Article

The Effect of Environmental Conditions on Pollution Deposition and Canopy Leaching in Two Pine Stands (West Pomerania and Świętokrzyskie Mountains, Poland)

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Abstract: This study analyzed the effect of atmospheric deposition on canopy leaching processes in stands predominantly composed of Scots pines. The research was conducted in two stands: the first located in the southwestern part of the Świętokrzyskie Mountains in the area known as Białe Zagłębie (Malik), and the second in the northwestern part of Poland in Western Pomerania (Czarne). The study was conducted in the hydrological years 2010–2013. The goal of the study was to assess the chemical transformation of precipitation as a result of various human activities. In Malik, the main factor that determined the physicochemical and chemical properties of throughfall was the cement/lime dust emitted by nearby industrial plants, which not only affected the quantity of deposit but also contributed to the alkalization process of throughfall. By contrast, the main source of pollution in Czarne, where local emitters are absent, was long-distance transport. We conducted a principal component analysis (PCA) in both stands that produced components representing local pollution (Malik) and long-distance transport (Czarne). For the stand in Czarne, sea aerosols were an important source of Na⁺ and Cl[−] ions in precipitation. In both stands, the highest enrichment ratio (ER) values were recorded for K⁺ ions. The contribution of leaching processes to the bulk deposition of K⁺ ions in Malik was 85.8%, whereas in Czarne, it was 73.8%. Regardless of the degree of anthropopressure, the intensity of quantitative and qualitative transformation in pine stands was comparable.

Keywords: throughfall; bulk precipitation; ion deposition; canopy budget model; Scots pine

1. Introduction

Atmospheric deposition is considered one of the controlling factors that determine the circulation of matter in forest ecosystems. As a result of contact with the surface of plants, rainwater undergoes a transformation that depends not only on species composition (conifers, deciduous trees) but also on the degree of atmospheric air pollution. In the temperate climatic zone, vegetation strongly affects the biogeochemical cycles of elements. These cycles are associated with water circulation and the chemical composition of water and dust that reaches tree stands, among other processes. Atmospheric pollutants affect the chemical composition of rain both directly, through their chemical properties, and indirectly, by leaching compounds deposited on the surface of needles or leaves.

As a result of alkaline pollutants emitted over the last 50 years, significant changes in rainwater occurred in Malik [1], altering the floristic composition of forest communities as well as other

components of the natural environment including soils [1,2] and selected bioindicators, such as pine needles and lichens [3,4]. The results of precipitation chemistry monitoring since the end of the 1990s confirm a systematic decrease in both precipitation's level of electrical conductivity (EC) and its ion concentration. The observed low ion concentrations in precipitation reflect the better air quality in northern Poland than in the south. As a result of reductions in the domestic emission of sulfur, precipitation pH has increased in the studied area and a greater role in the acidification process of nitrogen compounds [5].

When rainwater contacts plant surfaces, materials deposited on the surfaces wash out the rainwater and change its physicochemical properties and chemical composition. Furthermore, extensive ion-exchange processes take place between rainwater and trees in the canopy [1,6,7]. In addition to these changes in chemical composition, there are also changes in the amount of water that reaches the soil due to interception by the canopy. The rainfall that reaches the soil is characterized by significant variability that depends on the species composition of the forest; the structure, levels, density, and shape of the canopy [6,8–10]; the degree of compaction of leaves and needles; and distance from the tree trunk [11,12].

Research on the dynamics of nutrient cycling in forest stands indicates significant quantitative and qualitative differences between bulk precipitation and throughfall [6,11,13–18]. The species composition of a stand and the acidity of precipitation are important factors that modify the intensity of precipitation transformation in a forest [6,11]. It is assumed that coniferous trees modify the chemical properties of precipitation much more than deciduous trees [19] and thus have a stronger effect on the load of nutrients supplied to the soil, which in turn contributes to an increase in the rate of soil leaching [6,11]. The intensity of the leaching process depends, among others, on species composition [8,10], size of immission [20], and size of deposition [1]. According to Ukonmaanaho and Star [21], the leaching process mainly concerns monovalent K^+ ions, which are more mobile and less bound in cell walls, chloroplasts, and enzymes [22] than divalent cations, and whose intensity depends on the size of acid deposition.

The main research problem was to determine the deposition and processes occurring in pine stands in areas with varying degrees of atmospheric air pollution.

The manuscript tested the following hypothesis: the intensity of leaching components from pine tree crowns depends on cement-lime dust, emissions from agricultural areas, and marine aerosols.

2. Materials and Methods

2.1. Study Site

The research was conducted in two mixed stands composed predominantly of Scots pines (Table 1). Both research plots belong to the measurement network of the Integrated Monitoring Program (ICP; Czarne and Malik correspond to PL06 and PL09, respectively). The first, Malik, is located in the southwestern part of the Świętokrzyskie Mountains in the area known as Białe Zagłębie, while the other, Czarne, is located in Western Pomerania (Figure 1). The Czarne plot is situated in an area without local sources of industrial pollution. The dominant forms of land cover are arable land (43.4%) and forests (34.6%) under intensive management [5]. The largest urban center, Szczecinek (population 40,366), is located 15 km from the plot and can be a source of municipal pollution. Impact of pollutants from Szczecinek is limited only to the situation of inflow of air masses from the southeast direction. The share of this sector in a year is 5% on average.

Acidification and the ion concentration in rainwater are declining in the research area due to the reduction of SO_2 emissions that has been observed in recent years [5]. From 2010 to 2013, the annual mean concentrations of SO_2 and NO_2 ranged from 3.32 to 5.05 $\mu g \cdot m^{-3}$ and from 2.04 to 6.31 $\mu g \cdot m^{-3}$, respectively [5].

In the Białe Zagłębie area, the cement/lime industry is a major source of dust emissions. In the years 2010–2013, these plants emitted a total of 1487.1 tonnes of dust into the atmosphere, of which lime plants were 46.2% and cement plants were 53.8%.

Table 1. Characteristics of the experimental stands.

