VERSITA DOI: 10.2478/eces-2013-0003 ECOL CHEM ENG S. 2013;20(1):41-54

Rafał KOZŁOWSKI[1*] and Marek JÓŹWIAK[1]

CHEMICAL DENUDATION IN A GEOECOSYSTEM IN ACID IMMISION CONDITIONS

DENUDACJA CHEMICZNA W GEOEKOSYSTEMIE W WARUNKACH KWAŚNEJ IMISJI

Abstract: There is an analysis of the physico-chemical properties and the chemical composition of precipitation in a forest geoecosystem in acid immision conditions. The data used in the analysis was collected between 2000 and 2010. In that period, a drop in the immision scale of S-SO_2 in the atmospheric air had been observed, which consequently was one of the reasons for a drop in the precipitation acidity. The conclusion was that rainwater, after penetrating treetops and trunks, undergoes a significant transformation whose intensity depends on species composition of the forest stand. Statistically relevant differences were found in coniferous stands, in which a substantial drop in pH was noted, in addition to an increase in the load of components accumulated in the soil in relation to atmospheric precipitation. The calculated indicators of the eco-chemical state of waters (Ma%) have revealed that throughfall waters in coniferous stands and fir and beech stemflow contain significant amounts of aluminium, manganese, iron and hydrogen ions in the sum of cations. Also the indicator of acid-neutralizing capacity (ANCaq) shows that these waters are more enriched with sulfate, nitrate and chloride ions than bulk precipitation. The recorded variation eventuates from processes related to dry and humid deposition, as well as ion-exchange processes occurring within the stand. The obtained results point to an intensification of chemical denudation within the trunks, triggering disadvantageous changes in both biotic and abiotic part of the ecosystem. The effects of the increased inflow of souring agents to the soil through stemflow are significant acidification of the top mineral soil horizon and an increase in the hydrolytic acidity.

Keywords: precipitation, throughfall, stemflow, soil acidification

Introduction

From both the theoretical and practical point of view, it is important to know the functioning of geoecosystems. Studying the circulation of matter and the flow of energy in the geoecosystems leads to information which allows to determine the internal structure and physiognomy of the geoecosystem. The energy reaching the geoecosystem triggers processes inside it, affecting both the abiotic and biotic parts of it. The quantitative share of the matter circulation in a geoecosystem is characterized by the mechanical and chemical denudation [1].

[1] Department of Environment Protection and Modelling, The Jan Kochanowski University, ul. Świętokrzyska 15G, 25-406 Kielce, Poland
[*]Corresponding author: rafalka@ujk.edu.pl

Taking into account the assumptions of geoecosystem functioning, it is necessary to determine the types of matter, the delivery sources, the route of circulation in the geoecosystem and the drainage system. In the denudation system of geoecosystems located in the temperate humid zone, the flora plays a significant role. The forest influence on the course of morphogenetic processes is relatively well recognized in the macro-scale, especially in relation to mechanical denudation. We do not, however, have much information about the course and intensity of chemical denudation, particularly in micro-scale. The geoecosystems, being open systems, create conditions for constant exchange of components between the surrounding systems, as well as within a particular one. They are, however, characterized by a relatively invariable set of components, being in a constant circulation between the abiotic and biotic pool of the ecosystem [2].

As the current research has proved [3, 4], in the Swietokrzyskie Mountains, we are dealing with a long-term acid immision of local and remote origin. The research on the substance circulation dynamics in forest ecosystems conducted thus far, points to significant quantitative and qualitative differences between open-space precipitation and that from under the top of a tree stand. With significantly lower sums of precipitation in a forest, the loads of mineral and organic components delivered to the soil are bigger manifold. The physicochemical properties and chemism of atmospheric precipitation, mostly influenced by pollution of atmospheric air, are some of the main elements shaping the current degradation of the natural environment. The reason for that is the fact that water, apart form functioning as a partner in physical reactions, is also a medium for anthropogenic transformation of the natural environment. In literature [5-9] there is much said about the problem of acid rain and its negative influence on forest ecosystems. An important element modifying the transformation intensity of precipitation in forests is species composition of the tree stand. Conifers modify the atmospheric precipitation much more severely [10], thus they influence the range of components delivered to the soil more intensely, which consequently contributes to an increase in the speed of chemical denudation of the soil. An increase in the deposition of souring substances, including S and N, may lead to an increase in the aluminium mobility and a more intense eluviation of calcium and magnesium ions from the soil. Acid deposition may also influence the decrease in the pH level and the indicator of acid-neutralizing capacity (ANCaq) in surface waters, leading to a drop in the number of living organisms in these waters [11].

The aim of the present thesis was to determine the dynamics of chemical denudation, occurring within a geoecosystem under the influence of a long-term anthropogenic impact on the environment. In the analysis, the data used originated from the Base Station of the Integrated Monitoring of Natural Environment Holy Cross, which is a part of the Faculty of Protecting and Shaping the Environment at UJK, including hydrological years 2000-2010.

Area and methods of research

The research was conducted in the central part of the Swietokrzyskie Mountains (southern Poland), within a fir-beech stand identified with the Carpathians Fagion sylvaticae unit of vegetation *Dentario glandulosae fagetum* [12], located on the territory of the Base Station IMNE Holy Cross. The station is placed within the Swietokrzyski National Park, on the Srodkowomałopolska highland, in the Swietokrzyskie Mountains Region (Fig. 1, Table 1).

