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Source Apportionment Modeling of Bulk Precipitation Chemistry on the Dupniański Stream Catchment Area (Silesian Beskid – Southern Poland) Within 1999-2003

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Abstract

The study was carried out over a period of 5 years (1999-2003) at the Dupniański Stream catchment area located in Silesian Beskid Mts. region (southern Poland) by analysis of chemical composition of bulk precipitation. A data set consisting: precipitation volume, conductivity, water reaction, Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{2+}, Mn^{2+} and Zn^{2+} deposition were treated by source apportioning procedure and time series analysis. Four latent factors explain over 67% of the total variance of the system, allowing identification of the dominant pollution sources. Sources of pollutants have been defined and apportioned as follows: "acidic emission" - 35% (7.19 kg·ha^{-1}·month^{-1}); "mineral dust" - 12% (2.45 kg·ha^{-1}·month^{-1}); "heavy metals – dust particles" - 33% (7.98 kg·ha^{-1}·month^{-1}); "ammonium" – 8% (2.15kg·ha^{-1}·month^{-1}). Multiple regression analysis indicates that predicted and observed deposition of inorganic species is well correlated and varies between 0.59 and 0.95. Fourier transformation of varimax rotated factor scores discovers 12-month cycle in seasonal variability of "acidic emission" source.

Keywords: bulk precipitation chemistry, deposition, The Silesian Beskid, source apportionment modeling, time series analysis

Introduction

Atmospheric pollution in the form of acid rain impacts the health of forest ecosystems [1-5], affects the chemical balance of surface waters and soils [6-8], causes erosion of building materials [9]. Atmospheric deposition of sulphur and/or nitrogen may damage sensitive terrestrial and aquatic ecosystems [10-12]. Because of this, both analysis of chemical profiles of bulk precipitation and cycling of elements in spruce stands, which are affected by industrial emission is still subject to numerous studies.

Very often it is difficult to recognize source profiles and the use of composition data from other locations is misleading. Thus, it becomes necessary to extract information on the sources from the ambient monitoring data. There is a number of factor analysis methods that can be used to identify and apportion pollutant sources from the environment [13]. The basic factor analysis approach is a classical chemometric method of principal components analysis (PCA). PCA does not provide, however, a direct monitoring data balancing and apportionment. Therefore, PCA is commonly being connected with a source apportionment analysis, which is an important environmetric approach aiming to estimate the contribution of PCA-identified factors and the particular analytes to the total (mass) deposition investigated. After the PCA extraction of the number and identity of possible sources impacting investigated

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samples, the source contribution is calculated by using multiple regression of sample mass depositions on the Absolute Principal Component Scores (APCS).

Basing on data set containing deposition of inorganic species in bulk precipitation collected over a five-years period (1999-2003) in the Dupniański Stream catchment area we would like to demonstrate the possibilities offered by some established environmetric methods in assessment of environmental quality by identification of pollution sources affecting monitoring site, quantitative contribution assessment of each identified source and recognition of temporal variability of their impact. In this work PCA-APCS and time series analysis have been applied to achieve mentioned objectives.

Materials and Methods

Sampling and Analytical Techniques

The Dupniański Stream catchment of 1.68 km^2 area is located in southern Poland in the Silesian Beskid Mts.

Table. 1. Sumarized physico-chemical bulk precipitations characteristics within 1999-2003, water reaction and SEC of water in the Dupniański Stream catchment area in particular seasons

