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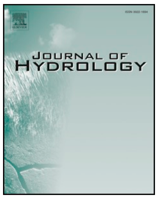

Research papers

17-Year study on the chemical composition of rain, snow and sleet in very dusty air (Krakow, Poland)

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ABSTRACT

The paper presents the results of long-term (1996–2017) studies of the chemical composition of rain, snow and sleet in one of the cities with the highest concentrations of particulate matter in the air in Europe. The study included measurements of 45 chemical constituents of precipitation as well as its pH and EC. Concentrations of PM10, SO_2 and meteorological parameters were also analysed. Differences in Cl and Na concentrations were found depending on the type of precipitation (snow or rain). These differences are most probably caused by anthropogenic factors, however, to a small extent (~18–19%), they are associated with the total variability of the concentrations of these chemical constituents. The differences between the concentrations of the remaining constituents of precipitation analysed are of lesser or negligible importance. The main processes affecting the chemical composition of precipitation are the chemical weathering of suspended dust and the formation of mineral acid aerosols. These processes shape the chemical composition of both rain and snow in a similar manner. The differences between the chemical composition of rain and snow are the result of the concentrations of and mutual relations between selected chemical constituents and precipitation pH. An important factor affecting the pH of precipitation is the effectiveness of the chemical weathering of suspended dust, which may make the precipitation more alkaline. It is very likely that pH-buffering will occur, which can prevent the pH of precipitation from decreasing, especially in cold periods. Long-term observations of variability in the concentrations of the chemical constituents indicate a slight, but rather constant decrease in concentrations of most of the chemical constituents analysed, as well as in the concentrations of PM10 and SO_2 in the air in Krakow. The directions of these changes reflect, to a certain extent, the complex transformations of industrial, economic and social conditions in Krakow within that period. The typical ranges of variability of the recorded values of concentrations/measurement values of 22 chemical constituents and the physical characteristics of rain, sleet and snow presented in the paper can be used as reference ranges of these parameters, typical for an area with a significant degree of atmospheric dust pollution.

1. Introduction

The chemical composition of precipitation is the result of complex, dynamic interactions between cloud formation processes, microphysical processes and a number of chemical reactions in the atmosphere. However, the concentration and origin of suspended dust as well as anthropogenic gaseous atmospheric constituents have a major influence on the chemical composition of precipitation (Seinfeld and Pandis, 2006). Motor vehicles, industry, mineral extraction and broadly defined agriculture constantly emit various chemical substances into the atmosphere (Mayer, 1999; Kuttler and Strassburger, 1999; Allen et al., 2001; Flemming et al., 2005). Due to high traffic volumes and industrialisation, urban areas are responsible for the emission of various types of particulate air pollutants to a greater degree than rural areas (Kim and Shon, 2011; Kim et al., 2012; Sharma et al., 2014). The use of fossil fuels as a power source for industry and internal combustion engines increases the emission of air pollutants such as: SO_2, NO_x, volatile organic compounds (VOCs) and various aerosols (Sillman, 1999; Atkinson, 2000; Marr and Harley, 2002; Murphy et al., 2007; Teixiera et al., 2008; Wang et al., 2013; Masiol et al., 2014). The combustion of petrol and diesel in vehicle engines results in the formation of particles with aerodynamic diameters ranging from below 0.1 to 2 μm (Lodge et al., 1981; Harrison et al., 1996). As a result, traffic-related aerosols are particularly visible in fine particulate matter. As a result of

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oxidation of SO_2 and NO_x contained in the exhaust gases from heating systems and vehicles, high concentrations of SO_4 and NO_3 can be found in precipitation (Kellman et al., 1982; Stockwell and Calvert, 1983). In densely industrialised areas, this has led to the large-scale occurrence of acid rain and/or photochemical smog (Lickens et al., 1976; Lickens and Butler, 1981; Daum et al., 1984; Low et al., 1991; Wang and Wang, 1995; Lickens et al., 1996; Hadi et al., 1999; Castillo et al., 1983; Galloway et al., 1976). The results from stable sulphur isotopes confirm that SO_4 in precipitation primarily originates from high temperature (minimum mean over sampling period 680 °C) combustion of fuels with $\delta^{34}S$ signatures $\leq 4.4‰$ (Górka et al., 2017). According to the above-mentioned authors, the stable oxygen isotope composition of sulphates and precipitation water indicates that the contribution of sulphate (generated directly by industrial processes) was $< 49\%$ during the long-term observation period, with a mean of ~20% during the non-heating and ~40% during the heating periods. Heavy metals are also important contaminants related to industrial processes. Heavy metals emitted in combustion processes are mostly soluble and reactive due to the small size of the transporting particles. Thus, they dissolve readily in the rain, especially under conditions of low pH (Herrera et al., 2009). A significant percentage of the total content of heavy metal particles falls with rain at the location where they were generated as a result of their high relative masses (Nurnberg et al., 1984). Lighter aerosols containing smaller particles of heavy metals, with low precipitation velocity, are easily carried by the wind (Smirnioudi et al., 1998). They remain in the atmosphere until they are removed by various purification processes, including dry and wet deposition (Hamilton-Taylor and Willis, 1990; Yoo et al., 2014). Some of the heavy metals contained in the precipitation are taken up by the plant root systems, and also by the leaf blades, and introduced into the food chain (Chaney et al., 1998). Some of these metals are essential for the proper functioning of living organisms (e.g. Cu and Zn), while others – such as Cd, Pb, As – are dangerous (Caussy et al., 2003; Adamus et al., 2004). Heavy metals introduced into the soil through wet and dry deposition inhibit the growth of local microorganisms, disturbing the processes of decomposition and transformation of organic matter (Hander et al., 2001; Becker et al., 2006). Understanding the mechanisms governing the chemical composition of the atmosphere is important for its short and long-term impact on the ecosystem as a whole and on human health in particular (Steinnea, 1990; Kanellopoulo, 2001; Ostro, 2004; Perera and Emmanuel, 2005; Samoli et al., 2008; Cooper et al., 2010; Apte et al., 2015; Lee et al., 2015). The load of chemical constituents carried by precipitation may have a significant impact on the natural environment, including animals and humans (Bytnerowicz et al., 2005). Studies of the chemical composition of precipitation can provide detailed data on the changes and other characteristics of local and/or regional atmospheric air pollution (Calvo et al., 2010; Budhavant et al., 2011; Cerqueira et al., 2014; Wu et al., 2015). Due to the large spatial and seasonal variability of meteorological conditions, the quantity of pollutants transferred by precipitation varies greatly. This differentiation results from, among other things, differing areas of origin of the pollutants, changing altitude for cloud formation, and the direction of movement of air masses. The dynamics of changes in air pollutant contents close to the Earth's surface (< 1.0 km) are high. The average aerosol residence time in the air is one to six days (Stefan et al., 2010). At the same time, it is estimated that in moderate latitudes, rain removes 70–80% of the mass of aerosols from the atmosphere (Falkowska and Lewandowska, 2009). The analysis of the chemical composition of precipitation is used to evaluate and estimate the impact of anthropogenic and natural emission sources on the atmosphere: wet deposition of toxic inorganic compounds, the weathering and dissolution of particulate matter (PM) as well as the long-distance transport of suspended dust. Studies analysing these aspects of the chemical composition of precipitation in urban areas were presented by multiple researchers (e.g. Kanellopoulo, 2001; Hu et al., 2003; Moulia et al., 2005; Song and Gao, 2009; Huang et al., 2010; Abdus-Salam et al., 2014; Mehr et al., 2019).

The aim of this study is to identify dependencies shaping the chemical composition and to determine the sources of origin of the chemical constituents in various types of precipitation (rain, snow, sleet) in Krakow, one of the cities with the highest level of particulate matter air pollution in Europe. The research can help to better understand the complex processes affecting the chemical composition of different types of precipitation and to determine the potential load of chemical compounds introduced into the environment in this manner. It is also important to determine the typical, most frequently occurring ranges of variation in the concentrations of selected chemical constituents and the values of the measurements of the physical characteristics of rain, snow and sleet. Another significant consideration is the analysis of the temporal variability of concentrations of selected constituents of precipitation in order to enable the general directions of changes in the concentrations of these constituents over the 1996–2017 period to be determined. This will provide grounds for an analysis of research results over time and the formulation of predictions regarding the potential directions and dynamics of changes in the recorded concentrations of the chemical constituents and the values of the measurements of the physical characteristics of precipitation.

