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Long-term trends and factors influencing rainwater chemistry in the Tatra Mountains, Poland

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Abstract: The results of rainwater chemistry monitoring in the Tatra Mountains, Poland, during the periods 1993–1994 and 2002–2019 were used to determine long-term trends and the factors influencing rainwater chemistry in the last two decades. In the early 1990's, the study area was characterized by prominent acid rains with a pH of 4.4 that affected surface water, meadows, and forest ecosystems. A rising pH temporal trend has been observed during the following years, indicating improving air quality. This trend has also been observed in measured ionic concentrations and reduced wet deposition loads of sulfur- and nitrogen-containing acid-forming compounds. The neutralization capacity of rainwater in Kasprowy Wierch increased over the last twenty years and has mostly been dominated by NH_4^+. The ammonium availability index has been steadily increasing between years 2002 and 2019 but remains less than 1. This statistically significant relationship also indicates that a portion of neutralization occurs in the lower part of the atmosphere due to ammonium-related neutralization processes. The acidic potential (AP) and the ratio AP/NP (acidic potential/neutralization potential) have been declining during the same time. The stated trends in rainwater chemistry reflect the transformation to more environmentally sustainable economies in the region. Similar changes have been observed in neighboring countries in the region, including Slovakia, the Czech Republic, and Lithuania.

Keywords: temporal trends, rainwater chemistry, atmospheric pollution, Tatra Mountains

INTRODUCTION

Urbanized and industrialized regions contribute to atmospheric pollution and the acidification of natural ecosystems. Gases, particles, and aerosols emitted into the atmosphere return to the surface of the Earth as either dry or wet deposits which interact with surface water, groundwater, groundwater-dependent ecosystems, soils, and the biosphere (Małecka 1991, Małecki & Matyjasik 2002, Stuchlík et al. 2006, Rzychoń & Worsztynowicz 2008, Warby et al. 2009, Oulehle et al. 2011, Yang et al. 2012, Krogulec & Zabłocki 2015, Krogulec et al. 2016, Tiwari et al. 2016). Long-term emission of acid-forming gases (SO_2 and NO_2) and their long-distance transport result in the alteration of rainwater chemistry. These processes mainly occur in gaseous phases where

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sulfur and nitrogen compounds are oxygenated to form sulfates and nitrates. Additionally, heterogeneous reactions occur on atmospheric particle surfaces and liquid phase reactions in cloud droplets that further modify rainwater chemistry (Charlson & Rodhe 1982, Wayne 1985). Sulfur dioxide and nitrogen oxides contribute to the acidity of rainwater, while solid particles typically cause its alkalization. Typically, higher atmospheric solid particle loads in urbanized areas contribute to increased pH, compared to regions with natural conditions (Porowska 2005, Walna 2015, Keresztesi et al. 2019). Temporal trends in rainwater chemistry are related to both natural climatic conditions and the transport of industrial gases in the atmosphere. Observed multi-year trends in rainwater chemistry have been significantly influenced by the transition of Poland and neighboring countries to more environmentally sustainable economies.

Dates used in this article include rainwater chemistry measurements conducted by Małecki (1998) in 1993–1994 in the Hala Gąsienicowa in the Tatra Mts. and rainwater data collected in 2002–2019 in Kasprowy Wierch, Tatra Mts. (GIOŚ 2015). These combined data provided information about recovery from the maximum acidification event and the long-term trends in rainwater chemistry in the Tatra Mts.

MATERIALS AND METHODS

Research site

The samples of rainwater were collected in two observation stations: Hala Gąsienicowa (1520 m a.m.s.l.) and Kasprowy Wierch (1991 m a.m.s.l.) (Fig. 1). Sampling sites were located in a flat, forestless place. The Tatra Mts. is a region with the highest annual precipitation in Poland. The average annual rain precipitation calculated from the years 1951–1995 is 1637 mm in Hala Gąsienicowa (Małecki 1998), and 1765 mm in Kasprowy Wierch (Małecka et al. 2002) with relatively small annual deviations. Precipitation in both stations is characterized by maximum monthly values from May to August.

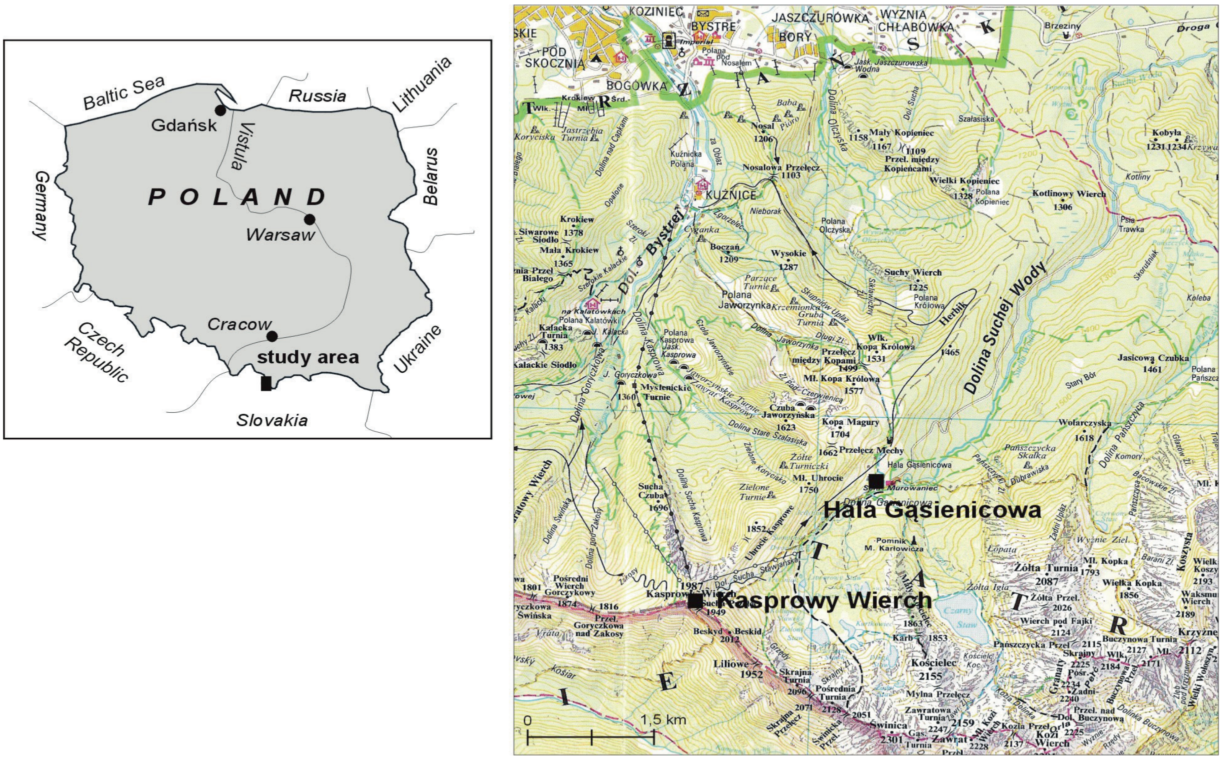

Fig. 1. Location of the study area (http://www.mapytatr.net/)

Methodology

In the years 1993–1994, samples of rainwater in Hala Gąsienicowa were collected after all rainfall events exceeding 3 mm (n = 205) at the same location. Measured parameters included: pH (pH meter CP-315 Elmetron; ±0.05 pH) and electric conductivity (conductivity meter CC-317 Elmetron; ±0.5%). Chemical composition analyses (n = 78) were conducted in the Polish Geological Institute in Warsaw and in the Department of Geology, Warsaw University. Ion chromatography was used to analyze the following anions (sulfates, chlorides, nitrates, nitrites, phosphates and fluorides). Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) was used to analyze trace elements (iron, manganese, copper, zinc, aluminum, strontium, barium), Atomic Spectrometry (FAAS) was used to analyze major elements (sodium, potassium, calcium, magnesium) (Jakimowicz-Hnatyszak & Pasławski 1996). The spectrophotometric technique was used to analyze ammonium. Bicarbonates were determined by titrating.

Measurements of rainwater chemistry in the Kasprowy Wierch station correspond to monthly samples collected in the years 2002–2019 and include pH and all ions measured in Hala Gąsienicowa (GIOŚ 2015). Samples were collected in the Kasprowy Wierch by the State Environmental Monitoring Program in accordance with the procedures described in the standard PN-ISO 5667-8:2003. Rainwater collected in 1993–1994 was compared with the results from Kasprowy Wierch for the years 2002–2019 (GIOŚ 2015). The interpretation of the sample results shows similar trends with the results of available studies on long-term trends in rainwater chemistry (Szczepańska & Kmiecik 1998, Kmiecik et al. 2007, Haylock et al. 2008, Wątor et al. 2018, Govender & Sivakumar 2020, Militino et al. 2020). The loads transported to surface water and groundwater with rainfall are a function of the concentrations of individual components and the amount of rainfall (Kostrzewski & Majewski 2021).