Year	V	Cl^-	NO_3^-	NH_4+	SO_4^{2-}	Na^+	K^+	Ca^{2+}	Mg^{2+}	Fe^{2+}	Mn^{2+}	Zn^{2+}	H^+	pH	SEC
Whole year (WY)															
	$mm \cdot m^{-2} year^{-1}$	$kg \cdot ha^{-1} year^{-1}$											$g \cdot ha^{-1} year^{-1}$		$mS \cdot m^{-1}$
1999	1119	24.72	62.49	10.76	65.19	7.68	8.41	38.61	5.53	0.90	0.14	2.86	54.72	5.31	3.30
2000	1094	20.26	31.14	18.57	29.25	6.89	7.49	29.63	3.46	0.71	0.14	0.53	67.85	5.21	3.12
2001	1210	21.40	34.60	26.61	46.88	5.16	6.61	34.18	4.19	0.10	0.16	7.26	66.88	5.26	3.01
2002	1145	16.19	42.51	12.78	37.57	10.06	17.39	47.07	7.37	0.23	0.07	0.22	45.57	5.40	3.14
2003	790	15.91	28.93	10.08	25.81	8.58	5.93	14.18	1.50	0.67	0.35	0.82	119.09	4.82	3.64
Growing season (GS)															
	$mm \cdot m^{-2} season^{-1}$	$kg \cdot ha^{-1} season^{-1}$											$g \cdot ha^{-1} season^{-1}$		$mS \cdot m^{-1}$
1999	640	21.56	49.88	5.28	47.87	5.55	7.08	30.35	4.91	0.77	0.11	2.56	16.00	5.60	4.17
2000	510	11.50	20.37	9.72	15.39	3.37	4.86	17.66	2.15	0.62	0.06	0.37	21.35	5.38	3.79
2001	799	15.19	24.87	20.82	27.95	2.87	5.21	24.75	2.61	0.03	0.10	7.18	8.70	5.96	3.20
2002	734	12.36	28.19	7.40	22.32	5.11	15.07	33.31	3.60	0.15	0.03	0.12	31.22	5.37	3.44
2003	512	11.55	19.40	6.18	15.26	1.67	2.44	8.27	0.68	0.38	0.24	0.52	100.53	4.71	3.86
Winter season (WS)															
	$mm \cdot m^{-2} season^{-1}$	$kg \cdot ha^{-1} season^{-1}$											$g \cdot ha^{-1} season^{-1}$		$mS \cdot m^{-1}$
1999	479	3.16	12.61	5.48	17.33	2.12	1.33	8.26	0.62	0.14	0.04	0.29	38.72	5.09	2.14
2000	583	8.77	10.78	8.84	13.86	3.52	2.63	11.97	1.30	0.10	0.08	0.15	46.50	5.10	2.54
2001	411	6.22	9.74	5.79	18.93	2.29	1.41	9.43	1.58	0.07	0.05	0.07	58.18	4.85	2.65
2002	411	3.83	14.33	5.38	15.24	4.95	2.33	13.76	3.77	0.08	0.04	0.10	14.35	5.46	2.59
2003	277	4.36	9.53	3.90	10.55	6.91	3.48	5.91	0.82	0.29	0.11	0.30	18.57	5.17	3.23
Average for 5 years															
	$mm \cdot m^{-2} year^{-1}$	$kg \cdot ha^{-1} year^{-1}$											$g \cdot ha^{-1} year^{-1}$		$mS \cdot m^{-1}$
WY	1072	19.70	39.94	15.76	40.94	7.67	9.17	32.73	4.41	0.52	0.17	2.34	70.82	5.18	3.21
GS	639	14.43	28.54	9.88	25.76	3.71	6.93	22.87	2.79	0.39	0.11	2.15	35.56	5.25	3.65
WS	432	5.27	11.39	5.88	15.18	3.96	2.24	9.87	1.62	0.13	0.06	0.18	35.26	5.09	2.57

Table 2. Varimax rotated factor loadings and mean source contribution to major ion deposition ($kg \cdot ha^{-1}\ month^{-1}$).