Krakow is a medium-sized European city (about 770 thousand residents) and a regional transport hub with a well-developed road and rail network. Large industrial plants located directly in Krakow and its immediate vicinity include ArcelorMittal Poland SA (steelworks, roasting or sintering installations) and power plants: EDF Krakow, EC Jaworzno, EC Skawina (CHP plants and other combustion installations). In 2000–2017, the average annual values of PM10 and PM2.5 in the centre of Krakow reached the following ranges, respectively: 56–96 and 38–61 $\mu g \cdot m^{-3}$. During this period, average annual concentrations of PM10 > 50 $\mu g \cdot m^{-3}$ were observed from 132 to 262 days per year. The characteristic feature of the air polluting dust in Krakow is the high content of carbon particles (soot) and very high content of fine particles PM2.5 and very fine particles PM0.1 (Wilczynska-Michalik et al., 2015). This is typical of the aerosols found in urban areas (Buseck and Adachi, 2008). As a rule, the PM2.5 concentration in Krakow is 60–80% of the value of the PM10 concentration (Wilczynska-Michalik et al., 2015). Very dusty air also leads to significant soil contamination. In Krakow, the level of heavy metals in the soils within the city centre is significantly higher than the natural level of these elements in soils (Gąsiorek et al., 2017; Ciarkowska et al., 2019). Air pollution in Krakow shows a clear seasonal variability and reaches its highest levels in the cold period. This is largely due to the heating systems found in most of the buildings in Krakow. Low-calorific coal (< 25 kJ), wood, coal waste with a high content of non-flammable dusts and iron sulphides, and in extreme cases even municipal waste are often used as fuel. The occurrence of episodes of high concentrations of air pollutants in Krakow in the cold period may indicate that this phenomenon is similar to the London type of smog, but a significant difference is the relatively low concentration of SO_2. The annual average winter SO_2 concentrations in the years 2007–2017 did not exceed 20 $\mu g \cdot m^{-3}$. Juda-Rezler et al., (2011) indicate that episodes of high concentrations of PM10 in cold periods in the cities of southern Poland (including Krakow) are more strongly associated with local pollutant emissions than in cities in central and northern Poland, where particles from distant sources (long-range transport and regional transport) constitute a more significant element of the PM10 composition.

Dense urban development and its location in a deep river valley, which reduces the possibility of natural ventilation and favours the formation of fogs, have a negative impact on the air conditions in Krakow. According to some authors, the main factor contributing to the high concentrations of particulate matter in Krakow is not usually a sharp increase in emissions (although this may indirectly be related to a decrease in temperature), but a deterioration in conditions conducive to the dispersion of pollutants in the near-ground layer of the atmosphere (Pietras, 2013).

Table 1
Descriptive statistics, LOQ, LOD and U.

	R				S				RS						
	n	Mean	Median	% < LOQ	n	Mean	Median	% < LOQ	n	Mean	Median	% < LOQ	LOD	LOQ	U (LOQ)
pH	590	5.51	5.57		203	4.91	4.71		40	5.14	5.07				
EC	590	28.23	22.70		203	31.90	25.30		40	43.60	32.45				
Ca	590	1.67	1.05	0.2	203	1.35	0.83	0.5	40	3.51	1.78	0.0	1.00E-04	5.00E-02	12.58
Mg	590	0.23	0.15	0.0	203	0.20	0.12	0.0	40	0.40	0.26	0.0	1.00E-06	1.00E-03	16.15
Na	590	0.56	0.26	1.0	203	1.70	0.98	0.5	40	1.22	0.73	2.5	1.00E-05	1.00E-02	12.15
K	590	0.86	0.41	2.7	203	0.60	0.36	2.5	40	1.14	0.66	5.0	5.00E-05	5.00E-02	11.98
HCO_3	590	3.61	2.10	49.3	203	2.41	0.90	70.0	40	4.25	2.80	40.0		2.00E+00	
SO_4	589	3.16	2.45	59.6	203	2.57	1.74	73.4	40	6.19	3.53	45.0	1.00E+00	3.00E+00	13.13
Cl	590	1.93	1.48	26.6	203	4.18	3.03	4.9	40	4.25	2.98	15.0		1.00E+00	10.00
PO_4	555	0.10	0.04	20.9	195	0.09	0.05	10.3	33	0.05	0.04	24.2	2.00E-03	6.10E-03	1.29E+01
SiO_2	590	0.37	0.18	5.6	203	0.29	0.18	2.5	40	0.31	0.24	5.0	1.00E-02	2.00E-02	11.91
Al	589	0.02	0.01	46.3	203	0.04	0.02	22.2	40	0.05	0.03	15.0	5.00E-03	1.00E-02	1.41E+01
B	585	0.03	0.01	35.0	203	0.02	0.01	45.3	40	0.03	0.01	40.0	1.00E-02	1.00E-02	1.59E+01
Ba	589	0.004	0.002	4.6	203	0.01	0.003	5.4	40	0.01	0.004	2.5	5.00E-04	5.00E-04	1.36E+01
Fe	517	0.02	0.01	39.3	177	0.05	0.03	12.4	33	0.05	0.03	6.1	2.00E-02	1.00E-02	1.42E+01
Mn	590	0.01	0.004	52.9	203	0.01	0.01	49.8	40	0.01	0.01	35.0	3.00E-03	5.00E-03	1.31E+01
Sr	573	0.004	0.002	2.3	197	0.003	0.002	0.5	39	0.01	0.004	0.0	3.00E-04	3.00E-04	1.29E+01
Zn	590	0.04	0.02	0.8	203	0.05	0.03	1.0	40	0.04	0.03	0.0	1.00E-03	1.00E-03	1.20E+01
Hg	499	1.62E-04	4.80E-05	73.3	196	2.85E-04	5.85E-05	65.3	33	4.55E-04	3.00E-05	84.8	5.00E-03	1.00E-04	1.35E+01
Cu	498	2.18E-03	1.35E-03	37.8	195	2.42E-03	1.36E-03	37.4	33	1.99E-03	1.84E-03	21.2	1.00E-03	1.00E-03	1.46E+01
Li	523	5.26E-04	2.82E-04	78.0	195	5.52E-04	2.95E-04	82.6	33	5.95E-04	5.16E-04	66.7	1.00E-03	1.00E-03	1.37E+01
Pb	499	1.51E-03	4.75E-04	17.0	195	3.87E-03	1.34E-03	7.7	33	1.62E-03	8.30E-04	12.1	1.00E-04	1.00E-04	1.53E+01
Ni	499	1.30E-03	1.73E-04	86.8	195	3.40E-03	1.19E-04	88.7	33	8.48E-04	4.09E-04	93.9	1.00E-03	1.00E-03	1.30E+01
Co	499	1.13E-04	7.10E-05	88.2	195	1.20E-04	7.60E-05	85.1	33	1.34E-04	9.70E-05	87.9	2.00E-04	2.00E-04	1.31E+01
As	499	1.34E-03	5.58E-04	66.5	195	9.73E-04	6.34E-04	68.2	33	1.39E-03	4.51E-04	78.8	1.00E-03	1.00E-03	1.18E+01
Be	499	1.27E-04	2.70E-05	96.0	195	9.96E-05	3.20E-05	95.9	33	2.91E-04	2.20E-05	97.0	5.00E-04	5.00E-04	1.42E+01
V	499	1.47E-03	4.18E-04	72.5	195	1.34E-03	7.07E-04	61.0	33	9.83E-04	5.19E-04	66.7	1.00E-03	1.00E-03	1.21E+01
Tl	499	1.42E-04	5.20E-05	71.1	195	1.12E-04	5.70E-05	70.3	33	1.04E-04	4.40E-05	72.7	1.00E-03	1.00E-04	1.43E+01
Se	499	3.73E-03	5.98E-04	92.2	195	1.97E-03	6.06E-04	95.4	33	4.96E-03	2.65E-04	90.9	1.00E-02	1.00E-02	1.42E+01
Mo	499	8.15E-04	1.16E-04	69.1	195	3.78E-04	7.50E-05	84.1	33	5.25E-04	8.40E-05	78.8	3.00E-04	3.00E-04	1.17E+01
Sb	499	4.57E-04	2.29E-04	42.5	195	4.04E-04	2.22E-04	46.7	33	4.07E-04	1.89E-04	51.5	2.00E-04	2.00E-04	1.74E+01
Ag	499	6.92E-03	2.94E-04	71.9	195	3.25E-03	2.64E-04	77.4	33	5.56E-03	3.04E-04	69.7	1.00E-03	1.00E-03	1.54E+01
Cd	499	5.02E-04	1.41E-04	75.6	195	4.27E-04	2.06E-04	63.6	33	1.72E-04	1.71E-04	93.9	3.00E-04	3.00E-04	1.34E+01
Br	499	1.08E-02	2.00E-03	99.0	195	2.27E-02	2.00E-03	99.0	33	5.08E-03	2.00E-03	100.0		1.00E-01	1.18E+01
I	499	9.48E-03	8.21E-04	89.2	195	3.50E-03	7.44E-04	95.9	33	1.37E-03	1.00E-04	97.0		1.00E-02	1.28E+01
Y	499	9.29E-06	6.00E-06	99.8	195	1.35E-05	9.00E-06	99.5	33	1.47E-05	1.10E-05	100.0	1.00E-04	1.00E-04	1.22E+01
Bi	499	8.62E-05	1.40E-05	94.8	195	4.66E-05	1.80E-05	98.5	33	6.93E-05	2.60E-05	97.0	5.00E-04	5.00E-04	3.48E+01
Ga	499	1.76E-04	1.14E-04	85.6	195	4.39E-04	1.64E-04	73.8	33	2.23E-04	1.87E-04	72.7	3.00E-04	3.00E-04	2.18E+01
Te	499	4.96E-05	2.00E-05	100.0	195	3.88E-05	2.00E-05	100.0	33	3.11E-05	2.00E-05	100.0	2.00E-03	1.00E-02	1.37E+01
Sn	499	1.76E-04	4.00E-05	98.0	195	2.15E-03	4.70E-05	86.7	33	9.79E-05	5.10E-05	100.0	1.00E-03	1.00E-03	1.26E+01
W	499	6.62E-04	5.00E-05	78.8	195	9.52E-04	4.50E-05	74.9	33	1.74E-03	2.00E-05	78.8	3.00E-04	3.00E-04	2.11E+01
Zr	499	2.45E-04	2.50E-05	98.6	195	5.86E-04	4.20E-05	90.3	33	4.42E-05	3.80E-05	100.0	2.00E-04	2.00E-03	1.23E+01
Rb	499	6.54E-04	3.95E-04	8.4	195	7.44E-04	4.45E-04	7.2	33	6.57E-04	4.58E-04	0.0	1.00E-04	1.00E-04	1.17E+01
U	499	6.67E-06	4.00E-06	100.0	195	8.92E-06	6.00E-06	100.0	33	1.00E-05	7.00E-06	100.0	1.00E-04	1.00E-04	1.22E+01
Cr	499	5.67E-03	1.21E-03	82.8	195	4.37E-03	1.76E-03	84.1	33	2.72E-03	1.49E-03	87.9	1.00E-03	5.00E-03	1.35E+01
Ti	482	9.06E-04	1.69E-04	99.8	189	4.98E-03	6.13E-04	93.7	32	1.65E-03	9.71E-04	100.0	1.00E-03	2.00E-02	1.26E+01
Cs	324	4.27E-05	1.10E-05	99.7	99	3.86E-05	1.10E-05	100.0	19	1.75E-05	2.00E-06	100.0	1.00E-04	5.00E-03	1.24E+01
PM10	506	39.7	32.0		181	70.3	53.8		30	62.5	47.0				
SO_2	362	6.28	4.34		149	20.34	15.78		19	14.98	15.46				
VISIB	589	8.95	9.33		203	5.59	5.15		40	7.32	7.24				
PRCP	552	0.86	0.56		199	0.35	0.23		40	0.49	0.29				
WDSP	590	3.30	2.88		203	3.74	3.50		40	3.97	3.50				
TEMP	590	11.88	12.28		203	-2.73	-2.11		40	1.56	1.69				
NH_4	110	0.51	0.32		52	0.56	0.16		4	0.25	0.05				
NO_2	110	0.03	0.01		52	0.02	0.01		4	0.01	0.01				
NO_3	130	3.85	3.30		72	3.39	3.40		6	5.46	6.13				