Temporal trend analyses are complex and often indicate individual sources interacting with synergistic pairs of sources indicated by primary component analysis (Goodwell & Kumar 2017). Overall trends indicate temporal changes of sulfates, nitrates, and ammonium over the last few decades (Lehmann et al. 2005), correlated high concentrations of sulfates with low pH (Manning et al. 2013), and enhanced weathering influencing observed trends of rain precipitation (Rogora et al. 2016, 2020). Waldner et al. (2014) demonstrates that monthly data, despite a higher data noise, provide more information than annual data. Strock et al. (2014) presented data from recovery from peak acidification in North America that can assist with anticipating similar changes in this study and in Central Europe in general, several years later.

Trend analysis water chemistry data was performed using GWSDAT software (GWSDAT n.d.). In this method, the statistical significance of trends is assessed by the Mann–Kendall trend test. If the Mann–Kendall p-value is below 0.05, then the estimated trend is statistically significant. A p-value above 0.05 should be interpreted as not a statistically significant trend (Jones & Spence 2013). This method is often used in the analysis of trends in changes in groundwater chemistry (Wątor & Kmiecik 2015, Lipiec & Rusiniak 2020).

The following parameters and methods were used to interpret the results of rainwater chemistry:

- acidic and neutralization potential,
- neutralization factor,
- ammonium availability index,
- marine contributions,
- non-marine contributions.

The acidic and neutralization potential was characterized using several different parameters, including the ratio of the acidic potential to the neutralization potential, the neutralization factor, and the ammonium availability index. The ratio of the acidic potential (AP) to the neutralization potential (NP) is calculated as:

$$\frac{\mathrm{AP}}{\mathrm{NP}} = \frac{\mathrm{NO_3^-} + \mathrm{nssSO_4^{2-}}}{\mathrm{NH_4^+} + \mathrm{nssCa^{2+}} + \mathrm{nssMg^{2+}} + \mathrm{nssK^+}} \qquad (1)$$

In this equation the term “nss” is the non-sea salt fraction (Roy et al. 2016). The concentrations are in moles per cubic decimetre [mol/dm^3].

The relative neutralization of rainwater can be characterized by the neutralization factor (NF)

(Zhang et al. 2007, Wu et al. 2012, Keresztesi et al. 2020, Zeng et al. 2020):

$$\mathrm{NF} = \frac{x}{\left[\mathrm{SO_4^{2-}} + \mathrm{NO_3^-}\right]} \tag{2}$$

where x is the concentration of the alkaline component, including Ca^{2+}, NH_4^+, Na^+, K^+, and Mg^{2+}, respectively. The concentrations are in microequivalents per cubic decimetre [μeq/dm^3].

The ammonium availability index (AAI) describes the relative neutralization of ammonium by sulfate and nitrate and is calculated as (Behera & Sharma 2010, Singh & Gupta 2017):

$$\mathrm{AAI} = \frac{\left[\mathrm{NH_4^+}\right]}{2\left[\mathrm{SO_4^{2-}}\right] + \left[\mathrm{NO_3^-}\right]} \tag{3}$$

The concentrations in this equation are in moles per cubic decimetre [mol/dm^3].

It has been shown that the acidity of rainwater is typically influenced by the presence of H_2SO_4, HNO_3 and organic acids, and the neutralization of these acids is caused by the presence of NH_3 and $CaCO_3$ (Xu et al. 2015, Wu et al. 2016, Chang et al. 2022). The neutralization occurs at higher elevations due to the reaction of $Ca(OH)_2$ and $Mg(OH)_2$ with H_2SO_4 and HNO_3 , and occurs below cloud level due to ammonia and the adsorption of SO_2 to suspended particles of Ca^{2+} and Mg^{2+} (Harrison & Pio 1983, Balasubramanian et al. 2001). The concentration of the H^+ ion reflects the acidity of raindrops after the neutralization process by Ca^{2+} and NH_4^+ (Chate & Devara 2009). When the rainwater is not neutralized and the acidity is related to H_2SO_4 and HNO_3 then the $H^+/(SO_4^{2-} + NO_3^-)$ ratio, or fractional acidity (FA) is often equal to one (Balasubramanian et al. 2001, Szep et al. 2018). FA in Central East Europe has a mean value of 0.29 (Keresztesi et al. 2019), indicating that the 71% of the inorganic acidity in precipitation is neutralized. FA and pH values have a strong correlation (Keresztesi et al. 2019).

The neutralizing factors (NFs) are typically stronger in Europe for ammonium and sodium (Wu et al. 2016, Chang et al. 2017, Keresztesi et al. 2019). Typical values of NFs are below one and typical values of AP/NP are between 1.2 and 2.2, indicating the significant role of acids. Typical values of ammonium availability index (AAI) are less than 60% in Central Europe, showing that there is not enough ammonium to neutralize acids (Chu 2004, Behera & Sharma 2010). Low values of AAI (below 100%) do not always correspond to low pH values as there might be neutralizing species present other than ammonium.

The marine contributions (%SSF) to the chemical composition of rainwater was evaluated using the following equation:

$$\%\mathrm{SSF} = \frac{100 \cdot (\mathrm{Na})_{\mathrm{RainKW}} \cdot \left(\dfrac{X}{\mathrm{Na}}\right)_{\mathrm{RainLeba}}}{(X)_{\mathrm{RainKW}}} \tag{4}$$

This is a modified version of the method used by Keresztesi et al. (2020) calculating the marine contributions in rainwater in Kasprowy Wierch (RainKW in equation (4)), where we assume that the concentration in rainwater in Łeba (RainLeba in equation (4)), located on the shoreline of the Baltic Sea, is 100% of marine origin. We have also selected the rainwater in Łeba as the marine origin reference baseline due to the dominant direction of the wind from the western and north-western sectors. We have selected the concentration of sodium rather than chloride as the reference marine element because annual concentrations of sodium were more consistent and characterized by a lower relative standard deviation (0.22) than the relative standard deviation of chloride (0.27). Sodium has been frequently used as the reference element for seawater (Keene et al. 1986, Conradie et al. 2016, Rao et al. 2016).

The non-marine contributions (%NSSF) are calculated as (Keresztesi et al. 2020):

$$\%\mathrm{NSSF} = 100 - \mathrm{SSF} \tag{5}$$

Atmospheric transport distance, the presence of nuclei of condensation, and proximity to sea water reservoirs are significant factors which influence the rainwater chemical composition. Rainwater occurring in close proximity to sea water typically includes dissolution products of sea aerosols. Statistical relations between rainwater chemical constituents gradually change with distance from ocean water (Möller 1990, Herut et al. 2000).

Concentrations of chloride decrease while those of sulfates, calcium and magnesium typically increase with increasing distances from shorelines. Molar concentrations of chlorides and sodium are typically equivalent because of their marine origin. Concentrations of chlorides and sodium are typically considered conservative and do not undergo a significant fractionation during their transport away from the shorelines (Möller 1990).

A fractionation factor is often used to evaluate ocean impact on rainwater chemistry. This fractionation factor is practically constant for sodium (Raemdonck et al. 1986, Wagner & Steele 1989).

RESULTS AND DISCUSSION

Factors influencing rainwater chemistry in the Tatra Mts. in 1993–1994

Values of pH in Hala Gąsienicowa in the years 1993–1994 ranged from 3.4 to 6.42 (Tab. 1), with most of the measurements below 5.6 (Fig. 2). The average value of pH was 4.39 with a standard deviation of 0.46, and coefficient of variation of 0.1.

The distribution of individual pH values in the analyzed period does not indicate seasonal changes (Fig. 2).

Overall, the presented pH values were typical for the entire region and similarly low values of pH were observed in other environmentally protected regions in Poland at that time, for example in the Borecki Forest (pH = 4.31) (Śnieżek & Degórska 1996), in the Wielkopolski National Park (Central-Western Poland) (pH = 4.23) (Walna & Siepak 1996), and in the Sudety Mts. (Southern-Western Poland) (pH = 4.79) (Dobrzyński 1997).

Rainwater in Hala Gąsienicowa was characterized by low values of electric conductivity (EC) ranging from 4.2 and 193 µS/cm, with an average value of 32.71 µS/cm (Tab. 2).