Ion	"acidic emission"	"mineral dust"	"heavy metals-dust particles"	"ammonium"	Estimated deposition ($kg \cdot ha^{-1}\ month^{-1}$)	Observed deposition ($kg \cdot ha^{-1}\ month^{-1}$)	R
	(factor loadings) mass contribution ($kg \cdot ha^{-1}\ month^{-1}$)						
SO_4^{2-}	**(0.75) 1.56**	(0.26) 0.74	(0.02) 0.60	(0.29) n.s.	2.90	3.41	0.85
NO_3^-	**(0.94) 3.06**	(0.03) n.s.	(0.11) 0.41	(-0.01) n.s.	3.47	3.33	0.95
Cl^-	**(0.91) 1.19**	(0.07) n.s.	(0.13) 0.19	(0.09) n.s.	1.38	1.64	0.92
Fe^{2+}	(0.13) n.s.	(0.25) 0.02	**(0.53) 0.04**	(-0.16) n.s.	0.06	0.04	0.59
Mn^{2+}	(0.02) n.s.	(-0.07) n.s.	**(0.80) 0.01**	(0.39) 0.005	0.016	0.014	0.89
Na^+	(-0.18) n.s.	**(0.72) 0.62**	(0.12) n.s.	(-0.13) n.s.	0.62	0.64	0.72
K^+	(0.24) 0.20	**(0.74) 0.85**	(0.01) n.s.	(0.03) n.s.	1.05	0.76	0.78
Ca^{2+}	(0.23) 0.40	**(0.83)1.95**	(-0.06) 0.39	(0.23) n.s.	2.74	2.73	0.89
Mg^{2+}	(0.09) n.s.	**(0.80) 0.32**	(-0.19) n.s.	(0.09) n.s.	0.32	0.37	0.80
Zn^{2+}	(0.09) n.s.	(0.02) n.s.	(-0.02) n.s.	**(0.68) 0.46**	0.46	0.19	0.68
NH_4^+	(0.10) n.s.	(0.10) n.s.	(0.01) n.s.	**(0.81) 0.74**	0.74	1.31	0.81

R is the correlation coefficient between estimated and observed deposition values
n.s. – not significant

(49°34'N, 18°50'E) not far from the main industrial centres. This region of the Polish part of the Carpathian Mountains is under their negative effect [14-15]. The catchment is covered with Norway spruce (*Picea abies* Karst) stands of different ages growing on dystric cambisols developed on Istebna sandstone. A bulk precipitation sampler was installed in the middle of the catchment at an elevation of 725 m a.s.l. The studies were conducted between 1999 and 2003 and the analytical methods applied were described in details elsewhere [16-17]. During the growing season, i.e. from 1st May to 30th October, samples of bulk precipitation directly reaching the catchment area were collected in special samplers (5 units with 15 cm inlet diameter each) installed in an open area 0.5 m above ground level, connected to a plastic tube with an outlet joining a container and a measuring device installed in a bunker. In Winter, staring from 1st November to 30th April (the following year) six collectors (plastic, chemically neutral snow bags with 15 cm inlet diameter each) were installed at 1.3 m above ground level in the open area at a distance of 120–150 m from the forest border.

The sampling was performed on the first day of each month. Water reaction and conductivity were measured in field (Eijkelkamp pH 13.37 and EC 18.34). Water was analysed using ion chromatography (Dionex-320) to determine the concentration of: Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{2+}, Mn^{2+} and Zn^{2+}. A low-pH acid rain sample from southern Ontario (Canada), RAIN.97 - No 409 served as a certified reference material (CRM) and was analyzed as well. Analytes' concentration ($mg \cdot dm^{-3}$) values were transformed to deposition ($kg \cdot ha^{-1}$) and in this form evaluated chemometrically.

Chemometrics

Principal Component Analysis transforms the original data matrix into a product of two matrices, one of which contains the information about the objects and the other about the variables. More often several principal components (PCs) provide a good summary of all the original variables. Usually, the limited number of components are subjected to rotation using a criteria such as varimax. After PCA rotation, the resulting components have been found to often be more representative of individual underlying sources of variation [18]. This, in turn, results in more interpretable and useful PCs.

The APCS procedure introduced by Thurston and Spengler [19] is well developed and often applied for apportionment purposes [20-22]. This balancing approach accepts that all sources have been identified by the principal components analysis and all of them participate in the source contribution procedure.

