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ORIGINAL PAPER

Long-term changes in atmospheric depositions in Slovakia

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Abstract

The aim of this paper was to analyse temporal changes in chemism of atmospheric deposition in Slovakia. Two kinds of deposition, bulk and throughfall were considered and analysed for the period of 1996–2010. Data acquired from permanent monitoring plots (PMP) of Level II were used for this purpose. These plots were established as a part of the ICP Forests Programme. The changes in the composition of deposition were identified for the spruce and beech plots. The results were compared among three spruce plots, two beech plots and one mixed spruce-beech-fir plot. Precipitation pH was higher on the beech than on the spruce plots and during the spotted period increased on both spruce and beech plots. Depositions of cations decreased significantly on the spruce and beech plots in bulk deposition for all elements except for calcium. The significant decline of sulphur and ammonium nitrogen was found on both spruce and beech plots, but the highest decrease of sulphur deposition was found in throughfall precipitation ($R^2 = 0.75$). The amount of nitrate nitrogen did not change during the study period.

Key words: temporal change of deposition; permanent monitoring plots; spruce; beech

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1. Introduction

In the early eighties of the last century, there has been observed the rapid deterioration of the European forest state which led in 1985 to the establishment of an International Cooperative Program for Monitoring and Evaluating the Impact of Air Pollution on Forests (ICP Forests). Plots of ICP Forests cover the whole territory of Europe. Monitoring of the forests vitality in Slovakia started in 1987 (Račko 1986, 1987) when there were established 111 permanent monitoring plots (PMP) of Level I in a grid of 16 × 16 km in accordance with manual of ICP Forests and the project "Partial Monitoring System of Forests".

The extensive large-scale monitoring of forest state on PMP of Level I has been characterised by low-intensity, so in 1994, according to Regulation No. 1091/94, the intensive monitoring was additionally implemented. It included widespread research surveys (crowns condition, atmospheric deposition, foliar analysis, soil, soil solution, air quality, meteorology, phenology, vegetation, ozone injury and litterfall). Intensive monitoring plots (Level II) in Slovakia has been on gradually based since 1995 in the most important forest communities with main forest tree species Turkey oak (*Quercus cerris* [L.] Karst), Sessile oak (*Quercus petraea* [L.]), European beech (*Fagus sylvatica* [L.]) and Norway spruce (*Picea abies* [L.]). Number of PMP of Level II has changed over the years due to objective reasons (calamities, harvesting, a cost of data collection). Only the data from spruce plots (*Picea abies* [L.] Karst.) and beech plots (*Fagus sylvatica* [L.]) on PMP of Level II, which were established in the 90s, were evaluated in our study. Temporal trends in the chemical composition of depositions in the period of 1996–2010 were investigated.

2. Material and methods

2.1. Study areas

PMP Level II are unevenly distributed across the territory of Slovakia to cover main tree species and the most important site condition (geology, soil, and climate). According to the methodology of ICP Forests, they were established outside the sites with intense immission load (Pavlenda et al. 2011, 2012). Basic information about the PMPs selected for the study is presented in Table 1. (Pavlenda et al. 2012).

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Table 1. Description of permanent monitoring plots of Level II in Slovakia.

	Plot	Year establishment	Altitude [m a. s.l.]	Aspect	Type of soil	Tree species	Age [year]	Tree species [%]	Avg. prec [mm]	Avg. temp. [°C]
PMP 203	Lomnistá dolina	1995	1250	SE	Skeletic Umbrisol	Spruce, Beech Maple	72	94%, 4%, 2%	1438	3.6
PMP 204	Poľana – Hukavský Grúň	1991	850	NE	Andic Cambisol	Beech, Spruce, Fir, Ash, Maple	90–120	45%, 42%, 6%, 5%, 2%	886	5.4
PMP 206	Turová	1997	575	E	Eutric Cambisol	Beech, Oak	70	99%, 1%	853	6.9
PMP 207	T. Lomnica	1998	1150	SE	Dystric Hyperskeletic Leptosol	Spruce, Larch, Pine, Fir,	60–140	50%, 45%, 3%, 2%	1207	3.8
PMP 208	Svetlice	1999	570	W	Haplic Cambisol	Beech, Larch, Oak, Pine	53	78%, 16%, 4%, 2%	994	6.3
PMP 209	Grónik	1998	875	W	Albic Podzol	Spruce	94	1	1129	4.9