Table 1
Selected statistical pH rainwater (after all rainfall exceeding 3 mm), 1993–1994

Extreme values [–]		Amplitude	Average value ($n = 205$)	Median value	Standard deviation	Coefficient of variation	Lower quartile	Upper quartile
max	min							
6.42	3.4	3.02	4.39	4.31	0.46	0.10	4.15	4.48

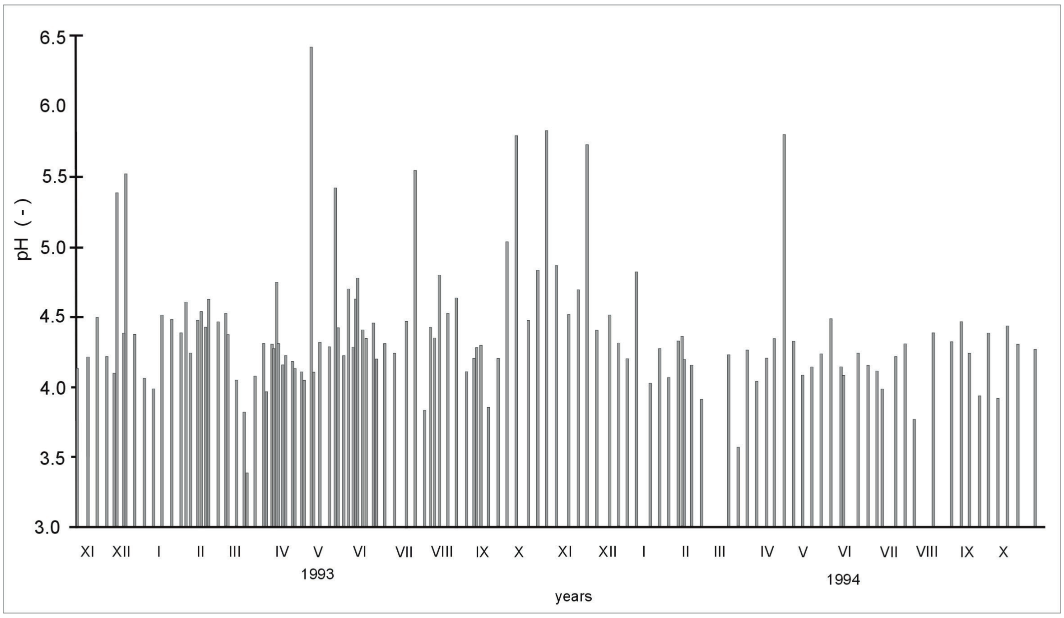

Fig. 2. *Reaction pH values of rainwater, Hala Gąsienicowa, 1993–1994*

Table 2
Selected rainwater electric conductivity statistical parameters, 1993–1994

Extreme values [µS/cm]		Amplitude	Average value (n = 205)	Median value	Standard variation	Coefficient of variation	Lower quartile	Upper quartile
max	min							
193.0	4.2	188.8	32.71	23.9	30.60	0.94	16.2	36.8

A maximum value of electric conductivity reached 193 µS/cm in March 1993, preceded by long period without precipitation which resulted in accumulated atmospheric pollution. Most of the measurements were below 50 µS/cm (Fig. 3).

Similar values of electric conductivity also occurred in other regions in Poland which were not affected by anthropogenic activity, i.e. Wielkopolski National Park (EC = approx. 50 µS/cm) (Walna & Siepak 1996), and in the Sudety Mts. (EC = approx. 45 µS/cm) (Dobrzyński 1997).

Analysis of the water ionic composition in the Hala Gąsienicowa station indicated that dominant anions included sulfates, nitrates, bicarbonates and chlorides. Dominant cations included: calcium, ammonium, and in smaller concentrations, sodium, magnesium, and potassium (Tab. 3).

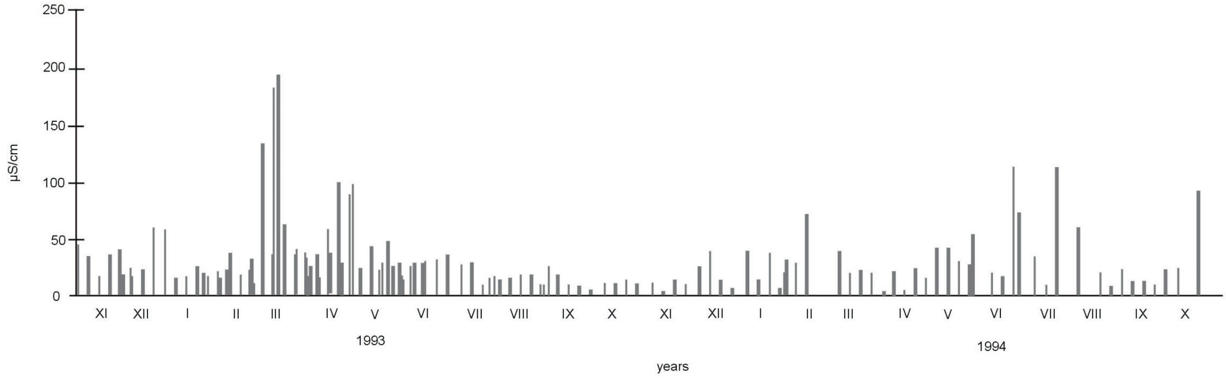

Fig. 3. *Electric conductivity of rainwater, Hala Gąsienicowa, 1993–1994*

Table 3
Chemical composition of rainwater collected in Hala Gąsienicowa (average values, n = 78)

Units	Anions							Cations*					
	HCO_3^-	Cl^-	F^-	NO_2^-	NO_3^-	SO_4^{2-}	PO_4^{3-}	Na^+	K^+	NH_4^+	Ca^{2+}	Mg^{2+}	Al^{3+}
mg/dm^3	1.60	0.91	0.02	<0.01	2.38	4.30	0.10	0.26	0.21	0.94	0.92	0.22	0.02
meq/dm^3	0.02	0.02	0.001	<0.01	0.03	0.089	0.003	0.012	0.006	0.065	0.056	0.019	0.002
% meq/dm^3	12.27	12.27	0.61	<0.01	18.40	54.60	1.86	7.32	3.65	39.64	34.14	11.58	1.32

* % meq/dm^3 for cations are corrected for the presence of trace elements.

The dominant ions in the analyzed samples were SO_4^{2-} and Ca^{2+}, which is typical for rainwater in Poland in general (Małecka 1991, Turzański & Godzik 1996, Dobrzyński 1997, Porowska 2005), also including other mountainous regions such as the Karkonosze Mts. (Tab. 4).

Calcium concentrations were similar in rainwater in both the Tatra Mts. and the Karkonosze Mts., while SO_4^{2-} concentrations were twice as high in the Karkonosze Mts. The observed difference in the concentration of this ion results from the transport of gaseous sulfur compounds from the west and north-west areas considered the most polluted of Europe, called the "Black Triangle", located between the Czech Republic, Germany and Poland.

Table 4
Concentrations of calcium and sulfates in the Tatra Mts. and the Karkonosze Mts. (1993–1994)

Name	**Ca^{2+} [mg/dm^3]**			**SO_4^{2-} [mg/dm^3]**		
	max	**min**	**aver.**	**max**	**min**	**aver.**
Tatra Mts.						
Hala Gąsienicowa	2.8	0.01	0.7	12.7	1.28	4.9
Karkonosze Mts.*						
Śnieżka	2.2	0.01	0.59	28.2	2.3	9.1
Jakuszyce	0.87	0.04	0.43	12.2	3.6	7.7
Karpacz	1.83	0.09	0.64	16.1	6.0	8.9
Przesieka	2.03	0.09	0.60	20.2	5.7	8.9

* Turzański & Godzik (1996).