Time series (TS) are sequences of independent random variables (observations) describing a phenomenon at successive points in time [23]. The purpose of TS analysis is: (i) a display of the series, (ii), preprocessing of the data, (iii) making a statistical analysis of relevant difference between successive observations, (iiii) to predict (forecast) future values of the TS [24-27], (iiiii) to detect mechanisms that govern changes in the observed phenomenon through time, in other words, to determine the nature of the phenomenon represented by the sequence of observations and to control the predicted values [28]. Data patterns are often expected to be smooth, that is, each data point is similar or well supported by the points in its vicinity. Smooth, modeled

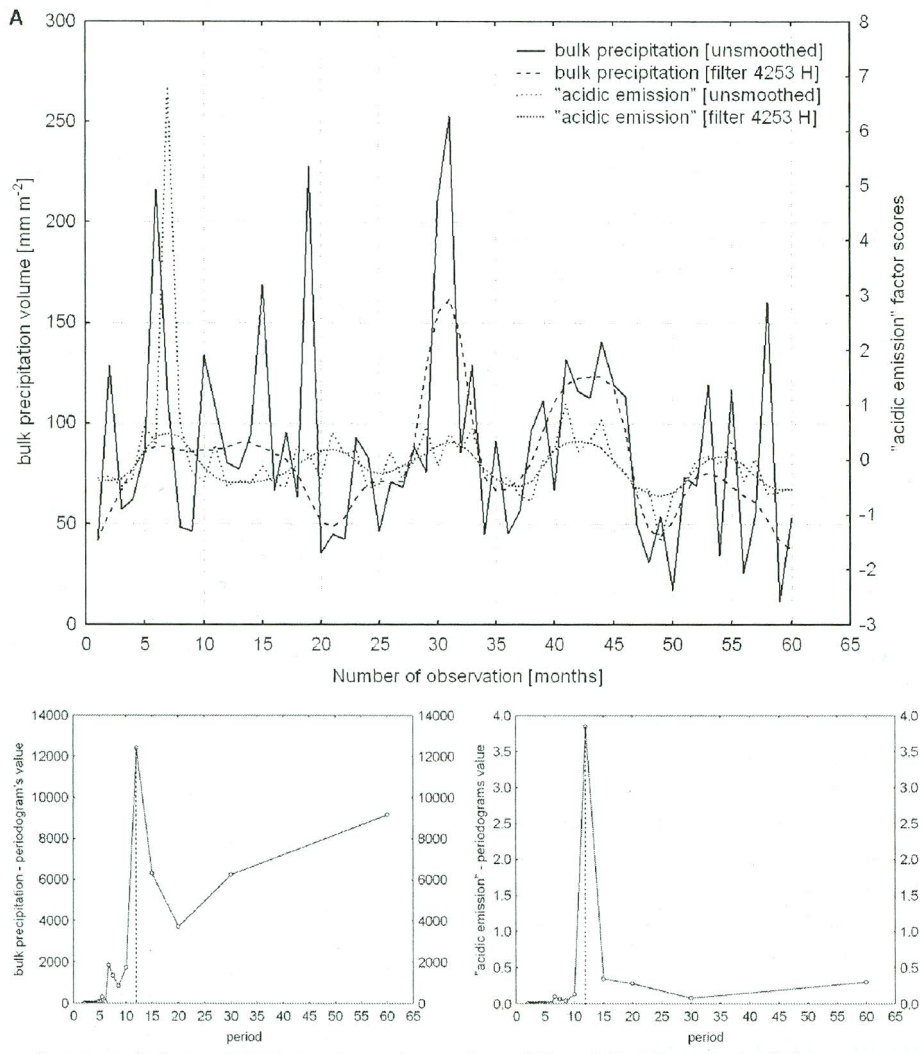

Figure 1. Distribution of average bulk precipitation volume ($mm \cdot m^{-2} month^{-1}$) and "acidic emission" factor scores during the period between I 1999 and XII 2003 determined on the basis of measurements carried out and corresponding periodogram's values.