Irrespective of the negative impact on human and animal health, atmospheric pollution also affects inanimate elements of the environment. Long-lasting high concentrations of sulphur compounds, but also of other gaseous constituents and dusts, in the air in Krakow have caused significant damage to the stone elements of many valuable historical structures. The process of destruction of the stone elements was associated primarily with the crystallisation of gypsum and other salts in the pore spaces of rocks, causing so-called salt weathering (Wilczyńska-Michalik, 2004).

2. Sampling and measurements

The precipitation sampling site is located in the centre of Krakow, within an area populated by blocks of flats (4-storeys) in close proximity (~50 m) to a very busy traffic route (road and tram traffic). The CIEP (Chief Inspectorate for Environmental Protection – data are from the JPOAT 2.0 air quality database) monitoring point for air pollution information is also located in the city centre, approximately 2 km from the precipitation sampling site. It is located in very similar conditions, in relation to topography, building development and urban traffic, by one of the main traffic routes of the city. Meteorological parameters were recorded at the airport meteorological station in Balice, located approx. 8 km from the place of precipitation sampling.

The samples of precipitation were collected in polyethylene (HD) vessels with a volume of 100 cm^3. Only the samples for which a sufficient amount of precipitation was obtained, i.e. at least 25–30 cm^3 of precipitation, were used for the titration and spectrometric analysis. In case of sleet or snow, approximately 100–500 cm^3 of precipitation was collected respectively, so that after melting of the snow, a sufficient amount of water was obtained for the test. Only fresh snow which had lain no longer than 6 h was collected for the study. If precipitation episodes (events) occurred several times during the day, samples were taken from individual precipitation episodes and examined independently from each other. The precipitation collected was divided into 4 separate samples for the analysis of cations, anions, alkalinity and other measurements. Electrical conductivity and pH were measured in situ (WTW indicator). Samples collected for chemical analysis were immediately passed through a 0.45-μm membrane filter into polyethylene bottles. Samples for cation analysis were acidified using a few drops of concentrated HNO_3 that had been purified by redistillation. Chemical analyses were conducted in 1996–2017, by the accredited laboratory of the University of Science and Technology in Krakow (Poland). Major dissolved elements were analysed by the ICP-AES method with an OPTIMA 7300DV Perkin Elmer and by the ICP-MS method with a ELAN 6100 Perkin Elmer. An ICP AES emission spectrometer with inductive coupled plasma (Plasma 40 Perkin Elmer) was used to measure the contents of: S, Ca, Mg, Na, K, Fe Sr, Zn and Si. The remaining microelements were measured using an ICP MS mass spectrometer (ELAN 6100 Perkin Elmer). The content of total sulphur and total phosphorus was converted to SO_4 and PO_4 concentrations, respectively. The Cl concentration was determined by the argentometric method. An automatic micropipette was used for titration. Alkalinity was determined in the laboratory following the volumetric method and using a mixed indicator. At pH values up to 8.6, in practice the alkalinity reflects the HCO_3 concentration.

3. Database

The database contains physical, chemical and meteorological data. Two research sub-periods can be distinguished in the dataset. In the period from 1996-04-03 to 1998-01-31, 57 cases were listed in the database. Then, there was no data until 2002. In addition, in the period from 2002-09-24 to 2017-07-11, 985 cases were listed in the database. The data refers to rain (R), snow (S) and sleet (RS) samples. Physical and chemical analyses include the measurements of 47 parameters. These include pH and EC, concentrations of the primary chemical constituents (Ca, Mg, Na, K, HCO_3, SO_4, Cl, PO_4, Si – as colloidal SiO_2) as well as secondary and trace constituents (Al, B, Ba, Fe, Mn, Sr, Zn, Hg, Cu, Li, Pb, Ni, Co, As, Be, V, Tl, Se, Mo, Sb, Ag, Cd, Br, I, Y, Bi, Ga, Te, Sn, W, Zr, Rb, U, Cr, Ti, Cs). Meteorological data include daily information (average from 24 h): air temperature (TEMP), visibility (VISIB), wind speed (WSPD) and precipitation volume (PRCP). VISIB is a parameter that determines the total dustiness of the air, regardless of the size of the particles of suspended dust. The mean (24 h) concentrations of PM10 and SO_2 measured on the day of occurrence of a precipitation episode at the CIEP monitoring point were also analysed.