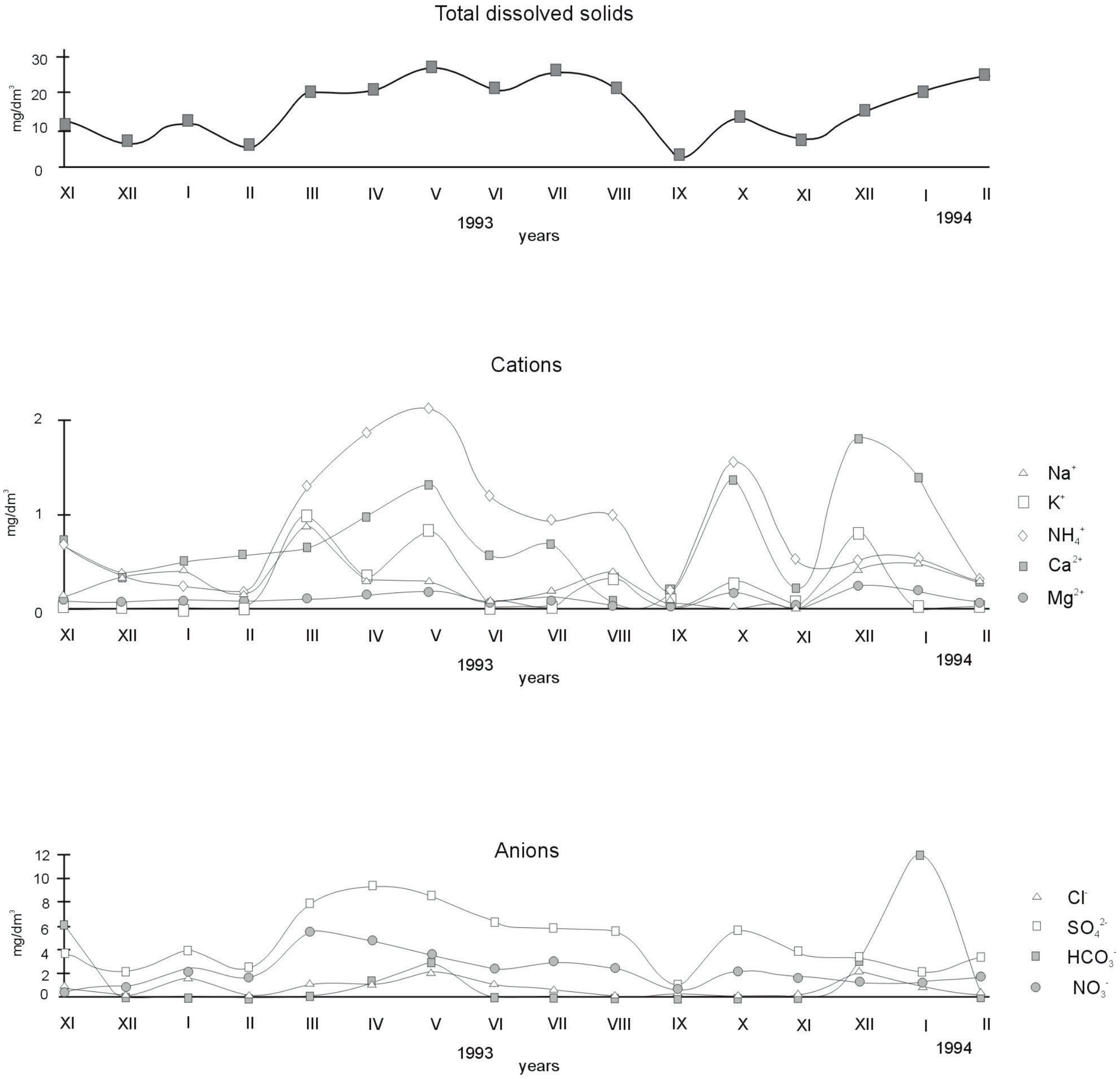

Fig. 4. *Average monthly concentrations of selected ions and total dissolved solids in rainwater in Hala Gąsienicowa*

Overall, the concentration charts confirm the dominance of ammonium, calcium and sulfate (Tab. 3, Fig. 4).

The total dissolved solids presented in Figure 4 are characterized by an overall normal distribution with similar median and mean values. The coefficient of variation suggests that a high statistical dispersion is observed for all measured elements and ions (Tab. 5).

The highest statistical dispersion was characterized by nitrites, fluorides, potassium and phosphates. Their distributions are skewed toward higher values and their maximum values are multiple times greater than the mean values.

Zinc, iron, and manganese are the most common trace elements in rainwater in Hala Gąsienicowa (Tab. 6). Copper, strontium, and barium occur at much lower concentrations. Coefficients of variation range from values less than 1 to slightly more than 2.

Concentration percentages of all selected ions which have a marine and a continental origin have been calculated by comparing rainwater concentrations in Kasprowy Wierch to the rainwater in Łeba (Fig. 5), assuming that the entire rainwater sodium concentration in Łeba is of marine origin (Fig. 6). Annual concentrations of sodium in Łeba are overall well correlated with the concentrations of chlorides (Fig. 5).

The results presented indicate that the influence of marine sources on rainwater chemistry in Kasprowy Wierch significantly declined in the years 2002–2018 and continental sources gradually become dominant (Fig. 7). Magnesium ions have the smallest contribution of continental sources among all measured cations.

Table 5

Chemical composition of rainwater in Hala Gąsienicowa (average values, n = 78)

Element	Concentration [mg/dm^3]				Standard deviation	Coefficient of variation
	max	min	amplitude	mean		
Na	1.2	<0.2	1.2	0.3	0.3	1.00
K	1.9	<0.5	1.9	0.2	0.4	2.00
NH_4	4.3	0.11	4.19	0.9	0.9	1.00
Ca	2.8	<0.1	2.8	0.9	0.6	0.86
Mg	0.33	<0.05	0.33	0.2	0.1	1.00
Cl	2.51	<0.1	2.51	0.9	0.9	1.00
SO_4	12.7	1.28	11.42	4.3	2.7	0.55
HCO_3	12.0	<0.1	12.0	1.6	3.0	1.88
PO_4	1.0	<0.1	1.0	0.1	0.2	2.00
SiO_2	0.23	<0.1	0.23	0.1	0.1	1.00
Al	0.11	<0.05	0.11	0.02	0.03	1.50
F	0.17	<0.1	0.17	0.02	0.04	2.00
NO_2	0.05	<0.01	0.05	0.003	0.01	3.33
NO_3	6.79	0.37	6.42	2.4	1.7	0.71
TDS	28.0	3.0	25.0	15.2	7.5	0.49

Table 6

Trace elements in rainwater in Hala Gąsienicowa – statistical parameters (n = 78)

Trace element	Concentration [µg/dm^3]				Standard deviation	Coefficient of variation
	max	min	amplitude	mean		
Fe	160	<0.01	160	41.9	32.3	0.77
Mn	80	<0.001	80	10.3	15.0	1.46
Cu	31	<0.05	31	4.3	6.8	1.58
Zn	1939	18.0	1921	55.0	699.5	2.07
Sr	12	<0.001	12	3.4	2.6	0.76
Ba	60	<0.001	60	7.9	11.6	1.47

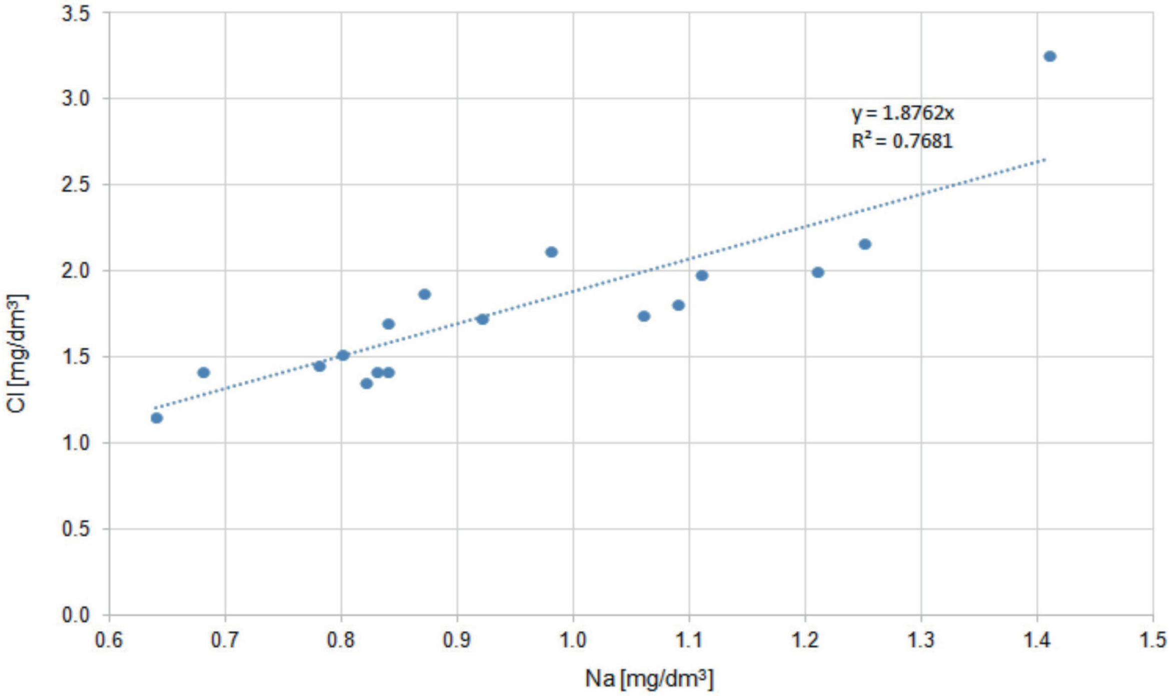

Fig. 5. *Annual average concentrations of chlorides versus concentrations of sodium in Łeba rainwater*

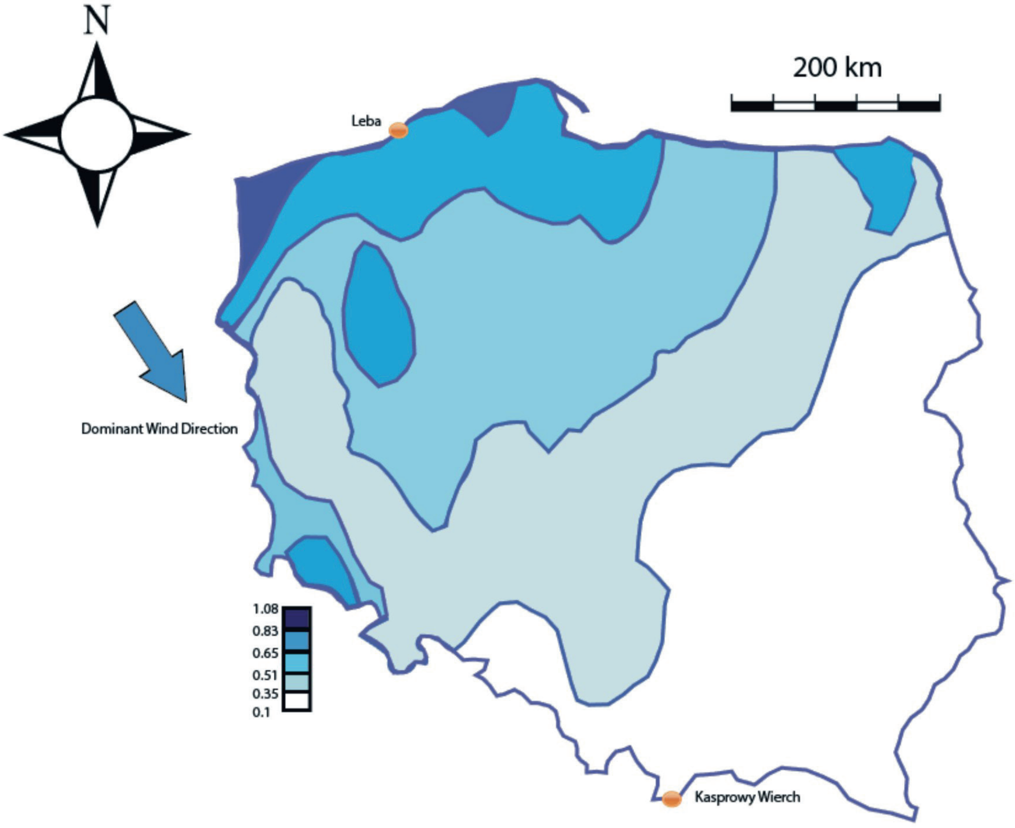

Fig. 6. *Example of annual sodium concentration in rainwater [mg/dm^3] in Poland in 2019 (GIOŚ 2019)*