2.2. Data collection and data analyses

The data from the deposition of PMP of Level II in program ICP Forests were collected and processed according to the Manual ICP Forests "Part XIV. Sampling and Analysis of Deposition, Manuals on Methods and Criteria for Harmonised Sampling, Assessment, Monitoring and Analysis of the Effects of Air Pollution on Forests", issued by the UN/ECE ICP Forests Programme Co-ordinating Centre in Hamburg (Clarke et al. 2010). Samples were taken in regular two-week intervals throughout the year (Pavlenda et al. 2011, 2012). Samplers for the collection of rainfall were located in respective forests under the canopy (throughfall – THR) and on the stands nearby the throughfall collectors without forest trees (bulk). The average sample of each collection has been formed by proportional mixing of samples from 3 collectors from the open area and 10 collectors from the throughfall stand, in order to capture the variability of the environment. The chemical analyzes were carried out in Central CHemical Laboratory of National Forest Centre according to appropriate methods ISO and STN for water quality: pH in water (STN EN ISO 10523), ammonium nitrogen by indophenol method in water (STN ISO 7150-1), sulphur and nitrate anions by liquid chromatography (STN EN ISO 10304-2), inorganic elements by ICP-AES (STN EN ISO 22036). The parameters were determined on the calibrated instrument pH on the pH-meter inoLab WTW 2, ammonium on PHARO Spectrometer 300, SO_4^{2-} and NO_3^- by Liquid chromatographic on instrument DIONEX IC CS-1000 and the elements Na, Ca, Mg, K by the atomic emission spectrometry AES-ICP- LECO. The results of specified parameters were in mg l^{-1}. This data based on total rainfall for the measurement intervals (14 days) in the observed area were converted into the deposition in kg ha^{-1} according to equation [1].

$$D_x = (C_x . M) / 100 \qquad [1]$$

D_x – deposition for following period, x – parameter in kg ha^{-1}, C_x – concentration of the element in mg l^{-1}, M – rainfall in mm.

Depositions in the measurement intervals (14 days) were evaluated in the program "Statistica" ANOVA, linear regression, where pH development in throughfall and bulk deposition (below the canopy and stands in an open area) were quantified. The data were processed separately for spruce, beech, and mixed stands. The differences between woody plants were evaluated by ANOVA and the trends by linear regression using the least square method.

3. Results

During the reporting period, the increase of pH has been seen in both the bulk and the throughfall deposition (Fig. 1 – 2). This fact is confirmed by the highest pH in 2010 on both beech stands (bulk and throughfall) and by the lowest pH in the throughfall depositions on the spruce stands in 1996. While the pH value is almost identical in both types of precipitations on beech areas, the pH on the spruce plots in the throughfall and bulk precipitation is different. It was recorded a higher pH up to 0.5 in the bulk precipitation than in throughfall on these stands.

The development of annual variability showed some differences between plots with different species composition and between two types of precipitation. At the beginning of the monitoring of deposition, the intra-annual variability of the tested parameters was higher, which was caused by methodology, as well as the number of evaluated data. In the first few years, the number of samples throughout year was considerably lower than 24. Data from beech plots had the comparable annual variability of the bulk and the throughfall deposition. The lowest annual variability was recorded in throughfall deposition on the spruce stands.

Table 2 shows the significance of the temporal trends in sulphur, nitrogen compounds and base cations in bulk and throughfall deposition. Statistically significant (95% confidence) trends are highlighted in bold. Statistically significant decrease ($P \leq 0.05$) was observed for both forest types in the most evaluated parameters.