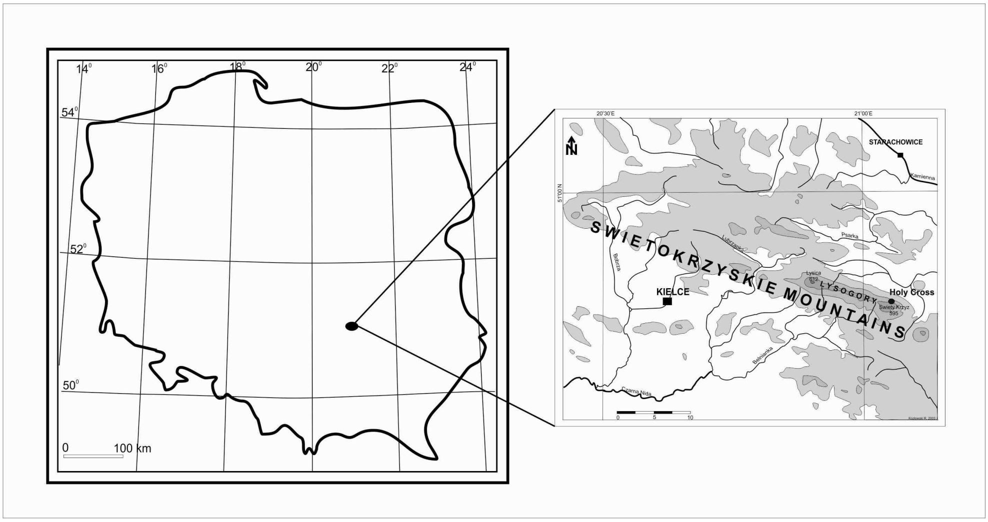

Fig. 1. Localization of investigative plot

The measurement methods used were in line with the requirements of the Integrated Monitoring of Natural Environment in Poland [13].

Table 1

Description of investigative plot

	Geoecosystem in central part of Swietokrzyskie Mountains		
Location	21°03'10''E, 50°51'20''N		
Area	1.26 km^2		
Height	268-595 m a.s.l.		
Precipitation (TF+SF/BP)	562.4 (*fir*) - 649.8 (*beech*) /717.9 mm a^{-1} [a]		
Temperature	7.3°C [a]		
Soils	Podzolic-rusty pseudogley		
Geology	Cambrian quartzites		
Vegetation	*Dentario glandulosae fagetum* [Beech (*Fagus sylvatica*), Fir (*Abies alba*), Acer (*Acer pseudoplatanus*), Hornbeam (*Carpinus betulus*)]		
pH [a]	BP pH 5.12	TF (*fir*) pH 4.41 SF (*fir*) pH 3.37	TF (*beech*) pH 4.88 SF (*beech*) pH 4.34
Deposition[a]	BP H^+ 126.4 g ha^{-1} a^{-1} S-SO_4 14.9 kg ha^{-1} a^{-1} N-NO_3 6.7 kg ha^{-1} a^{-1} Ca^{2+} 15.9 kg ha^{-1} a^{-1} Mg^{2+} 7.1 kg ha^{-1} a^{-1}	TF+SF (*fir*) H^+ 800.4 g ha^{-1} a^{-1} S-SO_4 43.4 kg ha^{-1} a^{-1} N-NO_3 24.7 kg ha^{-1} a^{-1} Ca^{2+} 36.2 kg ha^{-1} a^{-1} Mg^{2+} 13.5 kg ha^{-1} a^{-1}	TF+SF (*beech*) H^+ 439.6 g ha^{-1} a^{-1} S-SO_4 25.1 kg ha^{-1} a^{-1} N-NO_3 14.1 kg ha^{-1} a^{-1} Ca^{2+} 20.0 kg ha^{-1} a^{-1} Mg^{2+} 11.2 kg ha^{-1} a^{-1}

[a] = RH 2000-2010 hydrological years, BP - bulk precipitation (dry+wet), TF+SF - sum throughfall and stemflow

Field and laboratory research

This research was conducted on two experimental fields with a fir and beech stand at Holy Cross. The research of the size and quality of the atmospheric precipitation included rainwater in vertical section - atmospheric precipitation - throughfall - stemflow. To measure the immision scale (S-SO_2), an analyzer HORIBA APSA 350 E was used. The research was conducted in an automated cycle. The meteorological parameters (temperature, wind direction and speed, sums of precipitation) were analyzed automatically using a MILOS 500 station.

Inhouse studies

In the course of analysis, the indicators of the eco-chemical state of waters were calculated [14-16]. These were:

1. Acid-neutralizing capacity ANC_{aq} [$\mu Eq \cdot dm^{-3}$]

$$ANC_{aq} = K^{+}+Na^{+}+2Mg^{2+}+2Ca^{2+} - NO_3^{-} - Cl^{-} - 2SO_4^{2-}$$

This indicator, most commonly used in surface water analysis, is of great importance when analyzing the water acidification [17]. However, it can also be applied in atmospheric precipitation analysis [18].

2. Acidification level by Ulrich [19]

$$Ma\% = (Ma + H^{+}) : (Ma + Mb + H^{+}) \cdot 100\%, \text{ where}$$

$$Ma = Fe^{3+} + Al^{3+} + Mn^{2+} \text{ [mmol} \cdot \text{dm}^{-3}\text{]}$$

$$Mb = K^{+}+Na^{+}+Ca^{2+}+Mg^{2+} \text{[mmol} \cdot \text{dm}^{-3}\text{]}$$

The Moldan and Cerny model [20] was also used to estimate the size of sulfur load reaching the forest soil

$$NTF = (TF+SF)-BP, \text{ example}$$

NTF - throughfall netto, TF - throughfall, SF - stemflow, BP - precipitation.

Statistical study

In order to determine the trends, correlations and levels of statistical relevance between the selected parameters, the collected data was made subject to statistical study using Statistica and Origin software. To study the statistical relevance of the analyzed atmospheric precipitation samples, both parametric and non-parametric tests were used. The gathered series of variables were initially analyzed using the Shapiro-Wilk W test in order to determine the compatibility of data with the normal distribution. Once that assumption was met, the results were analyzed using the one-tailed variance analysis ANOVA, later tested *post-hoc* with the Tukey test. Also non-parametric tests were used, *eg* R. Spearman's non-parametric correlation test.