Table 1 presents descriptive statistics of the physical and chemical data as well as the limit of quantification (LOQ), limit of detection (LOD) and uncertainty (U) of measurement values for individual chemical constituents. The percentage of measurements $< LOQ$ is also included.

concentrations of chemical constituents, LOQ and LOD reported in $mg \cdot dm^{-3}$, EC in $\mu S \cdot m^{-1}$; PM10 and SO2 reported in $\mu g \cdot m^{-3}$; VISIB in km; PRCP in cm; WSPD in $m \cdot s^{-1}$; temperature in °C; LOQ for HCO_3 is value approximate – outside the scope of laboratory accreditation; U is reported in % for the appropriate concentration range of the tested chemical constituents, and for elements with two or more valencies, total concentration is reported.

For further investigations, chemical constituents with mean and/or median concentrations above the LOQ were selected. This criterion is approximately met by chemical constituents for which the number of measurements $< LOQ$ does not significantly exceed 50% (Table 1). The exceptions are SO_4 and partially HCO_3, which were used for further analysis despite a significant number of measurements $< LOQ$, as omission of these constituents makes interpretation of the results difficult. In general, 28 parameters were taken into account: pH, EC, Ca, Mg, Na, K, HCO_3, SO_4, Cl, SiO_2, Al, B, Ba, Fe, Mn, Sr, Zn, Cu, Pb, Sb, PO_4, Rb, TEMP, VISIB, WSPD, PRCP, SO_2 and PM10. Due to the small number of measurements of nitrogen compound concentrations, these results were not used for further analysis. Average and median concentrations of NO_3, NO_2 and NH_4 together with the number of measurements taken of them in particular types of precipitation are presented in Table 1.

The quality of individual results of the physical/chemical analyses of precipitation was evaluated by calculating the ion difference (ID), expressed as the following relationship:

$$ID = \frac{\Sigma C - \Sigma A}{\Sigma C + \Sigma A} \cdot 100\% \qquad (1)$$

where:

ΣA – sum of anions [% $eq \cdot dm^{-3}$];
ΣC – sum of cations [% $eq \cdot dm^{-3}$].

The following constituents were used to calculate the ID: Ca, Mg, Na, K, H_3O, HCO_3, SO_4, Cl and PO_4. Concentrations of H_3O ions were calculated on the basis of the pH. Concentrations of PO_4 were calculated on the basis of the concentrations of phosphorus (P) measured in spectrometric tests. Due to absence of measurements of nitrogen compounds concentration, the calculated ID values should be treated as approximate. The ID may also be affected by taking into account the uncertainty (U), which determines, with a probability of 95%, the concentration range of the chemical constituent analysed in the range ($x \pm U$), where x is the actual concentration of the constituent analysed. The potential values of ID increase/decrease resulting from the inclusion of U for the selected chemical constituents are presented in Table 2.

Taking into account the above, it was decided that the results of physical and chemical analyses with the ID in the range ± 30% will be used to conduct the tests. To some extent (~15% of cases) this exceeds the recommendations of Global Atmosphere Watch or European Monitoring and Evaluation Programme regarding permissible errors in physical and chemical analyses of precipitation. However, the data set defined in this manner does not limit the possibility of applying statistical methods by significantly reducing the number of cases analysed. The reduced database compiled as described contains 833 cases. Significant part of the data are cases with an ID ranging from -30 to -20% (Fig. 1), which results from significant problems with the precise measurements of anion concentrations in the ranges characteristic for precipitation. It is difficult to determine the impact of these measurements errors on study results and conclusions, among others thing, they can cause interpretation difficulties and reduce the quality of statistical inference. They can also cause the apparent "strengthening" of the anion influence, because most likely these errors come actually from overestimating the concentrations these ions.

For about 100 cases from different time periods, the measurements of trace element concentration are missing. These deficiencies are

Table 2
Effects of uncertainty U on the value of the ID – values (±) in %.

Ca	Mg	Na	K	SO_4	HCO_3	Cl
3.2	0.9	1.2	0.66	2.1	1.2	1.9

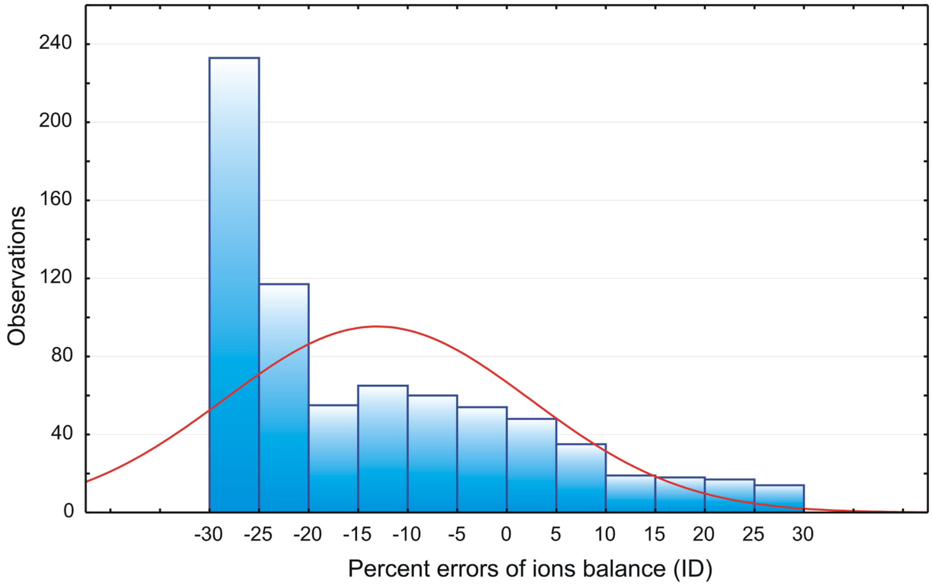

Fig. 1. ID histogram ID for the physical and chemical analyses of precipitation.

usually the result of a breakdown or the periodic inspection of the measuring equipment and the ensuing inability to perform the measurements.

Meteorological parameters, characterised by high local variability, are an important element of the database. This applies in particular to the range, direction and movement speed of precipitation zones. The complex nature of precipitation in the city, overlapping of several precipitation zones and variable movement speed of precipitation zones are frequently observed. These factors are a result of the cyclonic character of the weather in southern Poland in particular seasons of the year. Additionally, there are no trends in the directions of changes in precipitation levels for this region of Poland (Młyński et al., 2018). Precipitation zones are often only observed in certain parts of the city, while there is no precipitation at all in other parts of the city. Therefore, meteorological data, which are parameters with a potential error of a magnitude that is difficult to determine, should be treated as estimates.

4. Methods

4.1. The initial analysis and preparation of data

The Kolmogorov-Smirnov (K-S) test was used to analyse the normality of data. The results of the K-S test showed that all the parameters tested were characterised by a distribution different from normal. An attempt was made to normalise the distribution of these parameters using different types of transformations: logarithmic, Fisher and Box-Cox. The best results were achieved for the Box-Cox transformation, however, there are still many parameters with abnormal distributions (Table S1). Levene's test was performed in order to check the homogeneity of variance for parameters with normal distribution. The results obtained indicate that only some of the parameters analysed are characterised by the same variance ($p > 0.05$) (Table S2). This pertains to: Na, SO_4 Cl, Al, Fe, Cu , Rb, WDSP and PM10.

4.2. Statistical analysis

4.2.1. ANOVA

One-way ANOVA analysis was applied in order to identify any possible variability in the concentrations (or measurement values) of the selected parameters in particular types of precipitation. The parameters analysed were those that met the assumptions needed for parametric methods to apply, i.e. those that have both a normal distribution and homogeneous variance (Tables S1 and S2). These include: SO_4, Cl, Na, Al, Fe, Cu, Rb, WDSP and PM10. Precipitation type – rain (R), snow (S) and sleet (RS) were considered as independent variables. In order to determine the percentage of the variance of the parameters being analysed that is directly related to the type of precipitation, the following relationship was applied:

$$\omega^2 = \frac{SS_{effect} - df_{effect}\,(MS_{error})}{MS_{error} + SS_{total}}\cdot 100\% \tag{2}$$

where:

ω^2 – estimator of variance for the dependent variable explained by an independent variable in the entire data population; SS_{effect} – sum of squares associated with an effect; df_{effect} – degrees of freedom associated with an effect; MS_{error} – mean square of an error; SS_{total} – total sum of squares.