The trends of elements contents are reflected the changes of precipitation composition. The different trends between precipitations are caused by enriching the throughfall samples. However the throughfall deposition includes also the other elements which are coming from assimilation organs or from dry deposition on the foliage.

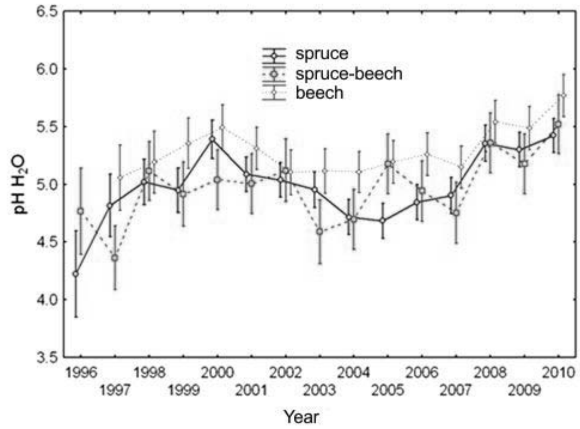

Fig. 1. Average value of pH in bulk deposition of PMP Level II.

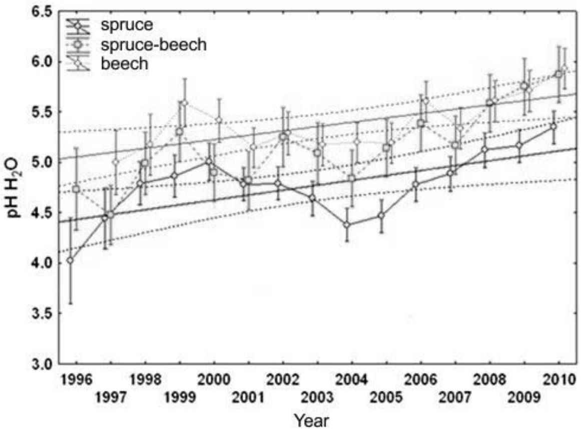

Fig. 2. Average value of pH in throughfall deposition of PMP Level II.

Table 2. Trends of annual deposition of basic cations, sulphur and nitrogen in the period 1996–2010 evaluated by linear regression.

Elements		Spruce PMP				Beech PMP			
		b_0	b_1	R^2	P-value	b_0	b_1	R^2	P-value
Ca	Bulk	269	−0.13	0.19	0.11	235	−0.11	0.20	0.09
	THR	500	−0.25	**0.27**	**0.05**	95	−0.04	0.02	0.63
Mg	Bulk	129	−0.06	**0.37**	**0.02**	79	−0.04	**0.32**	**0.03**
	THR	113	−0.06	0.21	0.08	32	−0.02	0.06	0.34
K	Bulk	846	−0.42	**0.53**	**0.00**	646	−0.32	**0.43**	**0.01**
	THR	-354	0.18	0.09	0.29	358	−0.17	0.07	0.30
Na	Bulk	269	−0.13	**0.64**	0.00	219	−0.11	**0.63**	**0.00**
	THR	187	−0.09	**0.35**	0.02	98	−0.05	**0.23**	**0.00**
S-SO4 2	Bulk	830	−0.41	**0.63**	0.00	781	−0.39	**0.57**	**0.00**
	THR	1173	−0.58	**0.75**	0.00	898	−0.44	**0.70**	**0.00**
N-NO3 -	Bulk	135	−0.07	0.16	0.14	111	−0.05	0.23	6.00
	THR	128	−0.06	0.18	0.10	72	−0.03	0.05	0.37
N-NH4 +	Bulk	606	−0.30	**0.61**	**0.00**	655	−0.32	**0.50**	**0.00**
	THR	756	−0.37	**0.42**	**0.00**	667	−0.33	**0.58**	**0.00**

Note: Bulk – open area, THR – throughfall. Statistically significant results P ≤ 0.05 are highlighted. PMP – permanent monitoring plots.