Parameters	Czarne	Malik
Location	53.7471° N, 16.5529° E	50.8144° N, 20.4966° E
Altitude (m above sea level)	152	267
Species composition at sampling site (%)	<i>Pinus sylvestris</i> (86), <i>Quercus robur</i> (7), <i>Fagus sylvatica</i> (5), <i>Betula pendula</i> (2)	<i>Pinus sylvestris</i> (52), <i>Carpinus betulus</i> (27) <i>Fagus sylvatica</i> (21)
Canopy cover (%)	70	60
Trees age (year) ¹	<i>Pinus sylvestris</i> (92), <i>Quercus robur</i> (20), <i>Fagus sylvatica</i> (40), <i>Betula pendula</i> (20)	<i>Pinus sylvestris</i> (80), <i>Carpinus betulus</i> (50), <i>Fagus sylvatica</i> (60)
Trees height (m) ¹	<i>Pinus sylvestris</i> (17–27), <i>Quercus robur</i> (5–10), <i>Fagus sylvatica</i> (10–15), <i>Betula pendula</i> (2–10)	<i>Pinus sylvestris</i> (25–35), <i>Carpinus betulus</i> (20–25), <i>Fagus sylvatica</i> (20–28)
Soils	Spodic Udipsamments ² , Albic Brunic Arenosol (Dystric) ³	Spodic Udipsamments ² , Albic Brunic Arenosol (Dystric) ³
Soils texture	Sand	Sand
Pines average breast height (cm) ¹	11–55	14–21
Average annual air temperature (2010–2013)	7.1°–8.1°	6.7°–7.7°
Average annual total of precipitation (2010–2013) (mm)	692.8	575.0

¹ Data for 2013, ² soil taxonomy [23], ³ World Reference Base for Soil Resources [24].

Figure 1. Location of the sampling site.

The Malik plot is situated 2.5 km from the Dyckerhoff cement plant in Nowiny and 5 km from the lime plant in Sitkówka-Nowiny. From 2010 to 2013, the mean annual concentration of PM10 in

Nowiny ranged from 32.0 to 40.3 $\mu\text{g}\cdot\text{m}^{-3}$, with a maximum daily mean of 186.6 $\mu\text{g}\cdot\text{m}^{-3}$ observed in 2012. The particulate matter in this area is highly alkaline ($\text{pH} > 11$), and calcium and magnesium ions are predominant [1]. In the analyzed period, the annual mean concentration of NO_2 at Nowiny ranged from 15.5 to 26.4 $\mu\text{g}\cdot\text{m}^{-3}$ [1].

2.2. Sampling and Laboratory Analyses

2.2.1. Rainfall and Throughfall Measurements

The results presented here cover a period of four hydrological years: 2010, 2011, 2012, and 2013. The measurement system included bulk precipitation (BP) and throughfall (TF). In Malik, throughfall was measured with five collectors with a total collection surface of 5670 cm^2 arranged in an “X” shape at a height of 1 m above the ground. In the second research plot, Czarne, the measuring system included 12 collectors with a total area of 1592 cm^2 regularly spaced on a grid. The inlet of each collector was placed at a height of 1 m above the ground. In both cases, the collectors were made of plastics (PTFE) that did not affect the chemical composition of rainwater. The collectors in the field were exposed monthly. In both the cases of bulk precipitation and throughfall, precipitation samples were collected after a monthly exposure of collectors in the field.

2.2.2. Chemical Analysis

Laboratory analyses measured the amount of precipitation and basic physicochemical parameters including electrical conductivity (EC), pH, and the concentrations of dominant ions (chlorides, sulfates, nitrates, sodium, magnesium, potassium, ammonium, and calcium). The amount of precipitation, pH, and EC were measured for each collector separately. The quantification of the other parameters was based on mixed samples. Samples were mixed proportionally, taking into account the precipitation amount at individual positions. After filtration, the samples were stored in a refrigerator at 4 °C. Chemical analyses were conducted in laboratories included in the Integrated Monitoring of the Natural Environment network of Poland. Samples from Malik were analyzed in the Environmental Research Laboratory of Jan Kochanowski University in Kielce, whereas samples from the Czarne plot were analyzed in the laboratory of the Geoecological Station at Adam Mickiewicz University in Storkowo (Table 2). During the research period, both laboratories participated in an inter-calibration process and the results obtained by each did not differ. Artificial rain samples from inter-calibration experiments organized by WMO/GAW (World Meteorological Organization/Global Atmosphere Watch Programme) were used. The difference in the results obtained in relation to the expected results was in the range of $\pm 10\%$.

Table 2. Experimental parameters, methods, and units.

Variable	Method and Instrument		Reporting Unit
	Czarne	Malik	
pH, EC	Potentiometry	Potentiometry	pH unit, $\mu\text{S}\cdot\text{cm}^{-1}$
Cl^- , NO_3^- , SO_4^{2-}	Ion chromatography (DX-120 by Dionex)		$\text{mg}\cdot\text{dm}^{-3}$
NH_4^+	Nessler spectrophotometric method (Spekol 1100, Carl Zeiss)		
Na^+ , K^+	AES Flame (SpectrAA-20 plus, Varian)		
Ca^{2+} , Mg^{2+}	AAS Flame (SpectrAA-20 plus, Varian)		

2.3. Data Analysis

2.3.1. Statistical Analysis

We calculated a weighted mean for each parameter, where the weight was the amount of precipitation. Unless otherwise stated, the reported statistics covered the entire measurement period and were calculated on the basis of monthly data. We performed statistical analysis to determine the statistical significance of differences between depositions under the canopy and in open areas. To identify the supply sources of chemical components in the analyzed water samples, we performed a principal component analysis (PCA) with Varimax factor rotation.

Variables were appropriately standardized before the PCA was performed. Finally, Pearson correlation was tested to determine the relationship between ion distributions.

2.3.2. Enrichment Ratio

In order to determine the degree of precipitation transformation in the forest, an enrichment ratio (ER) was applied (the ratio of the load of an ion in precipitation under the canopy to its load in precipitation in the open area).

2.3.3. Canopy Budget Modelling

To determine the loads of ions (K^+ , Ca^{2+} , Mg^{2+}) leached out of the canopy, we used the canopy budget model [25–28].