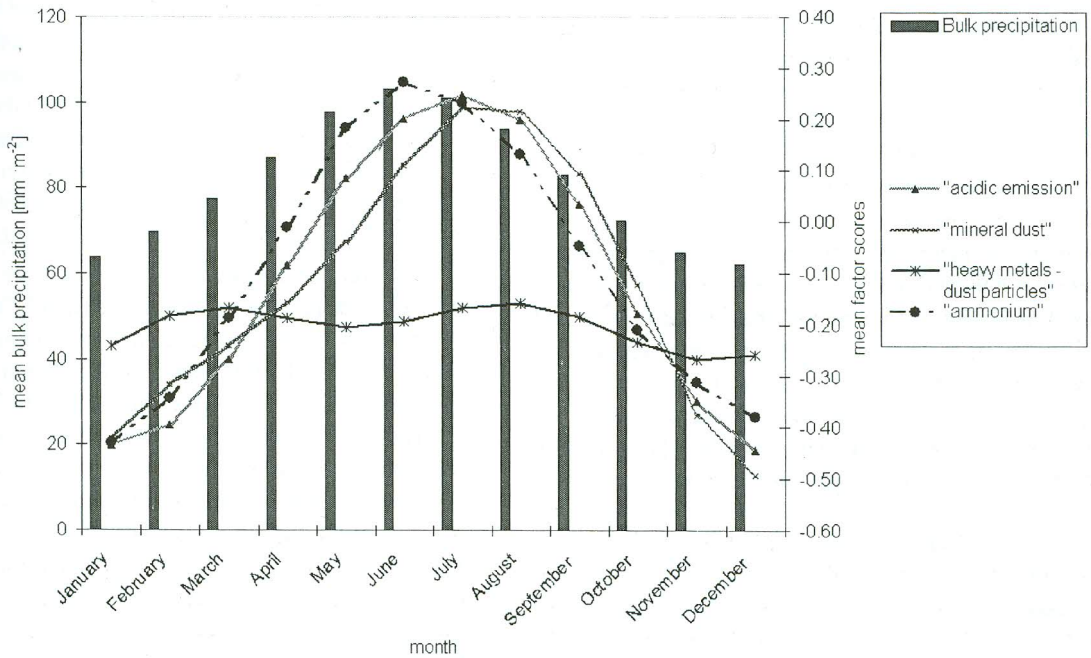

Figure 2. Distribution both of the seasonally decomposed mean bulk precipitation volume ($mm \cdot m^{-2}$) and PCs factor scores with particular months of the year taken into consideration.

sequences are typically locally monotone or gradually changing from point to point. However, in exploratory analysis, a small number of extreme data points not otherwise supported are usually not considered part of the main pattern (called as "noise") and thus necessarily should be isolated from the main pattern by application of various smoothing algorithms (i.e. moving averages, moving median, 4253H filter [29-30], Monte Carlo [31]. Transformation in the form of 4253H filter covers multiple smoothing based on moving average/median. This approach appears to be one of the most efficient in case of describing environmental data processing.

In this paper, analytes' monthly deposition values were treated initially by PCA and after that latent factors were included in the APCS apportioning procedure. Basing on the scree plot and Kaiser criteria only those PCs were included in the model, which posses an eigenvalue higher to or close to 1. The obtained regression coefficients were then employed to convert absolute monthly factor scores and estimate PCs mass contributions. The weighted least square regression ($p<0.05$) was performed for majority of investigated inorganic species deposition values. Next, in order to examine the structure of a TS both bulk precipitation volume and PCs scores were smoothed using a 4253H filter [29-30] and in this form subjected to Fourier spectrographic analysis, using the Hamming criteria to assess significance of the spectral concentrations [32].

All calculations in this study were performed by applying Statistica 6.0 [33] and Microsoft Excel 2000 application running on MS Windows 2000 platform.