A post-hoc test was used to interpret the results of the analysis of variance. Tukey's extended test for uneven sets (Unequal N HSD) was selected as the most suitable. Tukey's test is more conservative than the LSD test and is recommended for the comparison of pairs of averages.

In order to analyse the regularity of the distribution of the selected parameters over time, an analysis of variance for factorial designs (Factorial ANOVA) was performed. Parameters with normal distributions and homogeneous variances were selected for analysis. These include: SO_4, Cl, Ca and Na. The first set of independent variables are time criteria, the cold and warm periods. It is usually assumed that the cold period in Poland lasts from 24 October to 29 March, while the warm period lasts from 30 March to 23 October. This division reflects the variability of weather conditions in Krakow with a good approximation. The second set of independent variables are two temperature ranges corresponding to the average daily temperature on the day of the occurrence of a rain episode: > 10 °C and < 10 °C, respectively. The adopted boundary point (temp. < 10 °C) is one of the criteria for the start of the heating season in Krakow by multi-family housing managers. This is a contractual criterion and does not include single-family houses and buildings with individual heating systems, which constitute a significant proportion of the buildings in Krakow. In order to determine the percentage of the variance of the parameters under analysis that is directly related to the cold/warm period and/or the adopted temperature ranges, relationship 2 was applied.

4.2.2. PCA

In order to determine the processes shaping the chemical composition of various types of precipitation, principal component analysis (PCA) was used. This method does not require normal distributions for large data sets. Two data sets were used for PCA. Set (R) ($n = 590$) contains the results of physical and chemical analyses of rain as well as metrological parameters and concentrations of PM10 and SO_2 measured on the days of rainfall. Set (S) ($n = 203$) contains the results of physical and chemical analyses of snow as well as metrological parameters and concentrations of PM10 and SO_2 measured on the days of snowfall. PCA was not conducted for sleet (RS) due to the low volume of data ($n = 40$) for this type of precipitation. In order to determine the adequacy of PCA application and the selection of parameters for the analysis, Bartlett's test of sphericity was carried out and Kaiser-Meyer-Olkin coefficients (KMO) were determined. For KMO values below 0.6, the use of PCA is ineffective, and therefore the parameters for which KMO > 0.6 were selected for further analysis. The Kaiser and Cattell criteria were selected as the methods of determining the optimal number of PCA factors. In determining the number of factors, the factors in the factorial scree and factors with a value of < 1.6 were rejected. Given that the data analysed often have significantly different values and are expressed in different units, a correlation matrix was used to carry out the PCA.

4.2.3. Time variability

Time variability of SO_4, HCO_3, Cl, Ca, Na, Zn, Cu, Pb concentrations and the pH observed in rain samples (R) were analysed. Furthermore, the variability of PM10 and SO_2 concentrations in days covering precipitation episodes was presented. The remaining data sets, i.e. (S) and (RS), were not analysed as there was an insufficient number of cases for a reliable assessment of long-term variability. Time variability was studied in the periods from 1996-04-03 to 1998-01-31 and from 2002-09-24 to 2017-07-11. All cases were used in the study, without excluding cases with anomalous values. The occurrence of a trend was identified by examining the correlation between the selected parameters and time variables. For this purpose, the non-parametric Kendall *tau* coefficient was applied which, as a rank method, is resistant to the occurrence of anomalous observations.

5. Results

The chemical composition of particular types of precipitation is presented in graphic form as Fig. 2.

Table 3 shows the ranges of variability in the recorded concentrations of selected chemical constituents and the measured values of the physical markers of rain, snow and sleet (Table 3). The criteria for selecting the parameters are described in chapter 3.

The results of the analysis of variance (Table S3) indicate that there are significant differences between the mean concentrations or measured values of most of the parameters analysed. This pertains to: SO_4, Cl, Na, Al, Fe and PM10. However, no such differentiation was found for Cu, Rb and WDSP. Using the relationship (2), it was calculated what percentage of the variance of the parameters analysed is related to the type of precipitation (Table 4).

The results of the HSD test are presented in the expected means (LS Means) chart in Fig. 3.

The use of a more conservative test (Scheffe test) leads to similar results.

Fig. 4 presents the own values of the factors (Principal Component Analysis), the cumulative percentage of variance explained by particular factors is reported in parentheses.

The results of the PCA are presented in Table 5.

The variability of the concentrations of selected chemical constituents (SO_4, HCO_3, Cl, Ca, Na, Zn, Cu, Pb and pH) in rain samples occurring in the years 1996–1998 and 2002–2017 is presented in Figs. 5 and 6. The variability of the concentrations of PM10 and SO_2 in shorter observation periods, 2002–2017 and 2002–2012 respectively, is also presented.

The results of trend analysis using the non-parametric Kendall's *tau* coefficient (τ) are presented in Table 6.

6. Discussion

6.1. Chemical composition of precipitation and its range of variation

The Fig. 2 shows general relationships in the chemical composition of particular types of precipitation. Snow and sleet are generally characterised as a population with a lower pH and an increased content of Cl and Na compared to rain. Despite their high variability, the results of the studies are grouped into partially overlapping clusters, which differ in shape. This is particularly true for rain and snow. Therefore, despite the changing conditions shaping the chemical composition of precipitation in the years 1996–2017 (increase in the number of cars, closure of industrial plants, change in household heating technology, etc.), it can be assumed that the factors affecting the chemical composition of particular types of atmospheric precipitation are similar. Furthermore, these factors are similar irrespective of the large time interval between the studies. Taking into account the observations described above and a very large number of test results, it was assumed that the range of $\pm 1\sigma$ from the mean value should, as a good approximation, reflect the typical, most frequent range of variation in concentrations/values of the individual precipitation constituents (see Table 3). 68% of the data population is within the range between the 16th and 84th percentiles and this range is the same as the range of $x \pm 1 \sigma$.

Due to the large number of measurements (particularly for rain and snow) that average and reduce the impact of anomalous values, the information provided may be used as reference ranges for other areas with high air dustiness.

6.2. Analysis of variance

The values ω^2 obtained (Table 4) indicate that only a small part of the variation in the concentrations or measured values of the parameters analysed is related to the type of precipitation. The largest values of the variance related to the type of precipitation are observed for Na and Cl (19% and 18% respectively). A similar value of variance that is explained (16%) is also observed for PM10. Therefore, it can be assumed that in other cases of the study parameters, the variability of their variance is related to other sources that were not analysed. Taking into account the observations discussed above, the multiple comparison test (post-hoc) was conducted only for Na, Cl and PM10. The results of the HSD test (Table S4) show that there are differences in average Na concentrations and PM10 values between rain (R) and snow (S). For Cl, however, there are differences in the means between rain (R) and snow (S) and between rain (R) and sleet (RS) – but here, the differences are close to the limit of statistical insignificance (0.04). The results of the HSD test are presented in the expected means chart in Fig. 3. The resulting dependencies most probably indicate the relationship between Na and Cl and the de-icing of traffic routes in cold periods using brine or a mixture of crystalline inorganic salts (primarily NaCl). As a result of car and tram traffic, aerosols with an increased content of Na and Cl are formed in such periods. This effect can later be seen as the occurrence of snow and/or sleet (or occasionally rainfall, during the thaw period) with an increased content of Na and Cl. This observation is somewhat in contradiction with the results obtained by other researchers (Wróbel et al., 2000), who indicate that the spatial variation of Cl in coarse aerosol (> 1.9 μm) related to traffic is substantially different from the other constituents of this aerosol and the origin of Cl is not related to traffic. However, according to the authors of this paper, this does not exclude the relationship of Cl with road traffic and rather indicates different processes controlling the concentration (or recrystallisation)