This model is based on two assumptions:

- Na^+ ions are not subject to any processes during the infiltration of precipitation through the tree canopy; and
- Particles containing Ca^{2+} , Mg^{2+} , and K^+ ions have the same size as particles containing Na^+ .

These assumptions make it possible to estimate the DDF (dry deposition factor) for these ions according to the following formula [23]:

$$DDF = (TF_{Na} + SF_{Na} - BP_{Na}) / BP_{Na} \quad (1)$$

where TF_{Na} is the throughfall flux of sodium, SF_{Na} is the stemflow flux of sodium, and BP_{Na} is the bulk precipitation flux of Na^+ .

The amount of leaching of individual CL_x ions was calculated on the basis of the following formula [27]:

$$CL_x = TF_x + SF_x - BP_x - DD_x \quad (2)$$

where DD_x is the ion loads from the wash-off of dry deposition from the surface of plants.

2.3.4. Neutralisation Indicators of Acidic Compounds

Some of the cations (Ca^{2+} , Mg^{2+} , K^+) and anions (SO_4^{2-}) measured over land partially originate from sea salt. The fractions of these ions, which originate from the sea, did not play any role in deciding acidity/alkalinity of rainwater sample. The non-sea-salt (nss) fraction ions concentrations were calculated as follows [29,30]:

$$\text{No-sea-salt (nss)} = X_{\text{bulk precipitation}} - Na_{\text{bulk precipitation}} \cdot \frac{X}{Na^+} \text{ seawater} \quad (3)$$

where $X = SO_4^{2-}$, K^+ , Mg^{2+} , Ca^{2+} .

Neutralization factors (NF_x) of the different alkaline constituents were calculated using the formula suggested by Parashar et al. [31]:

$$NF_x = \frac{X}{nssSO_4^{2-} + NO_3^-} \quad (4)$$

where $X = nssCa^{2+}, nssMg^{2+}, nssK^+, NH_4^+$.

Considering both SO_4^{2-} and NO_3^- as the main acidifying components of rain. Fractional acidity (FA) was computed according to Balasubramanian et al. [32] as

$$\text{Fractional acidity (FA)} = \frac{H^+}{nssSO_4^{2-} + NO_3^-} \quad (5)$$

FA = 1 indicates that the acidity is not neutralized, whereas FA = 0 indicates that the rainwater acidity generated by these strong acids is completely neutralized.

Relative contribution of NO_3^- to the acidification was calculated using a ratio

$$\text{Contribution indicator of acidic factors} = \frac{NO_3^-}{nssSO_4^{2-}} \quad (6)$$

All concentrations were expressed in $\mu\text{Eq}\cdot\text{dm}^{-3}$.

3. Results

3.1. Canopy Impacts on Rainwater Fluxes

During the study period, the average annual bulk precipitation was 692.8 (579.9–784.8) mm for the Czarne plot and 575.0 (476.5–736.4) mm for the Malik plot. The average throughfall was 503.5 mm for Czarne and 410.3 mm for Malik. Values for individual years ranged from 408.1 mm (2013) to 581.7 mm (2010) for Czarne, and from 372.7 mm (2012) to 547.2 mm (2010) for Malik. In both stands, the distribution of the amount of throughfall was strongly correlated with the distribution of precipitation (Figure 2).

Figure 2. Linear correlations between bulk precipitation and throughfall in the Czarne (a) and in the Malik (b). r is the Pearson correlation coefficient, p is the significance value, n is the sample size.

During the study period, the mean standard deviation of canopy interception was $28.7\% \pm 8.5\%$ (Czarne) and $27.1\% \pm 24.7\%$ (Malik). Extreme values ranged from 18.1% to 75.0% (Czarne) and from -36.9% to 83.6% (Malik). In some instances, monthly throughfall for the Malik plot was observed as being higher than monthly precipitation in the Malik plot's open area (canopy interception less than 0%). From 2010 to 2013, there were five such cases: in January and February 2010 (-31.5% and -18.9% , respectively), in November 2011 (-35.3%), in August 2012 (-23.0%), and in April 2013 (-36.9%).

3.2. Canopy Impacts on Rainwater Chemistry and Deposition Fluxes

The weighted mean EC of bulk precipitation during the study period, taking into account the standard deviation at Malik, was $37.6 \pm 23.2 \mu\text{S}\cdot\text{cm}^{-1}$ and $13.7 \pm 8.1 \mu\text{S}\cdot\text{cm}^{-1}$ for the Czarne plot. Under the canopy, the weighted average EC increased in comparison with bulk precipitation and was $65.9 \pm 61.5 \mu\text{S}\cdot\text{cm}^{-1}$ in the Malik plot and $34.4 \pm 50.5 \mu\text{S}\cdot\text{cm}^{-1}$ in the Czarne plot (Figure 3a).

Figure 3. Monthly values of electrical conductivity (EC) (a) and pH (b) for bulk precipitation (BP) and throughfall (TF). Boxplots indicate the lower quartile (Q1), median (Q2), upper quartile (Q3), and interquartile range (IQR).

The weighted mean pH of bulk precipitation in the period from 2010 to 2013 was 4.98 in the Malik plot and 5.16 in the Czarne plot (Figure 3b). After passing the canopy, the pH of the throughfall in Malik increased by 0.93 units and reached 5.91, with extreme values of 4.57 (January 2013) and 7.33 (December 2009). In Czarne, the pH value of the throughfall dropped by 0.23 units (4.93). Extreme values ranged from 4.47 (March 2010) to 6.49 (March 2011).

For all tested ions on both plots, except for hydrogen ions, the observed weighted mean concentrations in throughfall exceeded the concentrations in bulk precipitation (Table 3).

