteristic of the whole of Poland [9]. In the cold half of the year concentrations in the Niepołomice Forest were ~5 times higher than in the northern “clean” part of the country, and about ~4 times lower than that of the mining and metallurgy industrial district of Upper Silesia [9].

A negative linear correlation was established between the mean monthly concentration of SO₂ in the air and the amount of monthly atmospheric precipitation in the Niepołomice Forest during 1993–2000 (r= -0.49, log-transformed data). It seems that rainfall removes SO₂ mostly from higher strata of the atmosphere, and only small amounts of locally produced gas are washed away by rain.

For plants the critical levels of SO₂ for acute effects from short-term exposure (one day or less) and for chronic effects from long-term exposure (one year) are 70 µg m⁻³ and 20 µg m⁻³, respectively [2]. In 1975–1977 a level of 70 µg m⁻³ was exceeded on over 9% of the days, and more often in cold (15% of the days) than in warm (3%) periods [3]. At the beginning of the 1990s the concentration of SO₂ exceeded the critical level on only 3% of the days over the year, and at the end of the 1990s only on single days.

S Deposition with Precipitation

In 1999 and 2000 the mean yearly concentration of $S-SO_4^{-2}$ in bulk precipitation in the Niepołomice Forest was 1.11 mg l^{-1} , ranging between 0.99 and 1.27 mg l^{-1} in the complex (Fig. 5). The mean yearly sulphur deposition ($S-SO_4^{-2}$) was approx. 8.1 kg ha^{-1} , varying from 7.3 to 8.9 kg ha^{-1} (Fig. 5). The highest concentration and deposition of sulphur were found in the northern and western fragments of the Niepołomice Forest. The present mean yearly concentrations and deposition of $S-SO_4$ were 4 times lower than in the years 1974-1978 [3]. Just as in the 1970s, the concentration and deposition of $S-SO_4$ were higher in the western part of the forest as compared with its centre. This spatial distribution pointed to the influx of sulphur compounds to the Niepołomice Forest with air masses from the west [8].

The input of S from the atmosphere to European forests, estimated on the basis of bulk precipitation, may amount to a few or a few dozen kg ha^{-1} per year [16]. In Sweden, in forests situated far from industrial centres it was $2.6 - 15.9 \text{ kg ha}^{-1}$ [11, 1], while in forests growing in highly industrialized regions in Germany it was as much as 86.4 kg ha^{-1} in 1973 and 48.1 kg ha^{-1} in 1991 [12]. Compared with these forests, S deposition from the atmosphere to the Niepołomice Forest may be considered low at present, and average in the 1970s.

The concentration of SO_4^{-2} in bulk precipitation was negatively correlated with the amount of precipitation (water) ($r = -0.81$, log-transformed data), while deposition was positively correlated with the amount of precipitation ($r = 0.78$). The composition of rainwater is determined by two processes: rainout (in-cloud removal) and washout (below-cloud removal). The compounds below clouds are scavenged by precipitation and greatly contribute to the high concentrations found in lower rainfall. On the other hand, the impurities contained in clouds and removed by rainout predominate in the high deposition found particularly for high precipitation amounts. The negative correlation between the concentration and amount of precipitation indicated that dry deposition (local emissions) was an important source of S flux. The positive relationship between S deposition and precipitation amount suggested that long-range transport was an important source of the element.

Seven years of studies in the Niepołomice Forest have shown no distinct pattern of seasonal variability of SO_4^{-2} concentrations in bulk precipitation (test of randomness $p > 0.05$).