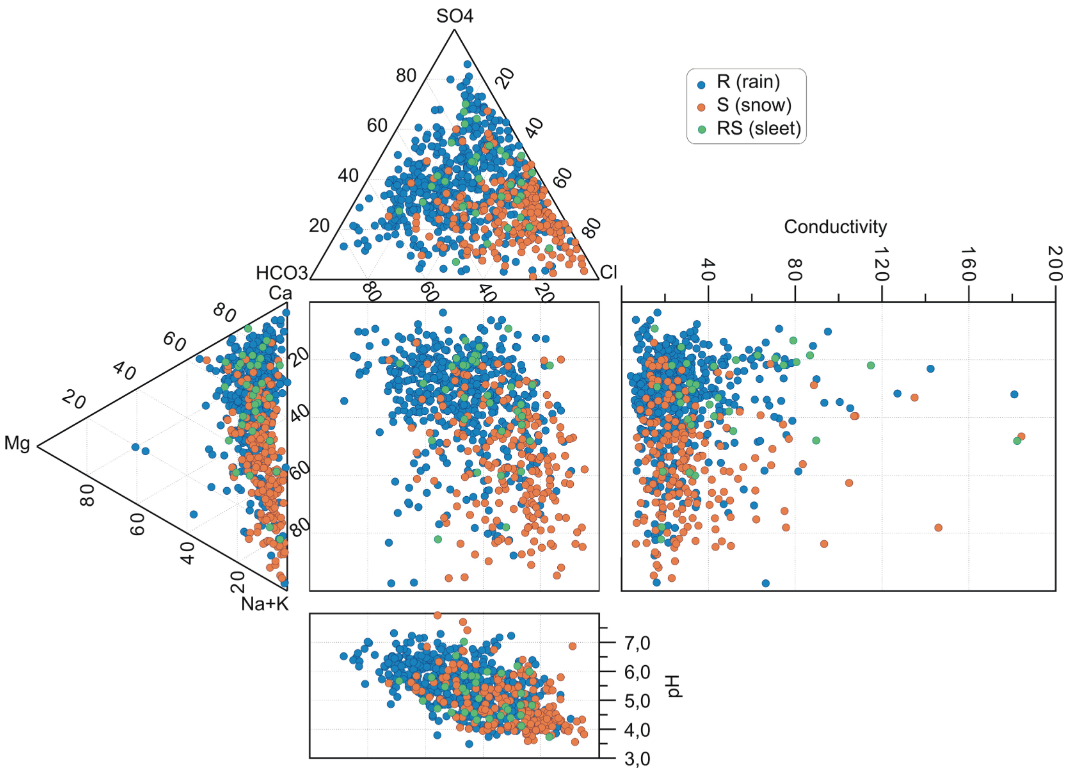

Fig. 2. Primary chemical constituents of the various types of precipitation on a Durov diagram.

Table 3
Variability of concentrations or measured values of selected parameters for particular types of precipitation (Values below LOQ are marked in red).

Var.	R			S			RS		
	n	Percentile 16	Percentile 84	n	Percentile 16	Percentile 84	n	Percentile 16	Percentile 84
pH	590	4.71	6.28	203	4.08	5.83	40	4.39	5.92
EC	590	13.10	42.20	203	15.02	45.70	40	18.30	74.71
Ca	590	0.40	2.69	203	0.36	1.91	40	0.26	5.81
Mg	590	0.06	0.35	203	0.04	0.30	40	0.04	0.67
Na	590	0.10	0.87	203	0.35	2.86	40	0.32	1.57
K	590	0.17	1.14	203	0.15	0.90	40	0.28	1.40
HCO_3	590	0.70	6.80	203	0.50	4.30	40	0.70	9.10
SO_4	589	0.97	5.02	203	0.84	3.99	40	1.25	9.22
Cl	590	0.82	2.64	203	1.58	6.36	40	1.03	6.41
SiO_2	590	0.05	0.45	203	0.08	0.40	40	0.10	0.48
Al	589	3.92E-03	3.96E-02	203	7.86E-03	6.00E-02	40	1.03E-02	8.48E-02
B	585	3.02E-03	6.24E-02	203	4.45E-03	4.65E-02	40	1.00E-03	5.11E-02
Ba	589	1.00E-03	6.26E-03	203	1.05E-03	9.10E-03	40	9.54E-04	8.49E-03
Fe	517	3.19E-03	3.50E-02	177	1.20E-02	7.20E-02	33	1.50E-02	7.80E-02
Mn	590	1.40E-03	1.22E-02	203	1.41E-03	1.35E-02	40	1.53E-03	2.59E-02
Sr	573	1.00E-03	5.84E-03	197	9.91E-04	5.10E-03	39	1.32E-03	9.65E-03
Zn	590	3.49E-03	5.67E-02	203	7.74E-03	9.04E-02	40	1.00E-03	7.40E-02
Cu	498	5.35E-04	3.25E-03	195	4.94E-04	4.25E-03	33	8.69E-04	2.86E-03
Pb	499	8.50E-05	1.98E-03	195	2.71E-04	5.52E-03	33	1.21E-04	3.23E-03
Sb	499	8.20E-05	7.72E-04	195	7.50E-05	5.73E-04	33	5.00E-05	3.75E-04
PO_4	555	1.00E-03	1.53E-01	195	1.58E-02	1.43E-01	33	1.00E-03	8.90E-02
Rb	499	1.50E-04	1.07E-03	195	1.94E-04	1.36E-03	33	2.93E-04	1.17E-03

Table 4
Variance explained by the dependent variable (%).

	SO_4	Cl	Na	Al	Fe	PM10
ω^2	1,30	17,83	19,03	10,10	11,92	16,17

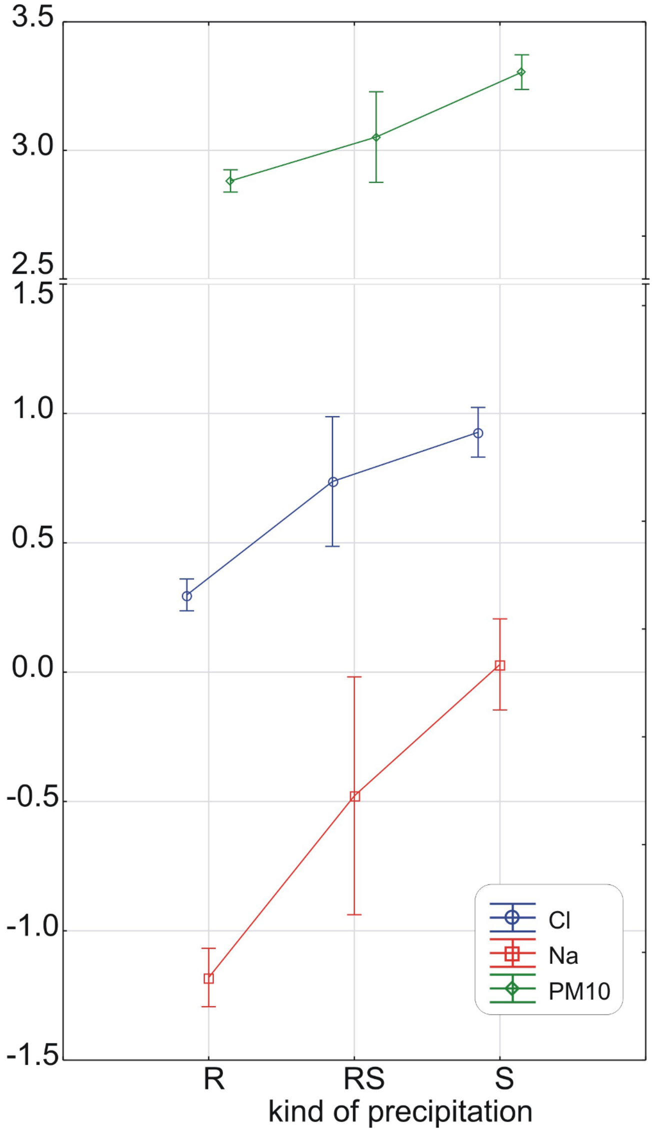

Fig. 3. Plot of LS Means and Conf. Intervals -effective hypothesis decomposition. (The negative values in the graph are the result of the Box-Cox transformation, vertical bars denote 0.95 confidence intervals)

of this element in aerosols. Chlorides in aerosols mainly occur in ionic form and do not undergo sorption or ion exchange processes, while in solid form they occur sporadically, mainly as secondary NaCl crystals (Wilczynska-Michalik et al., 2015). According to Wróbel et al (2000), studies on the chemical composition of aerosols carried out in the centre of Krakow (near one of the main traffic routes in the city) indicate that the share of road traffic in the concentration of coarse particles (> 1.9 µm) is from 20 to 80%, respectively between 1500 and 150 m from the road. The share of road traffic in the concentration of fine particles (< 1.9 µm) of individual elements was 50–70% close to the road (5 m), however, the fine aerosol pollution associated with road traffic affects the entire city.