4. Discussion

4.1. The pH development in depositions

The precipitation is the main factor affecting the quality of the environment (Thalman et al. 2002). Their composition is a result of many processes and chemical reactions associated with natural phenomena and emission of pollutants (Walna & Kurzyca 2006). If there are sufficient amounts of cations in the air, sulphide and nitrate anions are neutralized by the formation of salt. However, in the case of the excess of anion the strong acids (sulphuric and nitric) are formed which, as precipitation fall down, may cause acidification. The precipitation water has the natural acidity of pH = 5.65, whereby as the critical value for vegetation is considered pH below 3.5 (Kunca 2007). The acidity of rain is influenced by local sources of pollution from nearby chemical factories, as well as cross-border transmission.

The pH 5.65, which is considered as the natural value of precipitation, was reached only in the samples under the canopy of beech and in the mixed species stands since 2009. Most of the annual average pH values were below the value of natural acidity. Thus, these precipitations could be considered as acidic. At the open area, which reflected the characteristics of the atmosphere, including secondary pollution, a rain pH did not reach this value on any of the monitored plots. On the contrary, these values were achieved in the throughfall deposition, but this deposition was influenced by capturing of atmospheric pollution, as well as the leaching and washing of different components from the surface of assimilation organs (Pavlenda et al. 2011). Parker (1983) suggested that throughfall precipitation in coniferous forests usually have a lower pH than deposition in open area, which is mainly due to the acidic organic acids washout from the needles. This was also confirmed by our results.

H^+ depositions, which represented acidity of rainfall, are higher in the mountains and increases with the amount of rainfall (Walna & Kurzyca 2007). Our results also support this finding. H^+ deposition on the spruce plots, which were located at higher altitude (820 – 1150), with average precipitation of 1254 mm, was higher than the H^+ deposition on beech plots (altitude 570 meters) with the average rainfall of 909 mm.

The increase of pH value for both types of precipitation and at all stands was evident during the reporting period.

4.2. The development of basic cations and sulfur and nitrogen compounds

The contents of alkaline cations in deposition are influenced by natural sources e.g. wind erosion of dry soil, volcanic eruptions and biological mobilization (pollen) and in the coastal areas by sea sprays (Gorham 1994). They are affected also by the anthropogenic sources from the agricultural soil tillage (plowing, liming, planting and harvesting), burning of biomass, traffic on unpaved roads, from construction and demolition of buildings and roads, but also from the burning of oil and coal with the formation of fly ash (Draaijers et al. 1997). The alkaline cations play an important role in the chemical process involving acidification (Hedin et al. 1994). Their neutralizing capacity is significant, whereby in central and north-western Europe the deposition of alkaline cations usually neutralized less than 25% of potential acid deposition (De Vries 1994). The basic cations Mg^{2+}, Ca^{2+} and K^{+} are important nourishment for forest ecosystems (Gorham 1994). The deposition of active basic cations can improve the nutritional status of the ecosystem (De Vries 1994). The influence of basic cations on forest ecosystem is positive, but in recent decades their amounts are reduced (Ferm & Hultberg 1999) as a result of the reduction of emissions from fuel combustion and industrial processes. Although our results showed no statistically significant changes in the deposition of calcium, except for the spruce throughfall, the changes of the other basic cations were proved significant. The sodium element had the largest decrease for the both forest types and depositions. The statistically significant decrease of the magnesium and potassium was detected only in bulk precipitation (Table 2).

According to Walna & Kurzyca (2007), rigid structure representation cations may indicate a stabilization of emission sources. Thöni (2008) did not find a reduction in the deposition of the elements Na, Mg, Ca and K but in Slovakia, the statistically significant changes were determined. These depositions in the past in Slovakia were affected by the situation in neighboring countries, where high values in the "Black Triangle" were recorded as a result of intense industrial activity (Draaijers et al. 1997). So the statistically significant decrease may be due to the reduction of industrial activity.