Total Deposition of S

Total deposition of sulphur, which is the sum of dry deposition of sulphur (calculated on the basis of mean yearly concentrations of SO_2) and wet deposition (calculated from BP $S-SO_4$ deposition) for the Niepołomice Forest over the years is shown in Figure 6. In the 1990s, sulphur deposition decreased to about half the deposition

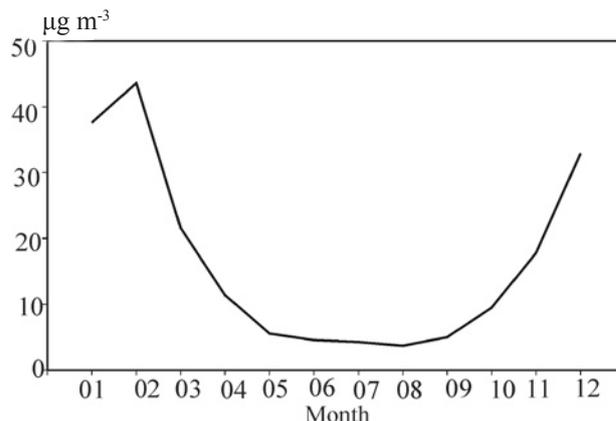


Fig. 4. Mean monthly concentrations of SO_2 (1989 - 2000) in the air in the Niepołomice Forest.

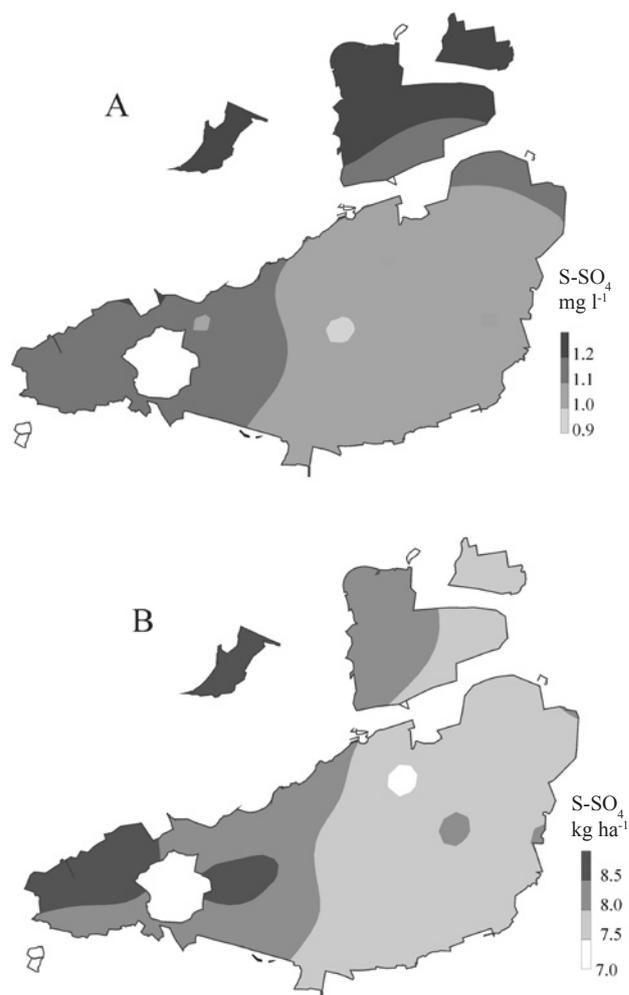


Fig. 5. Spatial pattern of $S-SO_4^{-2}$ mean yearly A - volume-weighted concentration, B - deposition in the Niepołomice Forest (1999 - 2000).

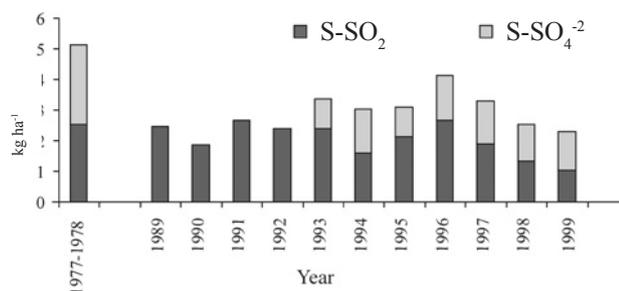


Fig. 6. S deposition from the atmosphere to the Niepołomice Forest.