There is a small, but noticeable, variation in mean concentrations of Al and Fe, which is most probably related to the different concentrations and different chemical composition of PM10 in the warm and cold periods. For SO_4, it can be assumed that the variation in concentrations of these ions dependent on the type of precipitation is negligible and of little significance.

The case of PM10 is different, as PM10 is not measured directly in precipitation samples but is important as an indicator of air pollution by particulate matter on the day of precipitation. The chemical composition of precipitation is largely dependent on the chemical composition and form of PM10 as well as the smaller fractions of particulate matter in the atmosphere. It was found that there were differences in average concentrations of PM10 between the days of rainfall and the days of snowfall. The highest PM10 values occur on the days with snow and/or sleet, i.e. in the cold period. High values of correlation between PM10 and SO_2 are also observed on the days of occurrence of particular types of precipitation (rain, $R = 0.73$ for $n = 336$; snow, $R = 0.73$ for $n = 140$ and sleet, $R = 0.72$ for $n = 18$). This confirms that a significant proportion of the concentration of PM10 is associated with low emissions and the combustion of fossil fuels, often containing sulphides, mainly pyrite and/or marcasite.

6.3. *Principal component analysis*

The results of the Bartlett's test of sphericity (p-values are $\leq 1.0 \cdot 10^{-5}$) for sets R and S indicate that the application of PCA to study the relationships between parameters in these sets is fully justified (Table S5). The sets of parameters that can be analysed with PCA were determined using KMO coefficients (Table S6). These sets include: pH, Ca, Mg, Na, K, HCO_3, SO_4, Cl, SiO_2, Al, Ba, Fe, Mn, Sr, Zn, Cu, Pb, Sb, PO_4, Rb, TEMP, VISIB, WDSP (snow only) and PRCP (rain only) as well as PM10. PCA was carried out for the thus selected parameters. Of the 793 cases used, 378 cases (R) and 157 cases (S), respectively, were processed during the PCA. The optimal number of factors was determined as three for set R and three for set S.

In the sets R and S, the following factors were distinguished: R1, R2 and R3 and S1, S2 and S3 (Table 5). The criterion for grouping parameters in factors was exceeding the value of ± 0.6 by the factor coordinates of these parameters. The grouping of particular parameters in the factors identified is to a large extent the result of processes common to these parameters, shaping their occurrence in the environment. Parameters with lower factor coordinates, i.e. ± 0.5–0.6, show similar dependencies, but their relationship with the factor identified is weaker or occurs only episodically more clearly. The separate factors only explain the variance of the parameters under analysis to a certain extent. For example, the R1 factor explains 28.8% of the variance, while the S1 factor explains 36.2% of the variance in the data sets analysed (Fig. 3). This means that the remaining variance is related to sources and/or processes other than those described below.

6.3.1. *R1 and S1 factors*

Within the R1 and S1 factors, several processes overlap which are common to both rain and snow, affecting the chemical composition of these types of precipitation. The key process is the chemical weathering of mineral particles floating in the atmosphere and dusts of anthropogenic origin. According to Wilczyńska-Michalik and Michalik (2015), the particulate matter in the air of Krakow is mainly composed of quartz, aluminosilicates, as well as carbonates and sulphates, occasionally pure chlorides. According to the authors cited above, Fe oxides, metallic iron and other metal-rich particles are common and carbonaceous particles (soot) are particularly abundant in the cold period. As a result of the chemical weathering of these particles and dusts, atmospheric precipitation is enriched with major (Ca, Mg and HCO_3) and minor (Ba, Sr, Mn and Rb) constituents. Other important processes are the reactions of inorganic anhydrides with water molecules and the formation of aerosols of mineral acids with the input of accompanying photochemical processes. These processes enrich the atmospheric precipitation in SO_4 and partly also in HCO_3. Aerosols of marine origin,

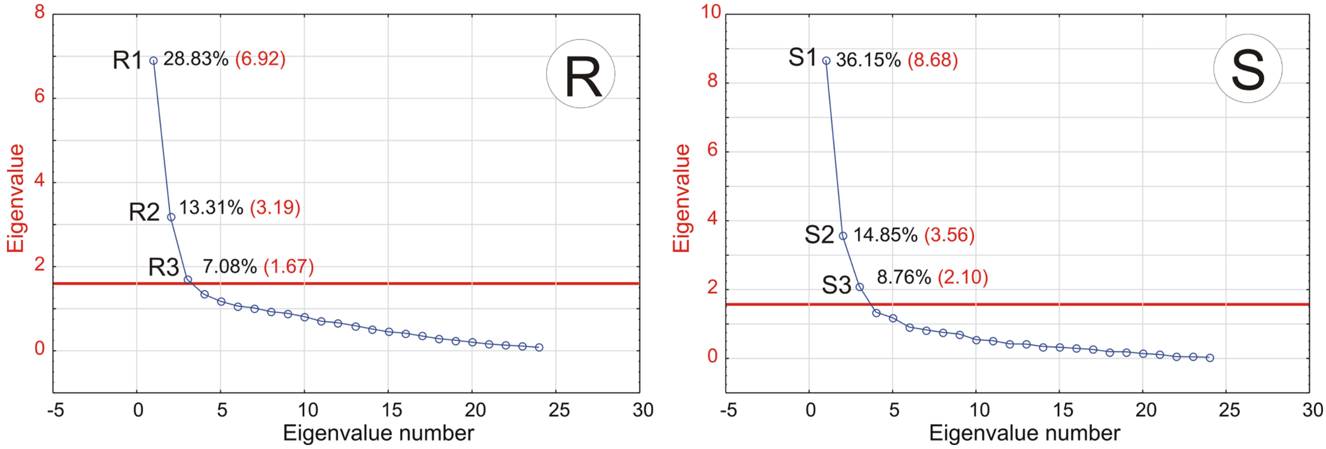

Fig. 4. The scree plot and eigenvalues.

Table 5
Factor coordinates of the variables/parameters. The parameters grouped in individual factors were marked in red.

	R factors			S factors		
	R1	R2	R3	S1	S2	S3
pH	0,14	**-0,67**	-0,16	0,49	**-0,60**	0,11
Ca	**0,75**	-0,47	-0,03	**0,91**	-0,29	0,01
Mg	**0,87**	-0,27	0,12	**0,92**	-0,25	0,04
Na	**0,66**	-0,08	0,37	**0,83**	0,02	-0,07
K	0,26	-0,22	0,06	0,14	-0,21	0,00
HCO_3	**0,62**	**-0,63**	0,07	**0,76**	-0,49	0,06
SO_4	**0,83**	-0,24	0,10	**0,85**	0,02	0,04
Cl	**0,71**	0,06	0,40	**0,87**	0,05	-0,06
SiO_2	0,45	-0,19	-0,13	**0,78**	-0,20	0,10
Al	0,48	0,59	-0,05	0,43	0,57	-0,03
Ba	**0,65**	0,35	-0,07	0,43	0,26	-0,10
Fe	0,46	0,56	-0,01	0,37	**0,75**	-0,16
Mn	**0,66**	0,24	0,02	**0,82**	0,19	-0,01
Sr	**0,79**	-0,26	-0,20	**0,94**	-0,15	-0,02
Zn	0,13	0,18	-0,24	0,31	**0,66**	-0,29
Cu	0,41	0,34	**-0,63**	0,40	**0,66**	-0,16
Pb	0,38	0,43	**-0,61**	0,17	**0,68**	-0,32
Sb	0,07	0,11	-0,03	0,45	0,04	0,17
PO_4	0,30	-0,22	-0,24	0,21	0,07	-0,04
Rb	0,51	-0,10	-0,29	**0,77**	-0,08	-0,09
TEMP	-0,28	-0,54	-0,44	-0,35	-0,08	-0,34
VISIB	-0,32	-0,44	-0,35	0,12	-0,30	**-0,76**
WDSP	-	-	-	-0,12	-0,40	**-0,68**
PRCP	-0,25	0,04	-0,03	-	-	-
PM10	**0,67**	0,30	0,07	0,12	0,35	**0,78**

which provide a significant load of Cl and Na, and the use of road salt for de-icing traffic routes in the cold period are also a significant factor in the shaping of the chemical composition of precipitation. Road salt may contain small amounts of carnallite ($KCl{\cdot}MgCl_2{\cdot}6H_2O$), which is a mineral with a relatively high Rb content. It is also worth noting that the effect of the volume of precipitation (PRCP) on the chemical composition of rainwater is hardly noticeable. However, this may in part be the result of the distance between the rainfall sampling points and the rainfall volume measurement points (see more Section 2). PM10 is important for the R1 factor, as it reflects the concentration of particles being an important source of the chemical constituents occurring in precipitation. SiO_2 is more important in the S1 factor, which probably indicates the effect associated with another form of SiO_2 and/or Si occurrence, which in cold periods may be more closely related to the emission of ashes and furnace slag than to particles of quartz and aluminosilicates. In statistical terms, a clear proportional relationship between PM10 and the main chemical constituents exists only for rain. The effect of PM10 on the concentration of these constituents in snowfall periods is practically unnoticeable, despite higher concentrations of PM10 and generally lower pH in these periods, which may increase the effectiveness of chemical weathering. These observations indirectly indicate a different chemical composition of PM10 in the cold period. This is confirmed by the results of other authors (Wilczyńska-Michalik and Michalik, 2015), who report that in Krakow the aerosol (suspended dust) composition shows significant seasonal variation.