As in the most European countries, also in Slovakia, the high sulphur depositions gradually decreased. Atmospheric sulphur compounds usually include sulphur dioxide, hydrogen sulphide, mercaptans and sulphates which come from human activity, volcanic emissions and from waterlogged soils. Sulphur dioxide originates mainly from industry and thermal power plants as the result of the combustion of fossil fuels. Nitrogen oxides (NOx and NO_2) are also the result of the combustion of coal, oil, gasoline (Asman et al. 1998). In the past, high levels of these compounds were detected in the so-called "Black Triangle", the area between Germany, the Czech Republic, and Poland, but also in Ukraine (Van Leeuwen et al. 1995). Statistically significant decrease in the sulphur content was determined for both types of precipitation and for the both beech and spruce forest types. The most significant decrease was found for sulphur deposition in throughfall on the spruce stands ($R^2 = 0.75$). This is probably the result of the abandonment as well as the modernization of industrial enterprises emitting significant amounts of sulphur oxides in the countries of Eastern Europe. It was also the reduced sulphfur content in fuels and coal fired power stations to be fitted with filters depicting sulphur (Thöni et al. 2008). However, the downward trend in sulphur deposition between 1998–2010 was found in the most areas of Europe confirmed as statistically significant mainly thanks to the applied measures (Lorenz & Becher 2012). The beneficial effect of reducing sulphur depositions on the growth of European silver fir (Elling et al. 2009; Bošeľa et al. 2014; Büntgen et al. 2014) as well as Norway spruce (Kroupová 2002; Kolář et al. 2015).

On the contrary the development of nitrogen components was not so clear. Although statistically significant decrease of ammonia nitrogen was identified on the both forest types, the changes of nitrate nitrogen were not detected. The total nitrogen in the atmosphere is mainly in the form of nitrate and ammonia nitrogen. While the ammonium nitrogen is formed in particular as the result of agriculture, nitrate nitrogen comes from NO_x emissions from vehicle, industrial and heating plants (Van Leeuwen et al. 1995). Increasing the number of animals (Behera et al. 2013), as well as the intensification of plant cultivation brings further increase of ammonium nitrogen emissions. Cape et al. (2004) suggested that the concentration of NO_x and NH_4^+ found near the road is proportional to the density of traffic. Ammonia nitrogen is the primary alkaline gas in the atmosphere, and it is therefore important for determining the total acidity of precipitation (Shukla & Sharma 2010; Behera et al. 2013). Statistically significant decrease in ammonia nitrogen on the monitored plots might have been caused by decline in the agricultural production in Slovakia since the 90s.

No trends in nitrogen deposition were found also in the Czech Republic (Hunová et al. 2014) and also the evaluation of data from all European ICP Forests plots Level II confirmed no significant changes in the development of nitrate deposition. The effect of the increasing traffic and also long-range transfer may cause permanently high deposition of this parameter.

5. Conclusion

Although there was a significant reduction of pollutants since the early nineties of the 20th century, the forest ecosystems continue to be influenced by anthropogenic activities. Depositions of sulphur on the territory of Europe are lower but they are still high in the area of the continental shelf of the North Sea to Central and Middle East Europe (Belgium, Netherlands, Denmark, Germany, Czech Republic, Poland and Slovakia). Depositions of sulphur which are considered as a part of the acid deposition still affects the forest and aquatic ecosystems and threat to the environment everywhere. pH precipitation has improved, namely to increase its value, but this is still considered acidic.

The forests in Slovakia are situated in the region that is constantly threatened by a high environmental impact from industry and transport. The higher sulphur depositions were recorded in the industrial areas and the increased nitrogen depositions are mainly in the areas with a dense transport network and intensive agriculture.

Since the 90s there has been a significant reduction in industrial emissions, particularly sulphur dioxide, as a result of the cessation of production with an environmental burden and the modernization of production processes, which was also confirmed by our data. However, currently, there are new factors affecting the forest ecosystems, in particular, climate change, the impact of various abiotic, biotic and anthropogenic factors, and the current atmospheric pollution caused by all types of transport, industry and agriculture producing emissions of nitrogen oxides and associated with elevated concentrations of ground-level ozone.

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