Results and discussion

The results of air pollution measurements conducted at the Holy Cross Base Station reflect the overlapping continental emissions, regional and local. The analysis of the S-SO_2 concentration from 1994-2010 showed a statistically relevant downward tendency of the immision scale (Fig. 2).

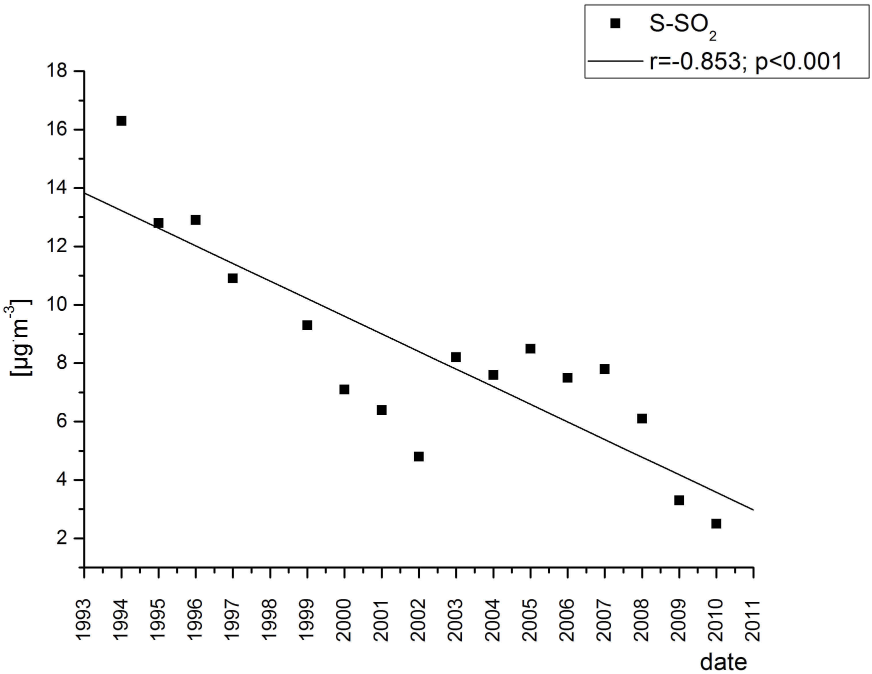

Fig. 2. Variation of S-SO_2 concentration between 1994 and 2010 in the studied geoecosystem

Particularly high concentration was noted in the 1990s, with an annual maximum of 16.3 µg · m^{-3} in 1994. The lowest annual average was 2.5 µg · m^{-3}, noted in 2010. In the concentration analysis of this component, there are three distinctive periods. The first one lasted until 2002 and was characterized by a dynamic drop in the concentration. The second one, between 2003 and 2007, distinguished itself with insignificant fluctuation. Since 2008, there has been a clear drop in the immision scale. As it comes out from research Kozlowski et al [4], such a course of S-SO_2 concentration in the atmospheric air is highly influenced by emitters located on the direction of dominant winds from W and SW sector. The detected tendency reveals a connection with the emission volume of sulfuric dioxide in Poland [21]. Based on the research conducted by Smith et al [22] and Smith and Fowler [23] in the UK, it was concluded that 50% of sulfur from the atmosphere is then delivered to the ecosystems via the atmospheric precipitation. As Huang et al [24] announce, the main reason for the precipitation acidity, displayed as the pH value, is the presence of (among others) sulfur dioxide in the atmosphere.

The analysis of the physico-chemical properties and the chemical composition of the atmospheric precipitation between 2000 and 2010 revealed that in the studied geoecosystem, we are dealing with occurrence of so-called acid rains. In accordance with the classification of Jansen et al [25], in the analyzed period, the weighted pH average of rainwater was determined normal (pH 5.12) (Fig. 3). The lowest value was noted in 2001 with pH 4.71, while the highest in 2004 with pH 5.67. In terms of electrolytic conductivity, the rainwater is classified as highly elevated. The highest value was noted in 2000, *ie* 9.58 mS · m^{-1}, while the lowest in 2010 with 2.53 mS · m^{-1}.

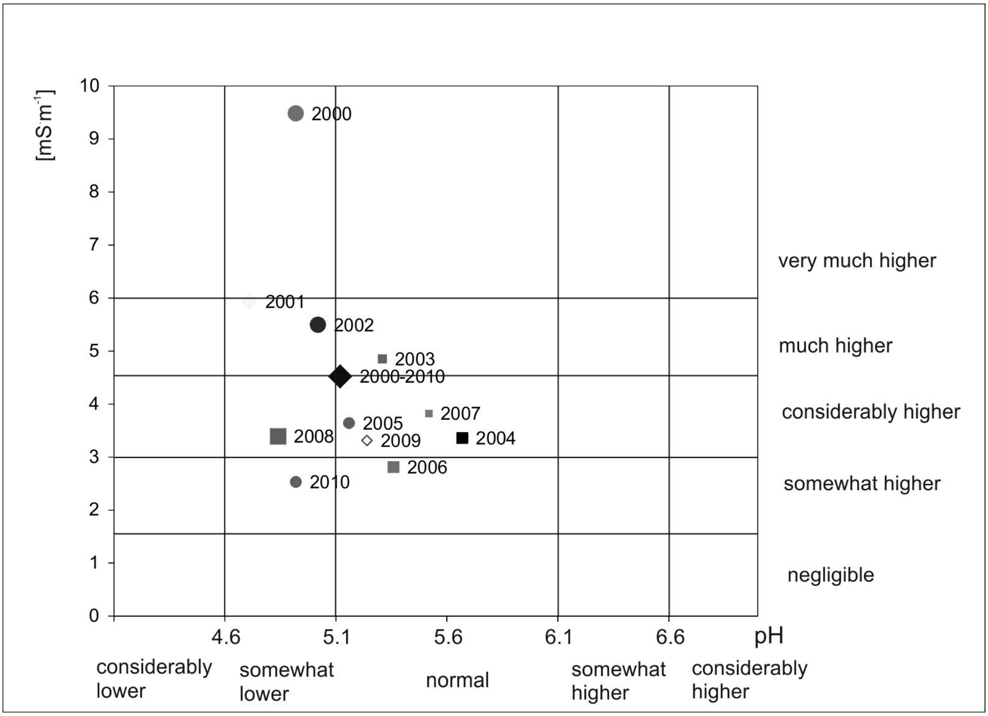

Fig. 3. Classification of precipitation in terms of pH and conductivity by Jansen et al [25]