The presented modified method (Appelo & Postma 1996), assumes that the entire concentration of sodium and chloride is related to oceanic origin. We have chosen to use the sodium concentration in Łeba as the baseline for marine origin because some chlorides might originate from anthropogenic sources from the combustion of plastic waste, coal burning, or from evaporation of coolants in the metallurgic industry (Lightowlers & Cape 1988). These results are consistent with observed data in the Sudety Mts. (Dobrzyński 1997). Both mountain ranges are located in Southern Poland which allows us to conclude that the predominantly continental origin of the majority of rainwater constituents characterizes the entire region of Southern Poland.

Trends in rainwater chemistry in the Tatra Mountains

One of the parameters which clearly indicates significant changes in rainwater chemistry in the studied area is pH, which increased from 5.22 in 2002 to 5.95 in 2019 (for comparison, the pH reached 4.39 in 1993–1994) (Fig. 8). The opposite trend was observed in electric conductivity, with values decreasing from 15.2 to 10.4 µS/ cm (for comparison, the EC reached 32.71 µS/cm in 1993–1994). The trend, assessed using the Mann–Kendall method, was statistically significant for both parameters (p-value < 0.05) The observed trends indicate an improvement in the quality of the atmospheric air, which is reflected in the chemical composition of rainwater in the years 2002–2019 (Figs. 8, 9).

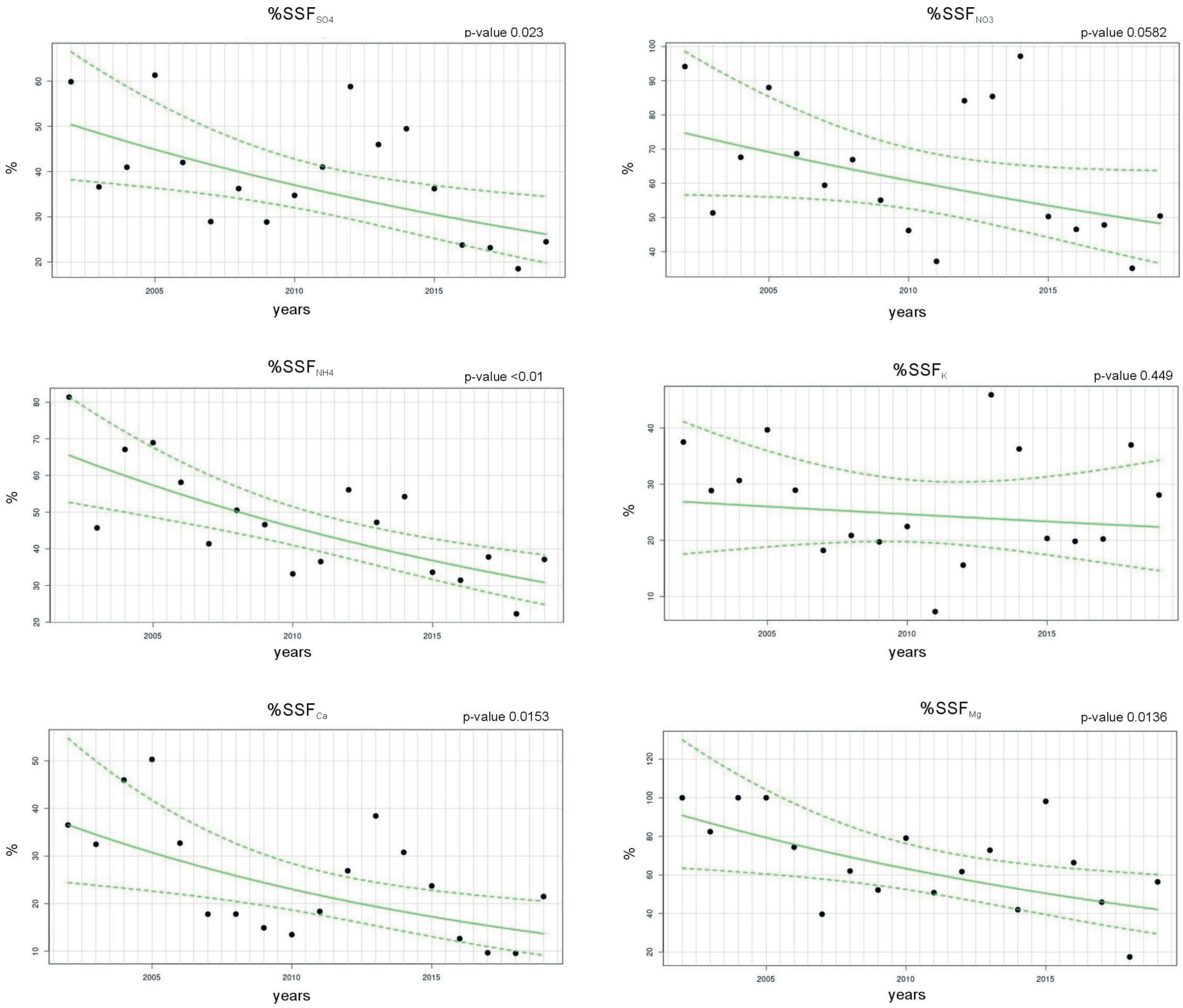

Fig. 7. Marine contributions [%SSF] in Kasprowy Wierch rainwater for selected ions

The differentiation of the presence of individual ions in the rainwater (Fig. 9) corresponds to the results of the temporal variability of concentrations in individual years (Fig. 10).

Concentrations of acid-forming sulfates and nitrates significantly decreased in the years 2002–2019 (Fig. 10), which correlates with an increasing pH trend (confirmed by the *p*-value < 0.05). The decreasing trend is also confirmed by the significantly higher concentrations of these components in the years 1993–1994 compared to the period 2002–2019. Concentrations of calcium, chloride, sodium, and ammonium also decreased over time, but the trend was not statistically significant (based on *p*-values above 0.05). Only concentrations of magnesium and potassium show a slightly increasing trend during the same time (but the trend was not statistically significant) (Fig. 10).

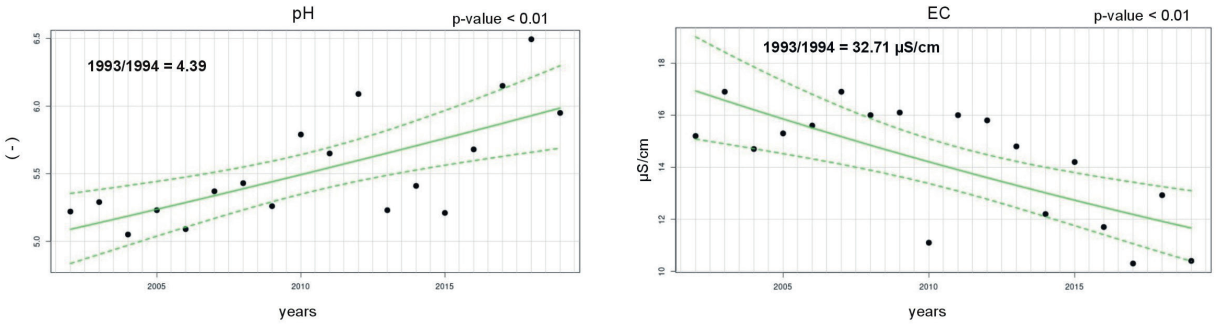

Fig. 8. *Observed values of pH and electric conductivity (EC) in rainwater in Tatra Mts.*