The concentrations of bulk precipitation and throughfall in the Malik plot were many times higher than the concentrations observed in the Czarne plot (Figure 4). For throughfall, the greatest differences were noted for SO_4^{2-} , with concentrations more than eight times higher (8.8); NO_3^- , with concentrations more than six times higher (6.2); and Ca^{2+} , with concentrations more than seven times higher (7.2). Similar concentrations were observed for Na^+ . For EC, the bulk precipitation values were almost three times higher (2.7) in the Malik plot than in the Czarne plot, whereas the throughfall values were almost twice as high (1.9). Higher values were only observed in the Czarne plot compared to the Malik plot for NH_4^+ (bulk precipitation and throughfall) and H^+ (throughfall). Taking into account the concentrations expressed in $\mu\text{Eq}\cdot\text{dm}^{-3}$, the following series of anions and cations were obtained for throughfall: $\text{Cl}^- > \text{NO}_3^- > \text{SO}_4^{2-}$; $\text{NH}_4^+ > \text{Ca}^{2+} > \text{Na}^+ > \text{K}^+ > \text{Mg}^{2+} > \text{H}^+$ for Czarne, and $\text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}^-$; $\text{Ca}^{2+} > \text{K}^+ > \text{Mg}^{2+} > \text{Na}^+ > \text{NH}_4^+ > \text{H}^+$ for Malik.

For both stands, statistically significant dependencies were found between ion concentrations, EC, and the amount of throughfall (Table 4). These were inversely proportional dependences that indicated the increase EC as a result of solution concentration. We observed no statistically significant relationships between H^+ and SO_4^{2-} or H^+ and NO_3^- in throughfall on either plot. However, a statistically significant and inversely proportional dependence between the distributions of H^+ and NH_4^+ was observed in Czarne. No similar dependence was observed in Malik, which may indicate that NH_4^+ plays a less important role in neutralising throughfall acidity. For throughfall in both plots, there were statistically significant dependencies between the distributions of Cl^- and Na^+ , K^+ and Mg^{2+} , and K^+ and Ca^{2+} .

Table 3. Statistical descriptors of the chemical composition of bulk precipitation (BP) and throughfall (TF).

	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	Ca ²⁺	K ⁺	NH ₄ ⁺	Mg ²⁺	Na ⁺	pH	EC
	mg·dm ⁻³								-	μS·cm ⁻¹
Malik—bulk precipitation BP										
Min	1.76	0.37	0.09	1.21	0.12	<0.01	0.25	<0.01	3.95	17.3
Mean	7.40 ±	3.32 ±	2.92 ±	3.99 ±	0.50 ±	0.67 ±	0.77 ±	1.47 ±	4.98	37.6 ± 23.2
± SD	8.85	4.17	1.48	3.32	0.39	0.79	0.47	1.72		
Q ₂	5.69	2.35	2.58	3.86	0.40	0.57	0.75	0.98	5.39	41.7
Max	39.3	19.0	7.40	14.96	1.67	3.65	2.52	7.84	7.70	109
N	43	43	41	42	43	43	43	43	46	46
Malik—throughfall TF										
Min	4.27	2.24	0.22	0.79	0.30	<0.01	0.28	0.01	4.57	28.0
Mean	17.3 ±	17.3 ±	3.29 ±	8.98 ±	4.96 ±	1.26 ±	1.41 ±	1.64 ±	5.91	65.9 ± 61.5
± SD	21.1	21.3	2.45	9.57	4.36	1.29	0.84	1.93		
Q ₂	15.0	21.3	3.39	10.25	3.83	1.39	1.41	1.26	6.33	74.8
Max	122.8	90.2	11.2	55.2	20.3	6.57	4.79	8.79	7.33	334
N	43	43	41	42	43	43	43	43	46	46
Czarne—bulk precipitation BP										
Min	0.45	0.60	0.19	0.16	0.08	0.12	<0.01	0.23	4.56	4.5
Mean	0.96 ±	1.50 ±	0.60 ±	0.79 ±	0.27 ±	0.69 ±	0.13 ±	0.63 ±	5.16	13.7 ± 8.1
± SD	0.88	1.12	0.35	0.64	0.26	0.87	0.06	0.32		
Q ₂	0.88	1.50	0.62	0.78	0.23	0.76	0.12	0.62	5.26	14.4
Max	6.15	6.95	1.64	3.59	1.25	4.22	0.35	2.32	6.57	51.3
N	46	46	46	46	46	45	46	46	44	45
Czarne—throughfall TF										
Min	0.53	0.43	0.54	0.56	0.50	0.46	0.18	0.58	4.47	17.0
Mean	1.97 ±	2.81 ±	2.01 ±	1.24 ±	2.06 ±	2.41 ±	0.36 ±	1.26 ±	4.93	34.4 ± 50.5
± SD	7.22	4.45	2.34	1.97	3.34	1.86	0.49	0.72		
Q ₂	2.08	2.90	2.03	1.40	1.79	2.44	0.38	1.32	5.15	36.7
Max	50.3	27.6	15.3	14.2	22.6	8.04	3.59	4.67	6.49	342
N	46	46	46	46	46	45	46	46	44	45

Mean ± SD—weighted mean ± standard deviation, Q₂—median, N—sample size.

Figure 4. Monthly variation of volume-weighted mean $\pm$ standard error ion concentrations in bulk precipitation (BP) and throughfall (TF) in Malik (a) and in Czarne (b). For comparison, monthly rainfall is presented at the bottom of the graph as well.

Table 4. Ion pair correlations in throughfall (regular represents Malik, bold represents Czarne).

	Rainfall	H ⁺	EC	Cl [−]	SO ₄ ^{2−}	NO ₃ [−]	Ca ²⁺	Mg ²⁺	Na ⁺	NH ₄ ⁺	K ⁺
Rainfall		0.209	−0.783 ****	−0.356 *	−0.489 ***	−0.515 ***	−0.563 ****	−0.387 **	−0.135	−0.208	−0.077
H ⁺	0.233		−0.215	−0.096	0.027	−0.148	−0.32	−0.413 **	−0.288	−0.138	−0.431 **
EC	−0.847 ****	−0.285		0.511 ***	0.665 ****	0.499 ***	0.726 ****	0.622 ****	0.000	0.095	0.226
Cl [−]	−0.625 ****	−0.279	0.713 ****		0.676 ****	0.288	0.602 ****	0.664 ****	0.409 **	0.168	0.184
SO ₄ ^{2−}	−0.777 ****	−0.137	0.870 ****	0.746 ****		0.270	0.591 ****	0.656 ****	0.034	−0.116	0.183
NO ₃ [−]	−0.642 ****	−0.115	0.779 ****	0.689 ****	0.801 ****		0.435 **	0.490 ***	0.074	0.346 *	−0.009
Ca ²⁺	−0.687 ****	−0.270	0.714 ****	0.492 ***	0.615 ****	0.493 ***		0.819 ****	0.087	0.181	0.456 **
Mg ²⁺	−0.740 ****	−0.188	0.814 ****	0.636 ****	0.682 ****	0.526 ***	0.821 ****		0.126	0.094	0.422 **
Na ⁺	−0.653 ****	−0.211	0.748 ****	0.947 ****	0.722 ****	0.649 ****	0.559 ****	0.717 ****		0.279	0.106
NH ₄ ⁺	−0.515 ***	−0.587 ****	0.607 ****	0.187	0.288	0.459 **	0.387 **	0.290	0.199		−0.381 *
K ⁺	−0.471 ***	−0.472 **	0.524 ***	0.378 **	0.365 *	0.193	0.668 ****	0.626 ****	0.366 *	0.553 ****	