The analysis of monthly pH values in precipitation waters revealed the existence of a statistically irrelevant upward tendency (Fig. 4). Also, an occurrence of seasonal dynamics of the pH value was observed. The highest values were noted in summer months, while the lowest in fall-winter months when there is an emission increase due to the so-called heating season. The observed downward tendency of S-SO_2 immision volume is reflected in the increase of pH values of precipitation. The conducted statistical analysis using the non-parametric Spearman's rank correlation test revealed the existence of a statistically relevant reverse correlation between the pH value and the S-SO_2 concentration (r = –0.232, p = 0.019). Rainwater, having gone through the treetops and trunks, underwent a significant transformation. The change spanned not only the quantity, but also the physico-chemical properties, expressed *eg* through the pH value or the electrolytic conductivity measurement (SEC).

The analysis of pH measurement revealed that rainwater, having gone through the treetops, underwent acidification to the pH level of 4.41 in firs and 4.88 in beeches. Stemflow were much more acidified. This process mostly concerns the fir stemflow. The weighted multi-annual average pH value was 3.37. The stemflow of deciduous trees has demonstrated lower acidity, with an average pH observed in a beech of 4.34. The lowest weighted average values in stemflow were noted in winter months.

During the research period, the monthly weighted average values of conductivity in bulk precipitation ranged from 0.95 to 23.3 mS · m^{-1}. Much more mineralized was the throughfall. The noted SEC values in throughfall water under beeches were almost 1.5 times higher, with the weighted average of 6.57 mS · m^{-1}. A higher enrichment factor was noted in waters penetrating the fir treetops. The bigger receptive area and the presence of assimilative organs all year, especially in winter months, caused the waters penetrating their treetops to be over three times as mineralized as water from atmospheric precipitation. The stemflow was quite specific, as the noted SEC values were higher in it manyfold than at the entrance. In the beech stemflow, an almost eight-fold increase was observed (34.53 mS · m^{-1}). The increase in mineralization was noted also in waters the beech stemflow. The gained values were only 2.4 and 3.6 times higher than those noted in water from bulk precipitation. The highest values were registered in winter months and the lowest in summer. The observed decay in conductivity should be linked mainly to the condensation process of solutions dripping down the tree surface. This process results from both ion-exchange processes in the plant-water system and washing away the aerosols embedded due to dry deposition on the tree surface. The intensity of the condensation process is much bigger in conifers than it is in deciduous trees. This results from, among other things, the differences in the morphological build of tree barks [26].

The obtained minimum pH values are linked to washing the acidogenic components of NO_3^- and SO_4^{2-} as well as the accompanying H^+ protons adsorbed on the plant surface as a result of dry deposition. Kozlowski [27] announced that this process particularly concerns coniferous trees which is related to the process of ridding the atmospheric air of pollution by the treetops. The obtained maximum pH values in the stands are linked to, among other things, the beginning and end of the vegetative season. In relation to the data from previous years, no statistically relevant tendency in the variation of acidity of precipitation penetrating the studied tree stands was noted.

Research on the chemical composition of bulk precipitation, throughfall and stemflow to significant differences in the concentration of particular components. The lowest values were noted in the bulk precipitation.

It is necessary to emphasize that using the precipitation load as the basis for estimating the total atmospheric deposition in forests may lead to acquiring uncertain values. It is the case since precipitation collectors gather both wet and dry deposition. However, dry deposition in a bell-mouthed inlet may be different than on the surface of assimilative organs in trees. That is why the precipitation method may underrate the total deposition of *eg* S and heavy metals, especially in highly polluted areas. Therefore, the total deposition of sulfur load in forest areas is calculated based on the sum of the throughfall and stemflow, reaching the forest floor [20], giving the value as the net throughfall.

Based on the obtained results, the conclusion is that the load of elements in rainwater usually undergoes differentiation - it increases or decreases after flowing through the tree zone. The increase of element load in throughfall is triggered by rinsing from plant tissue (mainly tree leaves/needles), washing away dust particles settled on trees, as well as solution condensation caused by the interception and evaporation of the rainwater. On the other hand, the load in a throughfall may decrease as a result of absorbing the elements included in the precipitation by the assimilative organs or their retention in the treetops.

In the studied ecosystem, the conclusion was that in the analyzed period, the annual average delivery from precipitation was 15.4 kg S-SO_4 · ha^{-1}. As a result of the processes related to rinsing the components of dry deposition in the treetops, the delivery to the forest floor in the coniferous stand was 44.0 kg S-SO_4 · ha^{-1}, which was 2.9 times more compared with atmospheric precipitation, and in the deciduous stand 25.1 kg S-SO_4 · ha^{-1}, revealing a 1.6 times increase. In every analyzed year, sulfur loads noted in the coniferous stand were higher compared with both the bulk precipitation alone and the rainwater reaching the soil in the deciduous stand (Fig. 4). The conducted statistical analysis using the ANOVA test revealed the existence of statistically relevant differences between the values of S-SO_4 load in bulk precipitation and that penetrating the studied stands. The one-tailed ANOVA analysis showed the significance of the differences (F = 54.79; p < 0.001). Using the *post-hoc* analysis (Tukey's test), it was concluded that within the research area, the statistical difference occurs in relation to the fir throughfall (p < 0.001) and fir (p < 0.001) and beech (p < 0.01) stemflow. No significance of the differences was found in relation to the beech throughfall (p = 0.707). The obtained results confirm the higher efficiency of conifers in modifying the chemical composition of precipitation reaching the soil in forest ecosystems.