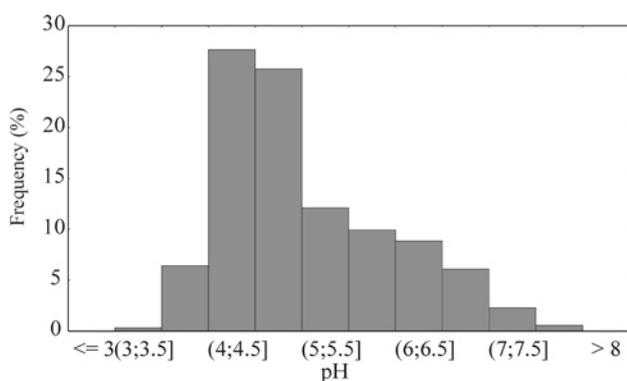


Fig. 7. Histogram of frequency distribution of pH of precipitation in the Niepołomice Forest in 1999 - 2000.



Fig. 8. Spatial pattern of precipitation with pH < 5.0 in the Niepołomice Forest, expressed as percents of all samples.

in the 1970s [3]. Dry S deposition was similar to or lower than wet deposition. A value 32 of kg ha⁻¹ per year may be judged the critical load of S to forest ecosystems in the environs of Kraków [14]; the present influx of sulphur to the Niepołomice Forest does not exceed this critical value.

pH of Atmospheric Precipitation

In the Niepołomice Forest the yearly mean pH of atmospheric precipitation amounted to 4.64 (1999-2000), and was rather consistent within the forest complex (4.52-4.93 pH). Figure 7 illustrates the frequency distribution of pH values for the Niepołomice Forest. These values range from 3.41 to 7.84; ~ 60% of the samples of bulk precipitation were acidic (pH < 5.0). A pH value of 5.0 is used to differentiate whether if the rain event is acidic and contaminated by anthropogenic sources [10], because some background sulphur components can further lower a CO₂-equilibrated pH of 5.6 to this level.

In the Niepołomice Forest, atmospheric precipitation is more acidic now than in the '70s [3]. At the measurement station situated on the northern border of the Niepołomice Forest (Hysne), mean pH was 4.66 and 5.20, respectively, and at the measurement station in the centre of the forest (Poszyna) 4.56 and 4.80.

Figure 8 shows the spatial distribution of precipitation with pH < 5.0 in 1999-2000, given as percents of all samples. Acid precipitation was least frequent (to 40%) in the northern fragments of the forest complex and most frequent (more than 70%) in the central part.

The pH of bulk precipitation varied over the year (test of randomness $p < 0.01$). In cold months the pH of precipitation was lower (mean 4.4) than in warm months (mean 4.9). Low pH is connected with high emissions of gas pollutants in cold months; in addition, snow is more effective in absorbing aerosols and gases than rain [6]. In this period, dry deposition of SO₂ to the samplers may also be important. On the other hand, in warm months one may expect high emissions of NH₃ and dust fall, which neutralize acid compounds.

The correlation coefficient between the concentration of hydrogen ions and amount of precipitation was $r = 0.11$ (log-transformed data), and between deposition of H⁺ and amount of precipitation $r = 0.42$, perhaps indicating that long-range transport is a source of H⁺ ions. There was no correlation between pH and SO₄²⁻ concentration in precipitation ($r = 0.02$).

The pH of atmospheric precipitation is determined by many processes influencing the production and neutralization of H⁺ in rain water. Strong acids in precipitation originate mainly from oxidized S and N compounds; acids are neutralized by particles and ammonia. In the case of bulk samples, pH is influenced by dry deposition of gases and particles to the funnel surface. Samplers placed on agricultural fields or other places with large local dust or gas emissions are affected by these emissions. Samplers placed in forests are less affected due to the permanent

vegetation cover around the samplers and the absence of emissions from local manure and fertiliser applications [5]. Many other processes may influence the pH value from bulk samplers, so one should be cautious in interpreting pH of precipitation based on bulk precipitation.