**** $p < 0.0001$, *** $p < 0.001$, ** $p < 0.01$, * $p < 0.05$.

Despite water loss due to the interception process, the average annual ion flux was higher under the canopy than in the open area in both stands. In Malik, the load was 229.6 (185.3–270.0) kg·ha⁻¹·year⁻¹, whereas in Czarne, the load was 71.3 (65.1–81.9) kg·ha⁻¹·year⁻¹. In both cases, these values exceeded the loads observed in the open area by a factor of two. The observed open area loads were 118.0 (98.8–158.1) kg·ha⁻¹·year⁻¹ in Malik and 39.8 (35.2–47.2) kg·ha⁻¹·year⁻¹ in Czarne.

The greatest differences in deposition between the studied stands were observed for SO₄²⁻, Ca²⁺, Mg²⁺, and NO₃⁻ (Table 5). Throughfall loads of these elements at Malik exceeded those observed in the second stand, except for NH₄⁺ and H⁺, whose values in Czarne exceeded those recorded in Malik. Comparable loads were observed for Na⁺ and Cl⁻ in both stands.

Table 5. Total element deposition, deposition ratios, and enrichment ratios (ER)—averages for the research period calculated on the basis of annual data.

Sampling Sites	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	Ca ²⁺	Mg ²⁺	Na ⁺	NH ₄ ⁺	K ⁺	H ⁺	Total Load
Bulk precipitation										
Loads in kg·ha ⁻¹ ·year ⁻¹										
Czarne	4.2	6.6	10.4	5.4	0.9	4.4	6.0	1.9	0.05	39.8
Malik	14.4	42.3	19.0	22.7	4.5	8.4	3.8	2.9	0.06	118.0
Ratio loads (-)										
Malik/Czarne	3.4 (2.0–5.6)	6.4 (5.1–9.8)	1.8 (0.8–3.7)	4.2 (2.6–5.8)	4.9 (2.9–6.5)	1.9 (1.2–3.0)	0.6 (0.2–1.0)	1.6 (1.2–1.9)	1.2 (0.9–2.1)	3.0 (2.1–4.5)
Throughfall										
Loads in kg·ha ⁻¹ ·year ⁻¹										
Czarne	10.2	10.0	14.2	6.2	1.8	6.4	12.1	10.4	0.06	71.3
Malik	13.4	71.0	70.9	36.4	5.8	6.7	5.1	20.3	0.01	229.6
Ratio loads (-)										
Malik/Czarne	1.3 (0.9–2.0)	7.1 (5.6–11.4)	5.0 (1.8–6.6)	5.9 (3.9–8.5)	3.2 (2.9–3.7)	1.1 (0.6–1.5)	0.4 (0.3–0.6)	2.0 (1.4–2.4)	0.1 (0.03–0.3)	3.2 (2.6–4.0)
Enrichment ratio (-)										
Czarne	2.5 *** (2.2–2.9)	1.5 *** (1.3–1.7)	1.4 * (1.3–1.4)	1.1 (0.8–1.5)	2.0 *** (1.7–2.3)	1.5 *** (1.3–1.8)	2.0 *** (1.2–3.3)	5.6 *** (4.4–7.6)	1.2 (0.8–1.6)	1.8 *** (1.5–2.2)
Malik	0.9 (0.5–1.7)	1.7 ** (0.9–2.9)	3.7 *** (2.3–9.4)	1.6 ** (1.1–2.0)	1.3 * (1.0–1.9)	0.8 (0.7–1.0)	1.4 (0.9–3.4)	7.0 *** (5.8–8.8)	0.1 *** (0.03–0.2)	1.9 *** (1.3–2.6)

In brackets the range for individual years is given. The significance of differences in the deposition in the open and under the canopy (Mann–Whitney *U* test) at *p* < 0.001 (***), *p* < 0.01 (**), and *p* < 0.05 (*).

The highest ER values were recorded for K⁺, with an observed ER of 7.0 in Malik and 5.6 in Czarne. ER values were close to 1 for Ca²⁺ (1.1) and H⁺ (1.2) in Czarne, and Cl⁻ (0.9) and Na⁺ (0.8) in Malik. In the case of H⁺ in Malik, the deposition under the canopy was an order of magnitude smaller compared to the open area (0.1) (Table 5). In both stands, the differences between deposition under the canopy and in the open area were statistically significant for most ions. The exceptions were H⁺ and Ca²⁺ ions in Czarne and Cl⁻, Na⁺, and NH₄⁺ ions in Malik.

The average four-year flux of nitrogen (N-NO₃⁻ + N-NH₄⁺) in Malik was 20.0 (10.9–25.3) kg·ha⁻¹·year⁻¹, 80% of which was in the form of nitrogen nitrate. In Czarne, the total flux of nitrogen was 12.6 (11.2–15.1) kg·ha⁻¹·year⁻¹, 75% of which was in ammonium form. Nitrogen deposition under the canopy as compared to bulk participation was twice as high in Czarne and almost three times higher in Malik. In Malik, the nitrogen load exceeded critical values for coniferous stands, 3–15 kg·ha⁻¹·year⁻¹ [33], whereas in the case of Czarne, the value did not exceed this range.