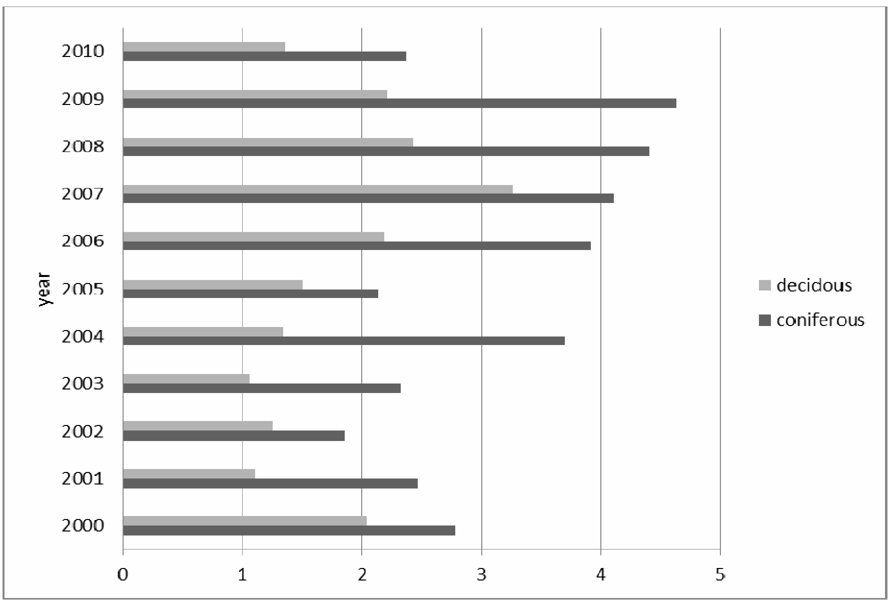

Fig. 4. Multiplicities of S-SO_4 load in rainwater reaching the soil in coniferous and deciduous stands (atmospheric precipitation = 1)

The size of S-SO_4 load in the net throughfall (NTF) in the studied stands varied in the coniferous stand between 11.4 in 2005 and 49.6 kg S-SO_4 · ha^{-1} in 2000. Significantly lower values were noted in the deciduous stand, where the net load varied between 1.2 in 2003 and 29.1 kg S-SO_4 · ha^{-1} in 2000 (Fig. 5).

The obtained results explicitly show that the assessment of the chemical denudation rate in forests requires taking into account the net throughfall, as these results span the entire sulfur load deposited through both wetly and dryly. As announced by Johnson and Lindberg [28], washing the sulfur out of the plant tissue is usually marginal and amounts to between 10 and 20%. Hitherto research shows that the increase of sulfur load in waters reaching the soil is triggered by dry deposition washed away with rainfall [29]. The dry deposition of sulfur is of particular importance in highly polluted areas and may amount to 40-60% of the total deposition [28]. Furthermore, it is much higher in conifers than in deciduous trees, as a consequence of all-year presence of assimilative organs and higher efficiency in capturing the air pollution.

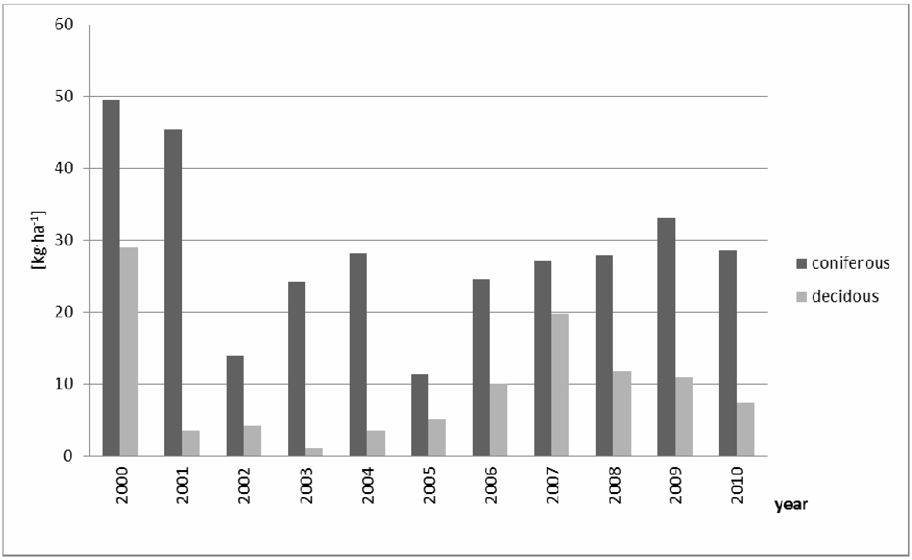

Fig. 5. Size of S-SO_4 load in the net throughfall within the studied stands

For the analysis of the chemical denudation intensity, the indicators of eco-chemical state of waters were calculated. The acidity degree by Ulrich [19] shall mean the percentage of acid cations and hydrogen ions in the sum of cations. The calculated indicator of the solution acidification in the studied waters allowed them to be classified as weak acid (Table 2).

Table 2

Values of the Ma [%] indicator in 2000-2010

	BP	**TFfir**	**TFbeech**	**SFfir**	**SFbeech**
Mean	11.8	18.3	15.5	27.3	22.2
Min	0.2	0.4	0.4	2.2	1.1
Max	79.3	96.2	95.6	67.8	80.2
SD	13.7	19.3	19.5	12.9	20.8

BP - bulk precipitation, TFfir - throughfall fir, TFbeech - throughfall beech, SFfir - stemflow fir, SFbeech - stemflow beech

Nevertheless, in the analyzed series, the trunk zone clearly marks itself with the highest average values of the Ma [%] indicator, pointing to a significant burden of acidifying components (Fig. 6). It is essential as these waters supply the soils in the trunks vicinity, causing their considerable acidification [29], which in consequence may lead to an increase in the amount of heavy metals [30].