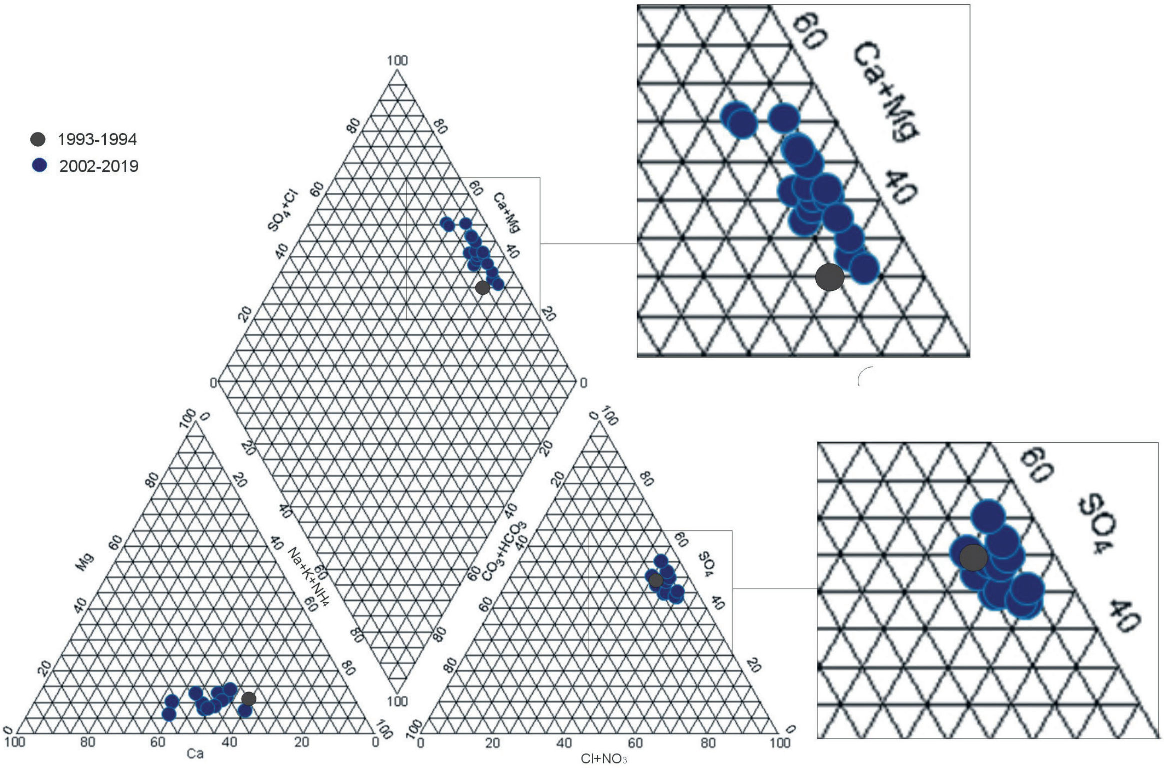

Fig. 9. *Piper diagram of rainwater samples in the Tatra Mts. (annual mean values)*

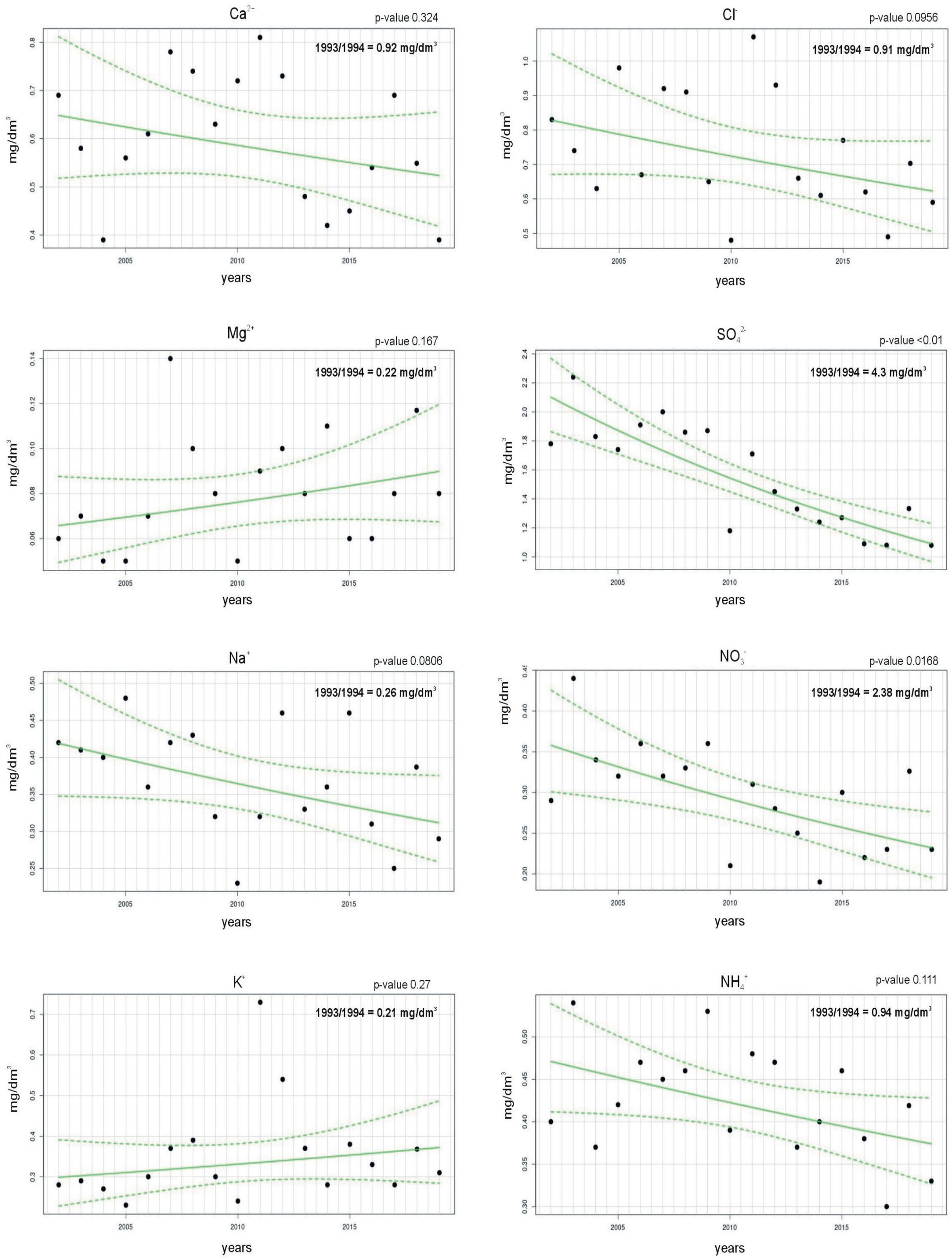

Fig. 10. *Chemical composition of rainwater in the Tatra Mts. (Kasprowy Wierch monitoring station)*

The chemistry of rainwater largely affects the chemistry of surface waters, spring waters, and shallow groundwater in the Tatra Mts. Annual ionic loads (considered as a product of the concentrations of individual components and the amount of rainfall) are presented in Figure 11.

The loads of sulfates tend to decrease, while magnesium and potassium show a slight increasing tendency (confirmed by the p-value < 0.05). Nitrates show a slightly decreasing, but not statistically significant load trend. No clear trends were established for the loads of calcium, sodium, ammonium and chloride. The comparison of the trends in ions concentrations (Fig. 10) and loads (Fig. 11) shows that the impact of sulfates on the soil and water environment is decreasing.