In the Malik plot, the average annual flux of K⁺ from throughfall reached 20.3 kg·ha⁻¹, of which 85.8% (17.4 kg·ha⁻¹·year⁻¹) was the effect of leaching. In the Czarne plot, the total annual average

K^+ deposition under the canopy was $10.4 \text{ kg} \cdot \text{ha}^{-1} \cdot \text{year}^{-1}$, of which leaching accounted for 73.8% ($7.7 \text{ kg} \cdot \text{ha}^{-1} \cdot \text{year}^{-1}$). In both stands, the highest K^+ loads were observed between May and October and, in the Malik plot, also in November and December (Figure 5).

Figure 5. Distribution of total K^+ load (TL), load leached from the canopy (CL), and load leached from the canopy as a percentage of total K^+ deposition in Czarne (a) and in Malik (b). ND—no data, Q2—median.

These months between May and October were also the period when canopy leaching made the greatest contribution to total deposition to the forest floor. In Czarne, the total Ca^{2+} load observed at the forest floor was related to the atmospheric inflow rather than leaching processes. In Malik, the contribution of these processes to total Ca^{2+} deposition ($36.4 \text{ kg} \cdot \text{ha}^{-1} \cdot \text{year}^{-1}$) reached 37.7% ($13.7 \text{ kg} \cdot \text{ha}^{-1} \cdot \text{year}^{-1}$). In addition to K^+ and Ca^{2+} , canopy leaching was also an important source of Mg^{2+} in throughfall. Significant canopy leaching of Mg^{2+} was observed both in Malik, where it reached 23.1% ($1.3 \text{ kg} \cdot \text{ha}^{-1} \cdot \text{year}^{-1}$), and Czarne, where it accounted for 26.0% ($0.5 \text{ kg} \cdot \text{ha}^{-1} \cdot \text{year}^{-1}$) of the throughfall.

To evaluate the fractions of the measured ions, which did not play any role in determining the acidity/alkalinity of the bulk precipitation, the non-sea salt (nss) fraction ion concentrations of Ca^{2+} , K^+ , Mg^{2+} , and SO_4^{2-} were calculated. Results showed that the nss fraction ion concentrations were 16.5 , 4.4 , 38.0 , and $6.3 \text{ } \mu\text{eq} \cdot \text{dm}^{-3}$ (Czarne), and 146.1 , 47.7 , 196.3 , and $11.4 \text{ } \mu\text{eq} \cdot \text{dm}^{-3}$ (Malik) for SO_4^{2-} , Mg^{2+} , Ca^{2+} , and K^+ , respectively. The percent contribution of the non-marine source amounted to 82.9%, 41.7%, 96.9%, and 91.2% (Czarne), and 94.8%, 76.6%, 98.6%, and 89.0% (Malik) for SO_4^{2-} , Mg^{2+} , Ca^{2+} , and K^+ , respectively.

In the Czarne plot, the $\text{NO}_3^-/\text{nssSO}_4^{2-}$ ratio in the bulk precipitation indicated the dominant role of nitrogen compounds in acidification processes (1.47). In Malik, a marked dominance of sulfur compounds was observed ($\text{NO}_3^-/\text{nssSO}_4^{2-} = 0.37$). The fractional acidity (FA) indicator calculated for bulk precipitation confirmed that 83% (Czarne) and 95% (Malik) of acidifying compounds were neutralized. In the case of Czarne, neutralization was associated with the presence of NH_4^+ ($\text{NF}_{\text{NH}_4} = 0.94$) and Ca^{2+} ($\text{NF}_{\text{Ca}} = 0.93$), whereas Mg^{2+} ($\text{NF}_{\text{Mg}} = 0.11$) and K^+ ($\text{NF}_K = 0.15$) had marginal effects. The ions determining neutralization at Malik were Ca^{2+} ($\text{NF}_{\text{Ca}} = 0.98$) and Mg^{2+} ($\text{NF}_{\text{Mg}} = 0.24$), whereas NH_4^+ ($\text{NF}_{\text{NH}_4} = 0.18$) and K^+ ($\text{NF}_K = 0.06$) had significantly lower impacts.

3.3. Source of Ionic Species

For each plot, three or four complementary components were distinguished using the concentrations of ions in bulk precipitation and throughfall (Table 6). For bulk precipitation, they explained 81% (Malik) and 76% (Czarne) of the total variance in the chemical composition of rainfall. For throughfall, the components explained 84% of the total variance for Malik and 89% for Czarne. On the basis of the results obtained from the Malik plot, the PC1 component represented the effect of local pollution on the chemical composition of bulk precipitation and throughfall. This component was correlated with base variables such as Cl^- , SO_4^{2-} , Ca^{2+} , and Mg^{2+} (Table 6). The effect of pollution was also apparent in Czarne, where it was represented by the main factor PC2 (bulk precipitation) and PC1 (throughfall). These factors included SO_4^{2-} , NO_3^- , NH_4^+ , and Ca^{2+} (only bulk precipitation).

Table 6. Factor loading and explained variance for bulk precipitation (BP) and throughfall (TF).