Results and Discussion

Investigated bulk precipitation characteristics (in $mm \cdot m^{-2}year^{-1}$/$mm \cdot m^{-2}season^{-1}$ and $kg \cdot ha^{-1}year^{-1}$/$kg \cdot ha^{-1}season^{-1}$ or $g \cdot ha^{-1}year^{-1}$/$g \cdot ha^{-1}season^{-1}$), water reaction and SEC (in $mS \cdot m^{-1}$) of water in the Dupniański Stream catchment area presented in Table 1, covers the period 1999-2003. According to Jansen classification [34] the annual mean conductivity measured in successive years (3.01-3.64 $mS \cdot m^{-1}$) was classified as high level mineralization. The maximum value was observed in 2003 when the precipitation volume was the lowest (790 $mm \cdot m^{-2}$). Water reaction in the period 1999-2002 varied between 5.21 and 5.40 was classified as normal, while in 2003 decreased to 4.82 and was classified as slightly acidic. In growing season bulk precipitation was characterized by conductivity classified as high level (3.20-4.17 $ms \cdot m^{-1}$) and normal pH (5.38-5.96) with exception in 2003 (4.71) when it changed into slightly acidic. In general, during winter season conductivity was lower than in growing one (2.14-2.65 $mS \cdot m^{-1}$), with an exception in 2003 when it was classified as high level (3.23 $mS \cdot m^{-1}$). Omitting 2001 year (pH of 4.85 – slightly acidic) water reaction in winter season was normal (5.09-5.46). According to Malzahn classification [35] bulk precipitation pH value in Dupniański Stream catchment area was comparable to other areas of Beskid Mts. [36], while different from Puszcza Borecka, Wigry, Storkowo, Koniczynka, Pożary, Święty Krzyż and Szymbark area comparing both pH and conductivity in analogical time interval [37-43].

The application of PCA has led to identification of four factors responsible for the data structure. PC_1 conditionally named as "acidic emissions", referring to co-emission of SO_4^{2-} and NO_3^- precursors (SO_x, NO_x) associated with the combustion of fossil fuels, automobile exhaust and burning of biomass, was strongly correlated with Cl^-, SO_4^{2-} and NO_3^- deposition. PC_2 conditionally named as "mineral dust", referring to soil-dust particles, was strongly correlated with Na^+, K^+, Ca^{2+} and Mg^{2+} deposition. PC_3, conditionally named as "heavy metals – dust particles", referring to heavy metals connected with ash emissions includes linked Fe^{2+} and Mn^{2+} deposition. The PC_4, conditionally named as "ammonium", was strongly influenced by NH_4^+ deposition. Identified factors explain 67.1% of the variance while particular PCs (PC_1-PC_4) explain 28.1%, 17.9%, 10.7% and 10.4%, respectively. Next, the varimax rotated PCs factor scores were subjected to APCS procedure. The intercept obtained in apportioning procedure (corresponding to the impact of undefined sources) was insignificant and equal to 2.45 $kg \cdot ha^{-1}month^{-1}$, while a correlation coefficient (R) between total estimated and measured deposition was equal to 0.87. The results indicate that 35% (7.19 $kg \cdot ha^{-1} \cdot month^{-1}$) of pollutants deposited with precipitation are caused by "acidic emission". The contribution of "mineral dust" and "heavy metals – dust particles" connected with ash emission is estimated as 12% (2.45 $kg \cdot ha^{-1} \cdot month^{-1}$) and 33% (7.98 $kg \cdot ha^{-1} \cdot month^{-1}$), respectively. Lower contribution comparing to "mineral dust" is related to "ammonium"–8% (2.15 $kg \cdot ha^{-1} \cdot month^{-1}$). In general, the Thurston-Spengler's procedure [19] indicates that the highest, comparable contribution to the total deposition mass have an acidic and ash emissions. It has to be stressed that this is a logical balancing keeping in mind that, for instance, fossil fuels combustion, burning of biomass and automobile exhaust emitters are commonly connected with an ash emission and as it could be recognized as anthropogenic activity and the main pollution source in the Silesian Beskid Mts. region. In Table 2 the PCA-derived source profiles are presented as a mass contribution for major anions and cations (SO_4^{2-}, NO_3^-, Cl^-, Fe^{2+}, Mn^{2+}, Na^+, K^+, Ca^{2+}, Mg^{2+}, Zn^{2+} and NH_4^+) determined in bulk precipitation samples, for which the obtained PCs were characterized as an "acidic emission", "mineral dust", "heavy metals - dust particles" and "ammonium". In general the predicted and observed deposition of inorganic species is well correlated (R higher than 0.55).