Acknowledgements

This work was financially supported by the Polish Committee for Scientific Research, grant no. 6P04F02315/p02.

References

- BERKVIST B., FOLKESON L. Soil acidification and element fluxes of a *Fagus sylvatica* forest as influenced by simulated nitrogen deposition. *Water, Air, Soil Pollut.* **65**, 111, **1992**.
- DE VRIES W., REINDS G.J., KLAP J.M., VAN LEEUWEN E.P., ERISMAN J.W. Effects of environmental stress on forest crown condition in Europe. Part III: Estimation of critical deposition and concentration levels and their exceedance. *Water, Air, Soil Pollut.* **119**, 363, **2000**.
- GRODZIŃSKI W., WEINER J., MAYCOCK P.F. (eds.). Forest ecosystems in industrial regions. Studies on the cycling of energy, nutrients and pollutants in the Niepołomice Forest, Southern Poland; *Ecological Studies* 49, pp.1-277, **1984**.
- GUS. Rocznik Statystyczny 1978-1998; pp.1-500, Warszawa. **1977-1999**.
- HOVMAND M.F. Cumulated deposition of strong acid and sulphur compounds to a spruce forest. *Forest Ecol. Management* **114**, 19, **1999**.
- JOHNSON D.W., LINDBERG S.E. (eds.). Atmospheric deposition and forest nutrient cycling; *Ecological Studies* 91, pp.1-688, **1992**.
- KASINA S. Rozkład stężeń dwutlenku siarki i opadu pyłu w rejonie zakładu przemysłowego Krakowa. *Ochrona Powietrza* **2**, 2, **1970**.
- KASINA S., RAPACZ J., FRANKOWICZ E. Opad siarki do podłoża Puszczy Niepołomickiej. *Człowiek i Środowisko* **9**, 235, **1985**.
- KICIŃSKA B. Wpływ cyrkulacji atmosferycznej na stężenie dwutlenku siarki w powietrzu w Polsce. *Prace i Studia Geograficzne* **28**, 223, **2001**.
- LIN N-H., LEE H.-M., CHANG M-B. Evaluation of the characteristics of acid precipitation in Taipei, Taiwan using cluster analysis. *Water, Air, Soil Pollut.* **113**, 241, **1999**.
- LOGREN S., KVARNAS H. Ion mass balance for tree small forested catchment in Sweden. *Water, Air, Soil Pollut.* **85**, 529, **1995**.
- MANDERSCHIED B., MATZNER E., MEIWES K.-J., XU Y. Long - term development of element budgets in Norway spruce (*Picea abies* (L.) Karst.) forest of the Germany Solling area. *Water, Air, Soil Pollut.* **79**, 3, **1995**.
- MOLDAN E., CERNY J. (eds.) Biogeochemistry of small catchments. A tool for environmental research; John Wiley & Sons: Chichester, New York, Brisbane, Toronto, Singapore, pp.1-419, **1994**.
- MILL M.J., WÓJCIK A., RZYCHOŃ D. Mapy krytycznych ładunków kwaśnych dla ekosystemów glebowo-leśnych Polski; PIOŚ: Warszawa, pp.1-29, **1994**.
- SCHLESINGER W.H. Biogeochemistry. An analysis of global change; Academic Press INC Harcourt Brace Jovanovich, Publishers: San Diego, New York, Boston, London, Toronto, pp.1-443, **1991**.
- SZAREK-LUKASZEWSKA G. Input of chemical elements to the forest ecosystem on the Carpathian Foothills (S Poland). *Pol. J Ecol.* **47**, 191, **1999**.
- TURZAŃSKI P.K., WERTZ J. (eds.). Raport o stanie środowiska w województwie Małopolskim w 1999 roku; WIOŚ: Warszawa, pp.1-283, **2000**.