Solute/Factor	Bulk Precipitation							
	Malik				Czarne			
	PC1	PC2	PC3	PC4	PC1	PC2	PC3	
Cl^-	0.84	0.23	0.11	0.08	0.17	0.91	−0.02	
NO_3^-	0.14	0.09	0.92	0.05	0.73	0.47	0.14	
SO_4^{2-}	0.85	0.03	0.36	−0.02	<i>0.63</i>	0.49	0.26	
Na^+	0.28	−0.22	0.18	0.82	0.27	0.85	0.14	
K^+	0.34	0.75	−0.05	−0.08	0.12	0.45	0.70	
Mg^{2+}	0.85	0.15	−0.21	0.12	<i>0.52</i>	0.39	0.33	
Ca^{2+}	0.89	−0.12	0.19	−0.02	0.89	0.03	−0.08	
NH_4^+	<i>0.56</i>	−0.12	0.30	<i>−0.64</i>	0.77	0.22	0.45	
H^+	−0.12	0.86	0.14	−0.07	−0.11	0.11	−0.87	
Eigenvalues	3.73	1.52	1.05	1.00	4.59	1.20	1.06	
Explained variance (%)	39	16	14	12	30	27	19	
Cumulative explained variance (%)	39	55	69	81	30	57	76	
Solute/Factor	Throughfall							
	Malik				Czarne			
	PC1	PC2	PC3	PC4	PC1	PC2	PC3	PC4
Cl^-	0.91	0.10	0.18	−0.07	0.27	0.91	0.19	0.13
NO_3^-	0.24	0.82	0.01	0.10	0.92	0.31	0.15	0.03
SO_4^{2-}	0.91	−0.09	0.00	0.10	0.76	0.49	0.16	−0.03
Na^+	0.01	0.80	0.08	−0.18	0.26	0.91	0.25	0.08
K^+	0.44	0.13	−0.70	−0.30	−0.13	0.28	<i>0.60</i>	<i>0.58</i>
Mg^{2+}	0.82	0.27	−0.29	−0.24	0.20	0.38	0.83	−0.07
Ca^{2+}	0.83	0.34	−0.09	−0.13	0.31	0.08	0.84	0.07
NH_4^+	0.18	0.18	0.90	−0.13	0.76	0.04	0.33	0.47
H^+	−0.08	−0.05	0.01	0.96	−0.15	−0.05	0.04	−0.93
Eigenvalues	3.80	1.51	1.28	0.95	4.60	1.32	1.15	0.92
Explained variance (%)	37	18	16	13	26	25	22	16
Cumulative explained variance (%)	37	55	71	84	26	50	73	89

Boldfaced values are strong (>0.70 or <-0.70) loadings; values in italics are moderate loadings.

For Czarne, PC2 components for bulk precipitation and throughfall were identified, which were correlated with concentrations of Cl^- , Na^+ , and to a lesser extent with Mg^{2+} concentrations. These components represented the effect of marine aerosol precipitation on chemical composition. In the case of Malik, this component was not distinguished. In both plots, we identified a component associated with H^+ but not with NO_3^- or SO_4^{2-} . In Czarne, NH_4^+ had a high contribution to the

formation of this component, but this dependence was of a different nature. Unlike for H^+ ions, the load had a positive mark (Table 6). In the matrix of factor loads, the PC3 component for Malik throughfall was noteworthy, as it was positively correlated with K^+ concentrations and negatively correlated with NH_4^+ (Figure 6).

Figure 6. Diagram (biplot) based on the principal component analysis (PCA) for throughfall in Czarne (a) and in Malik (b).

This component can be associated with the presence of K^+ leaching processes from plants. For Czarne, no main component that would clearly indicate the leaching processes was identified. K^+ contributed to the creation of two components: PC3 and PC4. In the PC3 component, high load values characterized Mg^{2+} and Ca^{2+} , whose presence in throughfall in the Czarne plot was primarily associated with atmospheric inflow. In the pine stand in Czarne, no Ca^{2+} leaching processes were observed. In addition to the PC3 component, K^+ ions contributed to PC4 component formation, which was correlated primarily with H^+ and to a lesser extent NH_4^+ .

4. Discussion

Interception, understood as the part of precipitation retained by the canopy, is an important element of water balance in forest ecosystems. During the study period, there were no significant differences in the amount of precipitation that reached the soil in the two observed stands. The parameter that differentiates these areas is the variation scale for interception. In the forest stand at Malik, located in a mountainous area with an elevation of up to 300 m above sea level, there were cases when interception was negative. Additional water inflow comes from fog deposition. This process is particularly effective in conifer stands, which have a larger reception area that facilitates the intake of water from fog [1,6,34].

Despite the loss of water in the interception process, we observed deposition of more than twice the values observed outside the forest in both stands. This difference can be explained by the effect of canopy leaching and the wash-off of aerosols that accumulate on tree surfaces through dry deposition [6,10,14,17,35–37].

In both plots, the highest load increase was recorded for K^+ ions: 5.6 in Czarne and 7.0 in Malik. These results are consistent with previous research [6,8,37–39] carried out both in coniferous and deciduous stands. The research conducted by Kowalska et al. [11] on stands of diverse species in Poland confirmed the enrichment of throughfall with K^+ at the level of 4.4 (pine), 4.7 (spruce), 7.2 (beech), and 11.5 (oak). The leaching process is primarily related to monovalent K^+ ions [20,21] due to greater mobility and weaker bonding in cell walls, chloroplasts, and enzymes compared to divalent ions [22,40]. The intensity of K^+ leaching depends on many factors, including the type and age of the stand [6,14,17], canopy [10,12], distance from the edge of the forest [41], and inflow of acidifying compounds from the atmosphere [6,14,18,26].

On the basis of the canopy budget model, we found that, in the case of total potassium deposition on the forest floor, 85.8% in Malik and 73.8% in Czarne came from canopy leaching processes. These values are comparable with the results of other authors. Draaijers et al. [26], Rothe et al. [42], and Kozłowski et al. [14] noted the contribution of leaching processes for spruce stands at levels of 89%, 80%, and 98.7%, respectively. For pine stands, Hermann et al. [10] reported values in the 44%–71% range.

The analysis of leaching intensity on the scale of the hydrological year indicates the occurrence of seasonal variation. In both stands, the maximum leaching values were recorded in the growing season, with the maximum falling between May and November. As Fober [43] reports, the contents of elements in plant tissues are subject to strong seasonal changes. According to Le Taconm and Toutain [44] and Kozłowski et al. [14], K^+ concentration in assimilation organs clearly decreases in the period from September to October, and increases in the summer months.

These observations are in line with the results of Kozłowski et al. [14] in a study of fir and spruce stands, where the maximum values of K^+ ions from leaching were found at the beginning and the end of the growing season. Moreover, Adriaenssens et al. [8] reported that the highest leaching intensity occurs during the growing season.