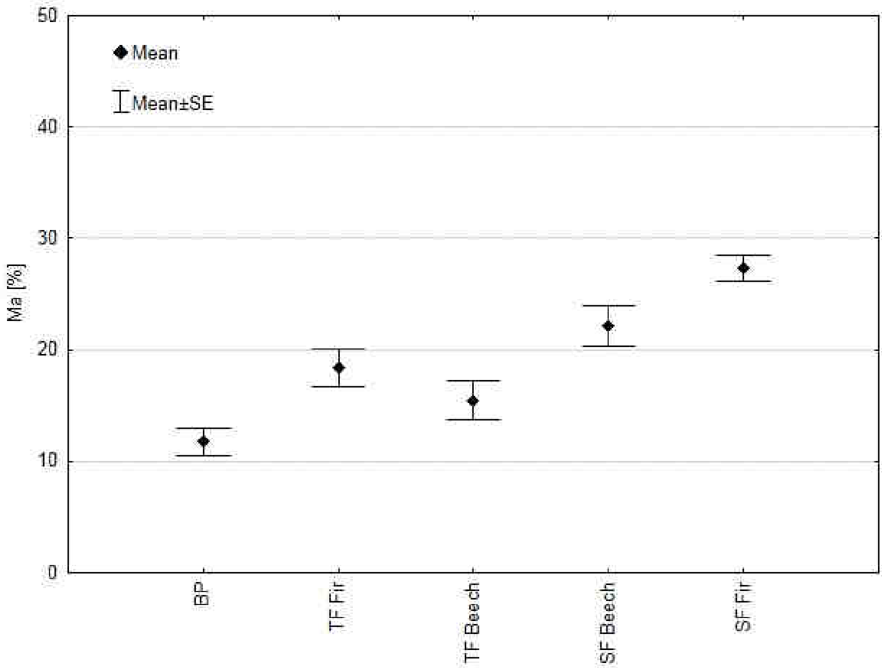

Fig. 6. Average values of the Ma [%] indicator with the standard error

The seasonal analysis proved that the highest values of the Ma [%] indicator occur in winter months, which causes them to qualify as highly acidic. The highest values were noted in the waters penetrating the treetops, where the maximum values exceeded 95%.

The analysis of the ANCaq indicator proved that in the studied geoecosystem, the lowest average values were noted in the fir stemflow with the multiannual average of -1499.8 μEq · dm^{-3} (Table 3). In these waters, also the highest diversity of the indicator was observed (Fig. 7). The negative ANCaq values were also spotted in the beech stemflow and fir throughfall. This fact points to a significant burden of acidogenic components originating from, among others, dry and humid deposition. Research conducted by Eshleman et al [18] in the state of New York (U.S.) proved that in snowmelt, the ANCaq indicator amounted from –4 to –121 μEq · dm^{-3}. In the research conducted at the Saint Cross, the lowest values in precipitation waters, coming down to even –1165 μEq · dm^{-3}, were noted just in winter months, which is a consequence of the increased presence of acidifying agents in the atmospheric air, resulting from the so-called heating season. Analogically to atmospheric precipitation, in the remaining series, the lowest values were noted in winter months, while the highest in summer.

The conducted statistical analysis using the ANOVA test proved the existence of statistically relevant differences between the ANCaq values in the atmospheric precipitation and throughfall in the studied stands. The one-tailed ANOVA analysis showed the significance of the differences ($F = 56.02$; $p < 0.001$) between the precipitation in the analyzed geoecosystem. Using the *post-hoc* analysis (Tukey's test), it was concluded that within the research area, the statistical difference occurs in relation to the fir ($p < 0.001$) and beech ($p < 0.01$) stemflow. No significance of the differences was found in relation to the beech ($p = 0.999$) and fir ($p = 0.246$) throughfall. These results confirm a significant burden of acidifying components on these waters, which leads to the intensification of chemical denudation within the tree trunks, triggering disadvantageous changes in relation to both biotic and abiotic part of the ecosystem.

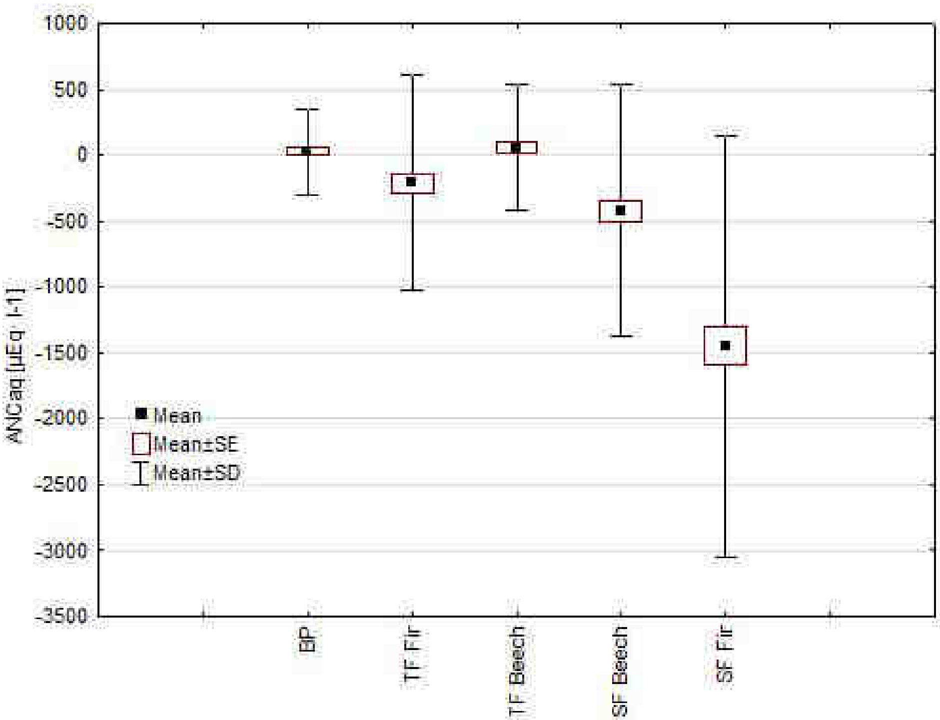

Fig. 7. Average values of the ANCaq indicator with the standard error and deviation