The data collected was detailed enough to make an assessment of seasonal behaviour of major pollution sources identified in Dupniański Stream catchment area. As a result of TS analysis (Fourier spectrographic analysis, Hamming criteria), distinct twelve-month time cycles were discovered in the TS structure of the bulk precipitation volume as well as in "acidic emission" factor. An existence of twelve-moth cycles is also observed for "mineral dust" and "ammonium" but with additional components differentiating these cycles from the previously described. No season-

al variability is observed for "heavy metals - dust particles". As an example, Figure 1 shows both distribution of monthly average bulk precipitation volumes and PC_1 ("acidic emission") factor scores for unsmoothed and smoothed variables. The periodogram's values (Figure 1) show the peak of volume of bulk precipitation and PC1, which clearly indicates a period T=12 months. Seasonal decomposition of the smoothed data allows the identification of the period's cycle in variation of bulk precipitation and PC_1. One of the findings is that some months have significantly higher volume rainfall events, while others have considerably lower. Figure 2 shows seasonally decomposed average monthly bulk precipitation volume and PCs scores for each of 12 months. Two clearly distinct periods are recognized: winter season (October-April) and growing season (May-September). An increase of the mean monthly bulk precipitation volume can be observed (91.8 $mm \cdot m^{-2}$) during growing season while in winter months the mean monthly bulk precipitation volume is approximately equal to 70.8 $mm \cdot m^{-2}$. Despite large emission reductions the Dupniański Stream catchment area still suffers from very high loads of acidifying input deposited during the past decades. Temporal fluctuations of "acidic emission" factor scores indicate increasing deposition of NO_3^- and SO_4^{2-} in growing season while decreasing in winter one. It has to be stressed at this point that NO_3^- deposition is prevailing in growing season, while SO_4^{2-} in winter season. As arises from Figure 2 four variables are positively correlated: bulk precipitation volume and "acidic emission", "mineral dust" and "ammonium" factor scores.

According to Jansen classification [34] an "acidic" compounds content assessment in rainwater samples indicates highest contribution of nitrates (62.49 $kg \cdot ha^{-1} \cdot year^{-1}$) and sulphates (65.19 $kg \cdot ha^{-1} \cdot year^{-1}$) in 1999, while ammonium in 2001 (26.61 $kg \cdot ha^{-1} \cdot year^{-1}$); with an escalation in growing season: 49.88 $kg \cdot ha^{-1}$ (1999), 47.87 $kg \cdot ha^{-1}$ (1999) and 20.82 $kg \cdot ha^{-1}$ (2001), respectively. Referring to entire period between 1999 and 2003 deposition of sulphates dominates (40.94 $kg \cdot ha^{-1} \cdot year^{-1}$) in the Dupniański Stream catchment area and similarly to results presented above this domination is more visible in vegetation season (25,76 $kg \cdot ha^{-1}$). Similar seasonality was observed by others [36] in Brenna and Salmopol areas. Increasing deposition of "acidic compounds" is an outcome of both high concentration and high bulk precipitation volume in growing season. Deposition of sulphates indicates decreasing tendency in consecutive years, both annual (65.19-25.81 $kg \cdot ha^{-1} \cdot year^{-1}$) and in winter (17.33-10.55 $kg \cdot ha^{-1}$) or growing season (47.87-15.26 $kg \cdot ha^{-1}$). Similar decrease was observed at Szymbark, Święty Krzyż and Storkowo stations [39, 42, 43]. Presented trend indicates decreasing air pollution level caused by SO_x both in areas mentioned above and in the Dupniański Stream catchment area [44]. The deposition of $S\text{-}SO_4^{2-}$ (13.67 $kg \cdot ha^{-1} \cdot year^{-1}$) in the Dupniański Stream catchment area was lower than in Święty Krzyż station (22.4 $kg \cdot ha^{-1} \cdot year^{-1}$) [42], which is characteristic to the areas of central-eastern Europe. Total nitrogen deposition ($N\text{-}NH_4^+$ 20.66-7.83 $kg \cdot ha^{-1} \cdot year^{-1}$ and $N\text{-}NO_3^-$ 14.11-6.54 $kg \cdot ha^{-1} \cdot year^{-1}$) exceeds total sulphur deposition ($S\text{-}SO_4^{2-}$ 21.76-8.61 $kg \cdot ha^{-1} \cdot year^{-1}$) in consecutive years. The maximum deposition of $N\text{-}NH_4^+$, $N\text{-}NO_3^-$ and $S\text{-}SO_4^{2-}$ was observed in 2001 similarly to the observations at Storkowo station [39]. Moreover, the contribution of $N\text{-}NH_4^+$ exceeds the one of $N\text{-}NO_3^-$ likewise in works presented by others for both Wigry, Storkowo and Silesian voivodship [36, 38, 39, 43, 45].