For both stands, air pollution was an important factor affecting throughfall's physicochemical properties and chemical composition. In Malik, the most important source of pollution is the cement and lime industry and the related local emission of dust pollution. Accordingly, the loads of SO_4^{2-} and Ca^{2+} recorded in Malik exceeded the values observed in the other stand by more than seven and six times, respectively. Ca^{2+} , SO_4^{2-} , and Cl^- present in throughfall at Malik are correlated with PC1, which represents an anthropogenic factor. Photographs of two-year-old pine needles from this area, taken with a scanning electron microscope, revealed incrustations near the stomata resulting from dust deposition. A point analysis of chemical composition conducted with an ED-XRF microanalyzer found sulfur and calcium in significant quantities in the samples whose tissue was nearest to the stoma [1]. Under favorable conditions, the process of gypsum formation takes place [1], which leads to partial clogging of the stoma [45] and may result in the deterioration of the stand's health and the increased leaching of biogenic elements.

In Czarne, the anthropogenic factor was represented by the PC1 and encompassed the concentrations of NH_4^+ , NO_3^- , and SO_4^{2-} . The presence of these ions in throughfall should be considered alongside the wash-off of substances deposited on the surface of plants [10,36,46].

The NO_3^- and SO_4^{2-} loads found in bulk deposition in the Czarne plot came from long-distance transport, as there were no local emitters in Czarne. Deposition of NH_4^+ , on the other hand, depends mainly on agricultural activities, as Rodrigo et al. [20] observed in Mediterranean forests, Huber and Kreutzer [47] in Germany, Neiryneck et al. [48] in a Scots pine forest in northern Belgium, Shen et al. [46] in two plantation forests in southeast China, and Cao et al. [49] in a cool-temperate deciduous broad-leaved forest (Japan).

Nitrogen is an element that differentiated the examined stands. In Malik, N- NO_3 accounted for 80% of the total nitrogen, whereas in Czarne, this figure was only 25%. The average annual load of NO_3^- in the stand at Malik was almost five times greater than in the Czarne stand. The source of NO_3^- in the throughfall at Malik, apart from the production of cement, are emissions associated with the S7 expressway located near the stand. The specific composition of the rainwater penetrating through the stand in Malik is a result of wash-off of alkaline dust, derived from the so-called White Basin cement and lime works, deposited on the surfaces of trees.

Sea aerosols represent an important factor that affects ion concentration in precipitation in Czarne, as they are an important source of Cl^- and Na^+ ions, and, to a lesser extent, Mg^{2+} and SO_4^{2-} ions. The studied area is located approximately 100 km south of the Baltic Sea coast. For Czarne, there were statistically significant dependencies between Cl^- and Na^+ distributions. For Malik, the analogous dependence turned out to be less statistically significant ($p < 0.01$). This was confirmed by the results of the PCA for the Malik plot, as Cl^- ions were correlated with PC1, representing anthropogenic impact,

but there was no correlation with Na^+ ions. In the second plot, both Cl^- and Na^+ were correlated with PC2, representing sea aerosols. The probable source of the high load of chlorides in the precipitation at Malik is dust emitted from two cement plants. According to [4], 800.4 Mg of cement dust was emitted from 2010 to 2013 in the area of Malik. Seo et al. [50] indicate that cement kiln dust (CKD) is a major by-product of cement manufacturing. In general, the maximum chloride content of cement is 0.10%, whereas the chloride contained in CKD may reach 0.25–15.4 wt % [51]. CKD consists of a set of oxidized, anhydrous phases, which include oxides, aluminosilicates, sulphates, and chlorides. Many of these phases, including calcium oxide (CaO), arcanite (K_2SO_4), and sylvine (KCl), are unstable or highly soluble. After the contact of dust with water, these phases can completely dissolve, followed by the precipitation of more or less stable phases [52]. As reported by Uliasz-Bocheńczyk [53], dust leachates from electrostatic precipitators are characterized by high concentrations of chlorides.

It is widely known that coniferous stands contribute to the increased acidity of rainwater [6,11,14,36,54]. The presence of cement/lime dust in the Malik plot caused the pH of precipitation penetrating through the canopy to increase by almost 1 pH unit as compared to bulk precipitation. The location of the Malik area at a distance of 2.5 to 21.0 km from the emission sources causes a periodic strong effect of cement and lime plants on this stand. The observed alkalization of precipitation after passing through the crown zone is conditioned by dry deposition of the cement and lime dust emitted by nearby industrial plants on the surface of the assimilation organs. This dust, characterized by high pH, is washed off the plant surface and deposited into the soil when precipitation occurs [3,4]. Research by Ots and Mandre [55] showed that deposition volume depends on the distance from the source of emission and the direction of the wind.

Neutralization ratios of acidifying compounds confirmed a significant contribution of ammonium nitrogen in the Czarne plot. For the Czarne plot, the basic factors influencing the chemical composition of precipitation are the lack of local industrial emitters, the local emission of agricultural pollutants, the inflow of pollutants to the study area, and its location near the sea. This was confirmed by low precipitation mineralization that was close to the background value, as well as a clear upward trend in pH observed in recent years, which is associated with the reduction of SO_2 concentrations in the atmosphere [5]. In this situation, the chemical composition of sub-crown precipitation is determined by the processes of ion leaching from assimilation organs (K^+ and Mg^{2+}), the presence of agricultural pollutants (NH_4^+), and the inflow of marine aerosols (Na^+ and Cl^-).

These values are similar to those obtained by Golobočanin et al. [56] in Central Serbia. In the case of the NF_{Ca} ratio, the higher values recorded on the Malik plot clearly indicate that calcium from the cement and lime industry has a significant effect on the natural environment of this area.

5. Conclusions

This study allowed us to verify the hypothesis formulated at the beginning of the manuscript. It was found that:

- The presence of cement/lime dust, mainly calcium and magnesium, emitted by industrial plants on Malik plot, affects conductivity, pH, and the chemical composition of precipitation, playing a key role in the neutralization processes of acidogenic compounds.
- Emissions from agricultural areas, mainly with ammonium ions, as well as chlorides and sodium, which are the source of marine aerosols, affected a low level of conductivity of atmospheric precipitation and the precipitation's composition on Czarne plot, playing a key role in the neutralization processes of acidogenic compounds.
- Regardless of air pollution, the intensity of quantitative and qualitative transformation of precipitation in both pine stands was comparable. In both cases, the total ion load in throughfall was twice as high as on the open area, with the highest leaching intensity in the growing season. The leaching processes of K^+ and Mg^{2+} did not depend on various anthropogenic pressures.

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