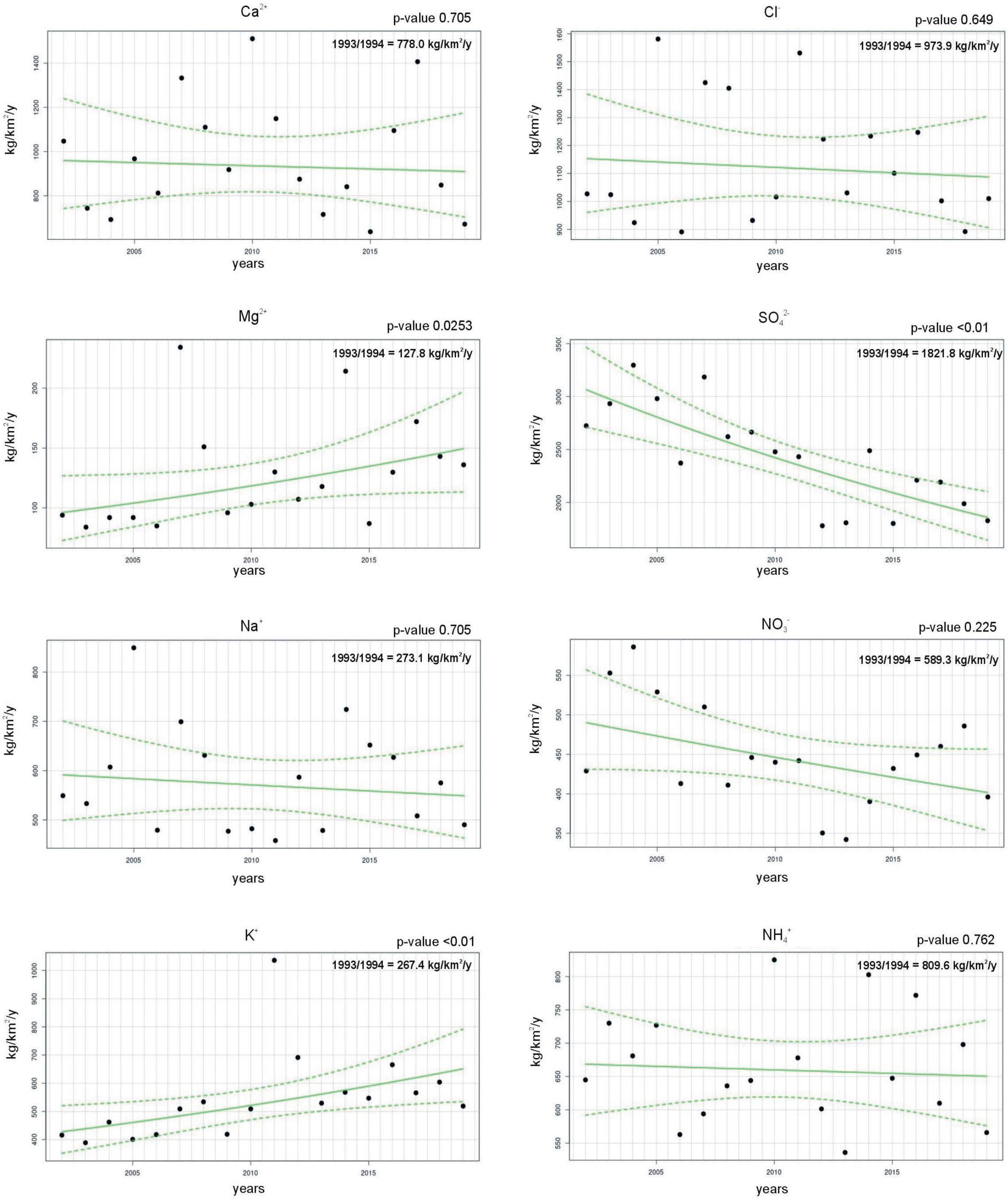

Fig. 11. *Annual loads of ions from atmospheric rainwater*

Annual loads of H^+ gradually decreased from 30 kg/km²/y in 1993–1994 to more than 17 kg/km²/y in 2004, and to approximately 2 kg/km²/y in 2019 (Fig. 12).

This trend (confirmed by the p-value < 0.05) is also reflected in the measured pH of rainwater in the Tatra Mts. which increased from pH = 5 in 2004 to pH = 6 in 2019.

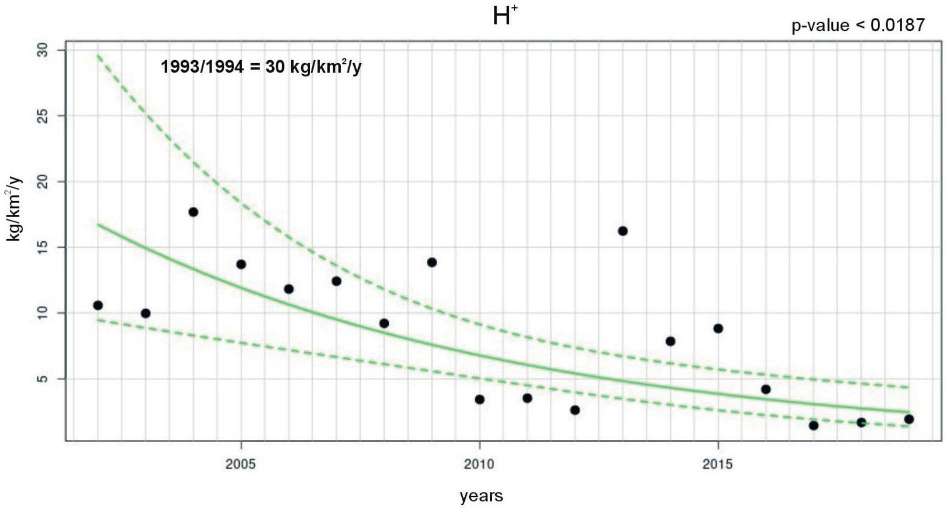

Fig. 12. *Annual H^+ loads from rainwater*

Factors controlling changes in rainwater chemistry

One of the controlling factors of rainwater chemistry are the decreasing pollution emissions resulting from the economic transformation of Poland. Decreasing trends in the deposition of sulfates and ammonium were also found in other regions in Poland (Walna 2015). Overall, this indicates an ongoing improvement in air quality since the 1990s (GUS-BDL 2022).

International agreements required the Czech Republic, Slovakia, Germany, and Poland to improve air quality. For example, the measurements conducted in the Bílý Kříž monitoring station, located in the Czech Republic about 70 km west of the Tatra Mts. showed that during the period 1996–2019, SO_2 concentration in the air decreased from 18 μg/m³ to 3 μg/m³, and NO_x concentration decreased from 10 μg/m³ to 5 μg/m³ (Hůnová et al. 2004, Hůnová 2020). These changes resulted in the reduced deposition of these compounds. The statistically significant decrease (p-value ≤ 0.01) of both forms of nitrogen and sulfur deposition was also determined in these studies in Slovakia. The decrease of $N\text{-}NO_3^-$ and $S\text{-}SO_4^{2-}$ depositions in the Czech Republic was less statistically outstanding (p-value ≤ 0.05) and the changes of $N\text{-}NH_4^+$ depositions was not statistically significant (Krupová et al. 2018, Marx et al. 2019). The German Federal Environment Agency stated that between 2002 and 2011, the total NO_x emission released by transport decreased by approximately 50% (Salthammer et al. 2018). Significant decreases in S deposition have subsequently been observed in other parts of Europe (Waldner et al. 2014, Vuorenmaa et al. 2018). However, the change in N deposition is more uncertain and it has often been difficult to observe clear trends (Bleeker et al. 2009, Pihl Karlsson et al. 2011, Colette et al. 2016). Similar changes in rainwater chemistry have also been observed in the regions outside of Poland (Sopauskiene & Jasineviciene 2005).

The neutralization factors for the cationic species for Kasprowy Wierch in the years 2002–2019 are shown in Figure 13. It was observed that NF was higher for NH_4^+, followed by Ca^{2+}, Na^+, K^+, and Mg^{2+}. The NH_4^+ neutralization factor remained the highest in all monitored years and accounted for between 35% and 49% of total neutralization factors from all cations (Fig. 13). Calcium and sodium concentrations remained relatively stable after 2009 and they alternated during the monitoring period as the second most dominant neutralization cation. Overall, the total neutralization factor has increased at statistically significant rates ($\rho = 0.0124$).

The ammonium availability index has been steadily increasing from 2002–2019 (Fig. 14). When AAI is less than 1, sulfates and nitrates are not entirely neutralized by ammonium, or other neutralizing cations are present.

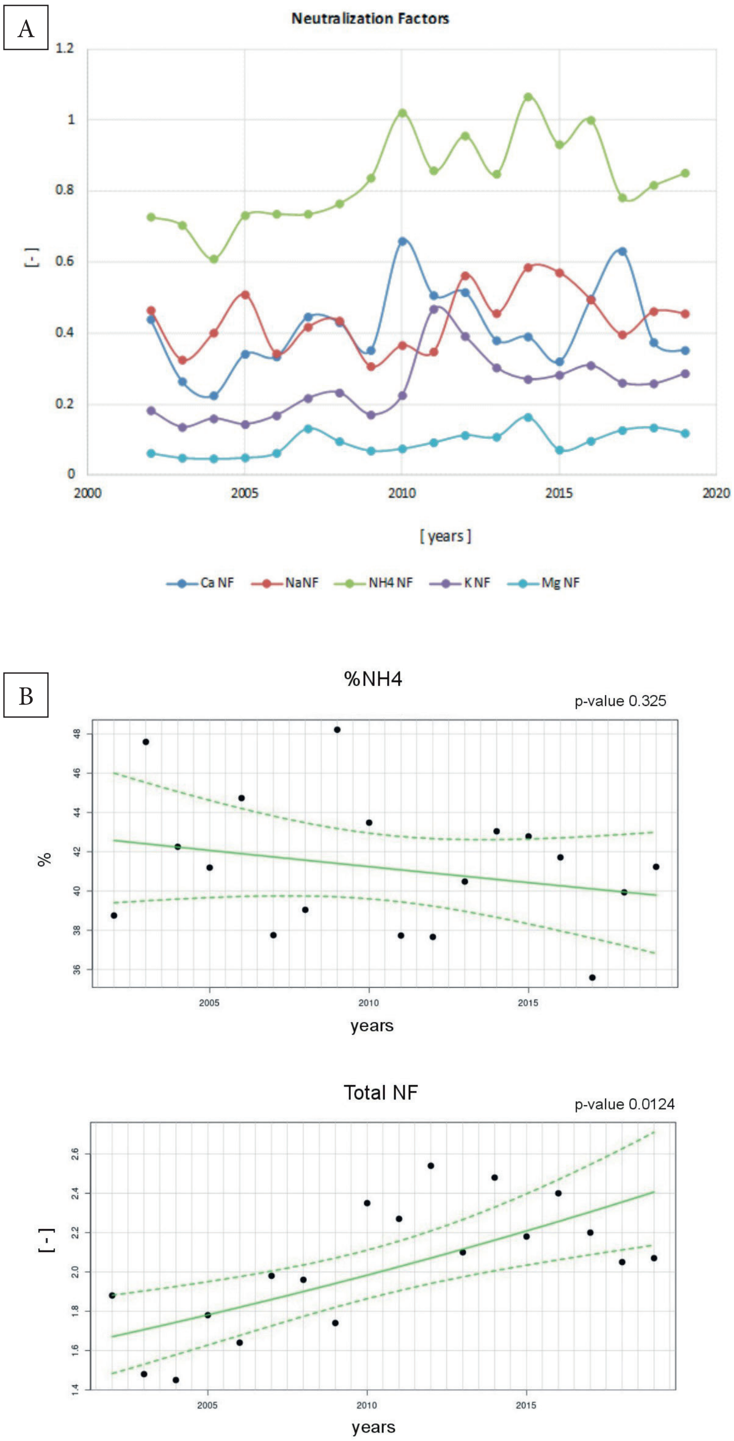

Fig. 13. *Neutralization factors for main alkaline ions in Kasprowy Wierch rainwater (A), and relative proportion of NH_4^+ neutralization factor as compared to the total neutralization factors (B)*