Table 3

Values of the ANCaq indicator [µEq · dm^{-3}] in 2000-2010

	BP	TFfir	TFbeech	SFfir	SFbeech
Mean	28.8	–209.0	58.0	–1499.8	–423.3
Min	–1165.5	–5656.7	–2513.7	–7266.5	–4992.0
Max	733.4	1392.2	1598.5	1337.1	874.9
SD	324.3	817.0	479.6	1595.9	955.6

BP - bulk precipitation, TFfir - throughfall fir, TFbeech - throughfall beech, SFfir - stemflow fir, SFbeech - stemflow beech

The effect of the intensified inflow of acidifying substances to the soil with the stemflow is significant acidification of the top mineral soil horizon and an increase in hydrolytic acidity. In the soil, concentric gradients of the pH value occur, with the minimum noted in the vicinity of tree trunks [29]. That is also where the maximum values of hydrolytic conductivity are observed [31]. A decrease of the pH value right next to the trunks was also noted in Germany [32] and Sweden [33].

Conclusions

1. The applied methods allow a cause-effect analysis of the chemical denudation rate occurring within the geoecosystem
2. The research has proved a significant role of dry and humid deposition in shaping the size of substance load reaching the forest floor
3. The seasonal dynamics of immision size has a modifying influence on the physicochemical properties and chemical composition of bulk precipitation, throughfall and stemflow
4. The waters from bulk precipitation, having gone through the treetop zone, undergo a significant transformation
5. The higher overall load of substances brought in to the soil occurs in a coniferous stand
6. As a consequence of dry, wet and humid deposition, considerable loads are brought in to the soil, including acidifying agents, contributing to an increase in the micromosaics of the pedon, especially in the close vicinity of the trunks

References

[1] Kostrzewski A, Zwolinski Z. The share of mechanical and chemical denudation in the modern system of geomorphologic upper Parseta (West Pomerania). Prace Geogr. IG i PZ PAN;1991:1-159.
[2] Grodzinska K, Laskowski R. Environmental Assessment and Biogeochemistry of a Moderately Polluted Ratanica Catchment (Southern Poland). Warszawa: Biblioteka Monitoringu Srodowiska; 1996:1-139.
[3] Jozwiak M. Functioning of the selected geoecosystem in the Holy Cross Mts. under acid immision (Central Poland). Przegl Geolog. 2001;49(9):775-779.
[4] Kozlowski R, Jozwiak M, Jozwiak MA, Rabajczyk A. Chemism of atmospheric precipitation as a consequence of air pollution: the case of Poland’s Holy Cross Mountains. Polish J of Environ Stud. 2011;20(4):919-924.
[5] Lorz C, Kowalkowski A, Jozwiak M, Kozlowski R, Schneider B. The recovery of acidified stream waters - A comparative case study from the Western Ore Mts. (Erzgebirge) and the Holy Cross Mts. (Swietokrzyskie Mts.). Hercynia N.F. 2005;38:41-58 (in German).
[6] Polkowska Z, Astel A, Walna B, Malek S, Medrzycka K, Gorecki T, Siepak J, Namiesnik J. Atmos Environ. 2005;39:837-855. DOI: 10.1016/j.atmosenv.2004.10.026.
[7] Augustin S, Bolte A, Holzhausen M, Wolff B. Europ J Forest Res. 2005;124:289-300. DOI: 10.1007/s10342-005-0095-1.
[8] Jozwiak M, Kozlowski R. Deposition of selected metals in the Świętokrzyskie Mountains and their influence on changes of soil pH. Ecol Chem Eng A. 2008;15(11):1239-1256.
[9] Polkowska Z, Blas M, Sobik M, Klimaszewska K, Malek S, Namiesnik J. Various forms of atmospheric precipitaion and deposits as a measure of environmental pollution in different geographic regions of Poland - Part II - Dew. Ecol Chem Eng S. 2008;15(4): 529-560.
[10] Wang MC, Liu CP, Sheu BH. J Hydrol. 2004;289:275-285. DOI: 10.1016/j.jhydrol.2003.11.026.
[11] Driscoll CT, Lawrence GB, Bulger AJ, Bulter TJ, Cronan CS, Eagar C, Lambert KF, Likens GE, Stoddard JL, Weathers KC. BioScience. 2001;51(3):180-198. DOI: 10.1641/0006-3568(2001)051[0180:ADITNU]2.0.CO;2.
[12] Broz E, Kapuscinski R. Protected and endangered species of vascular plants Swietokrzyski National Park and draft of Świętokrzyskie Landscape Parks Mountains. Rocznik Swietokrzyski. 1990;17:107-133.