The effect of nitrogen deposition may be an increasing problem in the future unless emissions of nitrogen oxides and ammonium are reduced [46]. Nitrogen deposition (sum $N\text{-}NO_3^-$ and $N\text{-}NH_4^+$) was above the critical load (15-20 $kg \cdot ha^{-1} \cdot year^{-1}$) for coniferous trees not only on the Dupniański Stream catchment area but also on Św. Krzyż [42] and in the middle and south of the Silesia Region – one of the most polluted area in Poland [45], which may change N/macronutrients ratios, decrease K and Mg and increase N concentration in foliar tissue [47]. Nitrogen deposition fluxes in this study were high, above critical loads, but still below the values reported for the heavily polluted Ore Mts. (Czech Republic) [48].

In rainy years (2001, 2002) a slight shift from decreasing trend of anions deposition was observed. In 2003 both minimum total bulk precipitation value and deposition of analytes ($kg \cdot ha^{-1} \cdot year^{-1}$) were observed (V - 790 $mm \cdot m^{-2}$, Cl^- - 15.91, NO_3^- - 28.93, SO_4^{2-} - 25.81, NH_4^+ - 10.08, K^+ - 5.93, Ca^{2+} - 14.18, Mg^{2+} - 1.50). In the group of alkali cations the highest deposition was observed for Ca^{2+} (47.07-14.18 $kg \cdot ha^{-1} \cdot year^{-1}$) and the lowest for Mg^{2+} (7.37-1.50 $kg \cdot ha^{-1} \cdot year^{-1}$). Comparing Ca^{2+} and Mg^{2+} deposition within seasons, higher values were observed in growing season (33.31-8.27 $kg \cdot ha^{-1}$), while lower during winter months (13.76-5.91 $kg \cdot ha^{-1}$) (Table 1). Soil in the Dupniański Stream catchment area is very acidic and has relatively small pools of exchangeable Ca^{2+} and Mg^{2+}. Soil recovery depends on future emissions, especially on base cation deposition. The recovery will be even slower if base cation deposition decreases further [5].

Conclusions

1. Nitrogen deposition was above critical loads for coniferous trees, which may change N/macronutrient ratios, decrease K and Mg and increase N concentration in foliar tissue.
2. Environmetric methods (PCA/APCS and TS) allowed identification of dominant pollution sources affecting monitoring site, quantitative contribution of identified sources as well as recognition of temporal variability of their impact.
3. Four latent factors explain over 67% of the total variance of the system. Sources of pollutants are defined and apportioned as follows: "acidic emission" - 35%; "mineral dust" - 12%; "heavy metals – dust particles" - 33%; "ammonium" - 8%.
4. Multiple regression analysis indicates that predicted and

observed deposition of inorganic species is well correlated and varies between 0.59 and 0.95. Fourier transformation of varimax rotated factor scores discovers 12-month cycle in seasonal variability of "acidic emission" source.

5. In growing season deposition of analytes connected both with "acidic emission", "mineral dust" and "ammonium" increases simultaneously with volume of bulk precipitation. It has to be stressed that NO_3^- deposition predominates in growing season, while SO_4^{2-} in winter season.

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