The acidic potential (AP) displayed a declining trend in the years 2002–2019 (Fig. 15). At the same time the neutralization potential (NP) has increased overall during the same period. The resulting ratio AP/NP has decreased, indicating an increasing trend of neutralization as compared to acidification of the rainwater. When we compare this figure to Figures 8 and 12 showing rainwater pH, we can deduce that AAI values have been increasing between 2002 and 2019 due to increasing rainwater pH values (Fig. 16).

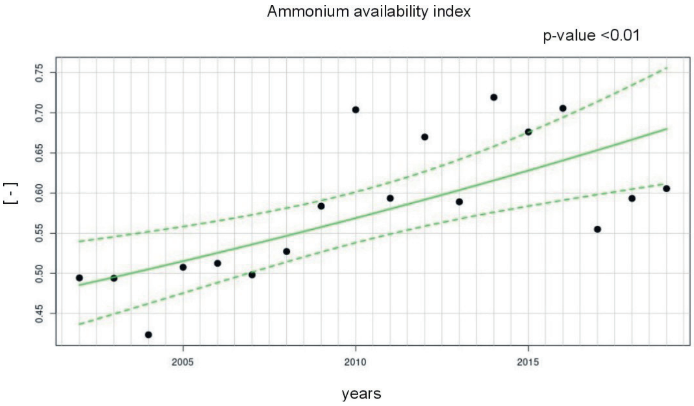

Fig. 14. Ammonium availability index in the annual Kasprowy Wierch rainwater

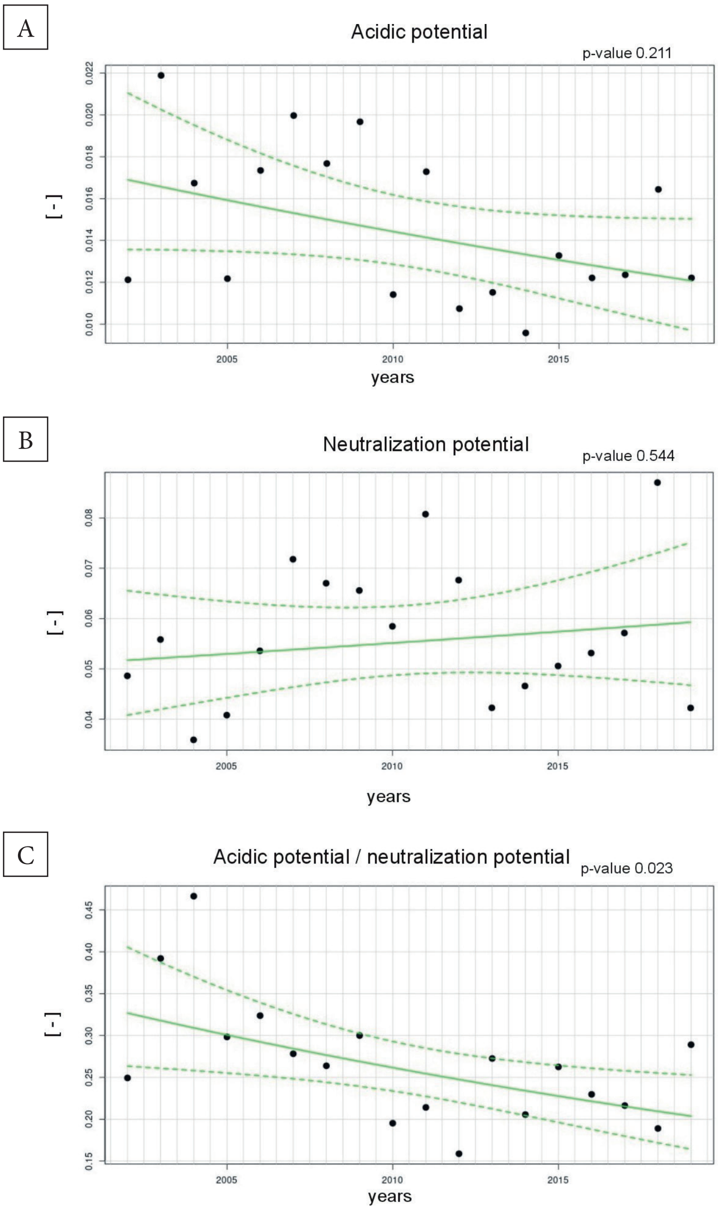

Fig. 15. The acidic potential (A), the neutralization potential (B), and the ratio of these parameters (C) corresponding to annual rainwater data in Kasprowy Wierch

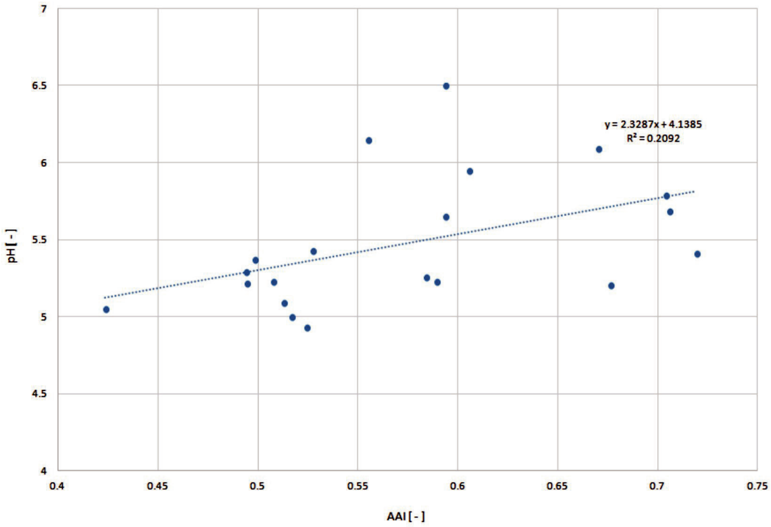

Fig. 16. *Relationship between ammonium availability index (AAI) and pH*

CONCLUSIONS

Rainwater chemistry in the Tatra Mts. is mostly controlled by continental sources, and its temporal changes since 1993 were mostly caused by anthropogenic processes. The study area is mostly affected by distant sources of pollution. Air quality has significantly improved during the period of observations, indicated by increasing pH values, the decreasing trend of electric conductivity, and ionic concentrations of sulfur and nitrogen in rainwater (assessed by the Mann–Kendall method using GWSDAT software). The magnesium and potassium loads show increasing trends, while concentrations and annual loads of calcium, sodium, and chlorides remain approximately unchanged.

Neutralization factors are highest for NH_4^+ in all monitoring years, followed by Ca^{2+}, Na^+, K^+, and Mg^{2+} in the Kasprowy Wierch monitoring station. Total neutralization capacity of all cations increased from 2002 to 2019 and is statistically significant ($\rho < 0.0124$). The ammonium availability index has been steadily increasing between 2002 and 2019. It remains less than 1, suggesting that sulfates and nitrates are not entirely neutralized by ammonium, which is likely caused by increasing pH values. The acidic potential (AP) and ratio with neutralization potential (AP/NP) have displayed declining trends from 2002 to 2019, while the neutralization potential (NP) has increased overall during the same period. Since the ammonium availability index has been steadily increasing from below 0.5 to more than 0.65 at a statistically significant rate ($\rho < 0.01$), and the neutralization occurs mainly below cloud level due to ammonia and the adsorption of SO_2 to suspended particles of Ca^{2+} and Mg^{2+}, it can be concluded that at least a significant part of the neutralization processes occurs in the lower atmospheric level.

The observed trends in rainwater chemistry result from reduced gas and dust emissions in Poland and neighboring countries. International agreements and global monitoring of rainwater quality are important due to the global nature of atmospheric pollution transport. Rainwater chemistry is a significant factor which influences aquatic, forest, and meadow ecosystems, as well as exposed soluble earth materials, including both human-made structures and naturally occurring outcrops.

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