[13] Kostrzewski A, Kruszyk R, Kolander R. Integrated Monitoring of Environment. The principles of organization, the measuring system, the selected test methods. 2006; http://www.staff.amu.edu.pl/~zmsp/dok.html (in Polish).
[14] Reuss JO, Johnson DW. Acid deposition and the acidification of soils and water. Ecol Stud. 1986;59:1-120.
[15] Cronan CS, Grigal DF. Use of calcium/aluminium ratios as indicators of stress in forest ecosystems. J Environ Qual. 1995;24(2):209-226.
[16] Kernan MR, Helliwell RC. Sci of the Total Environ. 2001;265(1-3):39-49. DOI: 10.1016/S0048-9697(00)00648-3.
[17] Bi SP, An SQ, Liu F. Environ Inter. 2001;26(5-6):327-333. DOI: 10.1016/S0160-4120(01)00008-3.
[18] Eshelman KN, Davies TD, Tranter M, Wigington PJ. A two-component mixing model for predicting regional episodic acidification of surface waters during spring snowmelt periods. Water Resour Res. 1995;31:1011-1021.
[19] Ulrich B. Z.Pflanzenern Bdkunde.1988;151(3):171-176.DOI: 10.1002/jpln.19881510304.
[20] Moldan B, Cerny J. Biogeochemistry of Small Catchments. A Tool for Environmental Research. Chichester-New York-Brisbane-Toronto-Singapur: Viley Sons; 1994:1-322.
[21] ENVIRONMENT 2010.Regional and Environmental Surveys Division. Warszawa: CSO; 2011:1-609.
[22] Smith RI, Fowler D, Bull KR. In: Acid Rain Research: Do We Have Enough Answers? Heij GJ, Erisman JW, editors, Amsterdam: Elsevier; 1995:175-186.
[23] Smith RI, Fowler D. Uncertainty in estimation of wet deposition sulphur. Water, Air, and Soil Pollut: Focus. 2001;1:341-354.
[24] Huang DY, Xu YG, Peng P, Zhang HH, Lan JB. Environ Pollut. 2009;157(1): 35-41. DOI: 10.1016/j.envpol.2008.08.001.
[25] Jansen W, Block A, Knaack J. Acid rain. History, generation, results. Aura. 1988;4:18-19.
[26] Kowalkowski A, Jozwiak M, Kozlowski R. Investigation method of the rain water influence on forest soil properties. Regional Monit Srodow Przyrod. 2002;3:45-52.
[27] Kozlowski R. Determining the role of fog deposits as conditioners of throughfall volume. Monit Srodow Przyrod. 2009;9:65-72 (in Polish).
[28] Johnson DW, Lindberg SE. Atmospheric Deposition and Forest Nutrient Cycling. Ecol Stud. New York: Springer-Verlag; 1992;91.
[29] Jozwiak M, Kozlowski R. Transformation of precipitation in chosen geoecosystems in the Swietokrzyskie Mountains. Regional Monit Srodow Przyrod. 2004; 5:199-217.
[29] Szarek-Lukaszewska G. Input of chemical elements to the forest ecosystem on the Carpathian Foothills (S Poland). Polish J Ecol. 1999;47(2):191-213.
[30] Stevens CJ, Dise NB, Gowing DJ. Environ Pollut. 2009;157(1): 313-319. DOI: 10.1016/j.envpol.2008.06.033.
[31] Kozlowski R, Adwent E. Spatial variability of selected physic-chemical soil properties in the central part of the Świętokrzyskie (Holy Cross) Mountains. Monit Srodow Przyrod. 2011;12:93-101
[32] Haase D, Neumaister H. Stoffdynamik in waldbestandenen Auenökosystemen. Erfassung und Bewertung: Leipziger Geowissenschaften; 1999;11:9-17.
[33] Matschonat G, Falkengren-Grerup U. Recovery pf soil pH, cation - exchange capacity and the saturation of exchange sites from stemflow - inducted soil acidification in three Swedish beech (*Fagus sylvaitca* L.) forests. Scand. J Forest Res. 2000;15(1): 39-48.

DENUDACJA CHEMICZNA W GEOEKOSYSTEMIE W WARUNKACH KWAŚNEJ IMISJI

Katedra Ochrony i Kształtowania Środowiska, Uniwersytet Jana Kochanowskiego w Kielcach

Abstrakt: Dokonano analizy właściwości fizyczno-chemicznych i składu chemicznego opadów atmosferycznych w ekosystemie leśnym w warunkach kwaśnej imisji. Dane przyjęte do analizy objęły lata 2000-2010. W ww. okresie stwierdzono spadek wielkości imisji S-SO_2 w powietrzu atmosferycznym, co w konsekwencji było jedną z przyczyn spadku kwasowości opadów atmosferycznych. Stwierdzono, że wody opadowe po przejściu przez strefę koron i pni drzew ulegają znaczącej transformacji, której intensywność zależy od składu gatunkowego drzewostanu. Istotnie statystyczne różnice stwierdzono w przypadku drzewostanu iglastego, w którym odnotowano znaczący spadek wielkości pH oraz wzrost ładunku składników deponowanych do gleb w odniesieniu do opadu atmosferycznego. Obliczone wskaźniki ekochemicznego stanu wód (Ma [%]) wykazały, że zwłaszcza wody opadu podkoronowego w drzewostanie iglastym oraz spływające po pniach jodeł i buków zawierają znaczne ilości jonów glinu, manganu, żelaza oraz wodoru w całkowitej sumie kationów. Również wskaźnik pojemności zobojętniania kwasów (ANCaq) wskazuje, że wody te są znacznie bardziej wzbogacone w jony siarczanowe, azotanowe i chlorkowe niż opad bezpośredni. Stwierdzona zmienność wynika z procesów związanych z suchą i wilgotną depozycją oraz procesami jonowymiennymi zachodzącymi w obrębie drzewostanu. Uzyskane wyniki wskazują na znaczne obciążenie tych wód składnikami zakwaszającymi, które doprowadzają do intensyfikacji denudacji chemicznej w obrębie pni drzew, wywołując niekorzystne zmiany zarówno w odniesieniu do biotycznej, jak i abiotycznej części ekosystemu. Efektem wzmożonego dopływu substancji zakwaszających do gleb z wodami spływającymi po pniach jest znaczące zakwaszenie wierzchniego mineralnego poziomu gleb oraz wzrost kwasowości hydrolitycznej.

Słowa kluczowe: opad atmosferyczny, opad podkoronowy, spływ po pniach, zakwaszenie gleb