6.3.2. *R2 and S2 factors*

The R2 factor shows a directly proportional relationship between pH and HCO_3, which indicates the influence of the effectiveness of chemical weathering of mineral particles on HCO_3 concentrations and the pH of rainwater. In the case of snow (factor S2), i.e. in cold periods, the relationship is much weaker. This is due to the occurrence of snow cover and/or frozen soil during these periods. In such conditions, it is much more difficult to deflate mineral particles containing numerous carbonates and aluminosilicates from the soil (the bedrock of Krakow and its surroundings is largely composed of limestones and marls, so carbonate particles are common in soils and found in significant concentrations). This is confirmed by the fact that the proportional relationship between pH and HCO_3 in relation to temperature is not very strong, however noticeable, and it does not occur in the case of snow. The most likely explanation is that the more pronounced temperature effect is more pronounced only episodically, in anomalous air temperatures. In this case, a greater influence of temperature on the solubility of mineral substances can also be observed. In a similar way, there may be a tendency to increase Al and Fe concentrations as the pH of precipitation decreases. In the case of the S2 factor, an inversely proportional relationship occurs between pH and most of the precipitation constituents (Fe, Zn, Cu, Pb, as well as secondary Al), indicating an increase in concentrations of these elements with decreasing pH of precipitation. The pH values of the cold precipitation are the lowest, which allows more effective chemical weathering of the particles suspended in air and increases the concentrations of these elements. The highest value of factor coordinates for Fe may be the result of chemical weathering of particles that are the products of the combustion of fossil fuels with high pyrite and/or marcasite content. These particles are rich in iron compounds and are more abundant in the atmosphere in the cold compared to the warm period. In both the R2 and S2 factors, the factor values of PM10 are not high, which

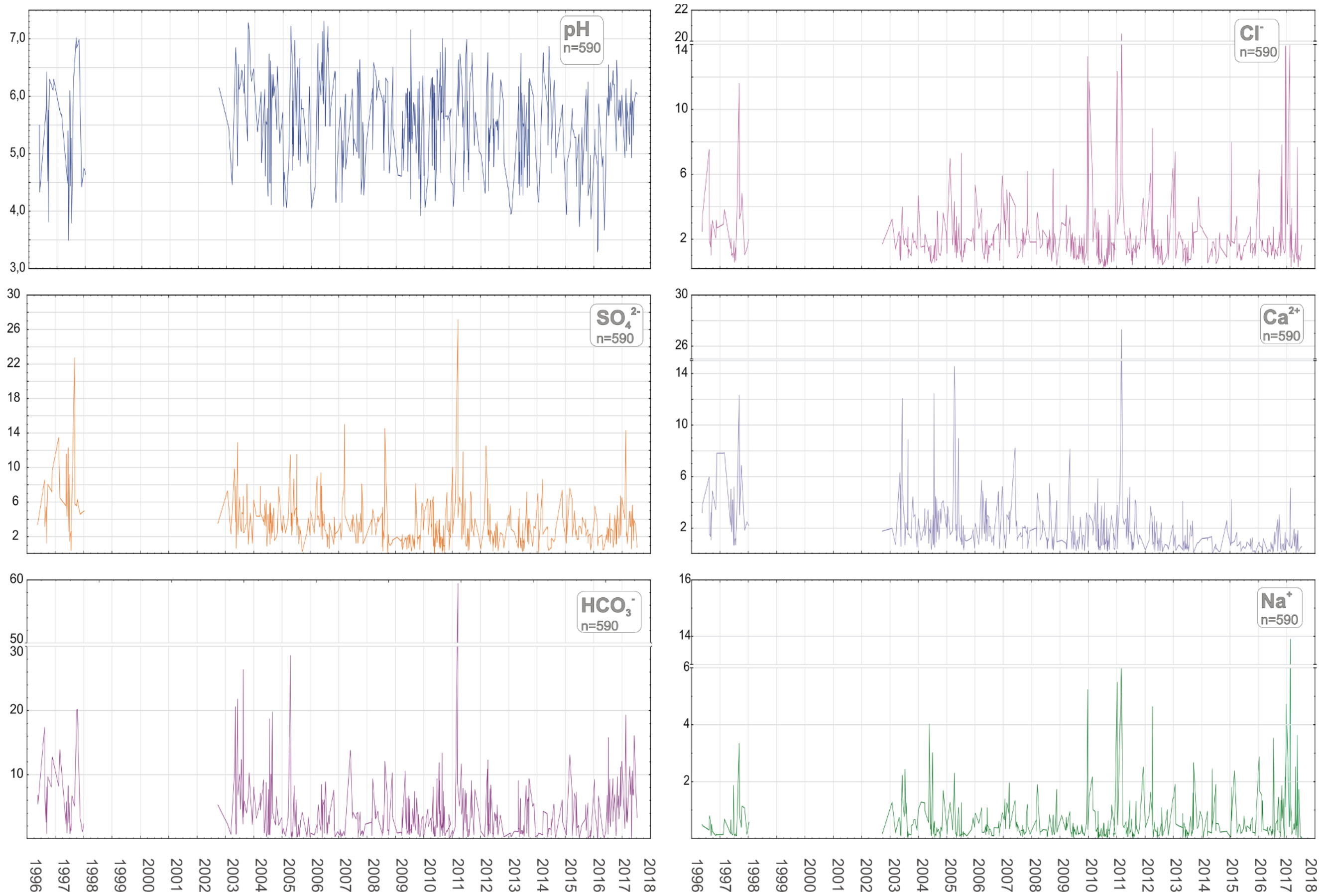

Fig. 5. Time variability of the concentrations of the primary chemical constituents.

indicates the lack of a significant influence of PM10 on the variability of parameters grouped in these factors. In Krakow, spatial variability of the average metal content in PM10 (Zn, Ca and K, Mn and Fe) is observed depending on the distance from the ArcelorMittal steelworks (Samek, 2012), which in the context of variable wind direction and strength may further complicate the pattern of the observed dependencies.

The pH value of both factors is not significantly dependent on SO_4. The correlation between SO_4 concentration and SO_2 content in the atmosphere is also very low ($R = 0.12$, $p = 0.006$, $n = 530$). This information supplements previous observations on the relationship between pH and other precipitation constituents and collectively indicates the buffering of the pH of precipitation. This buffering is a result of numerous precipitation-alkalising substances (mainly carbonates and aluminosilicates) in the atmosphere. A similar situation has already been observed in Krakow. In 1970–80s, apart from the high concentration of particulate matter, very high concentrations of SO_2 in the atmospheric air were recorded. At the same time, there were significant emissions of rainfall-alkalising constituents from numerous industrial and power plants (cement plant in Pleszew, Solvay sodium plant, ArcelorMittal steelworks (formerly the Lenin steelworks), CHP plant in Łęg, etc.). Therefore, typical acid rains with pH < 5.1 appeared sporadically in Krakow in the 1970s and 1980s. For example, between 1987 and 1989, the pH of precipitation ranged from 4.81 to 7.42, while precipitation had high EC values of 100 or more $\mu S \cdot m^{-1}$ (Turzański, 1995). The pH of precipitation is also affected by other factors that were not analysed in our paper. These are mainly nitrogen compounds: NO_x and NH_3. The concentrations of NO_3 or NH_4 in precipitation are similar to the concentrations of the main chemical constituents (Table 1). In Krakow, between 2009 and 2013, increased concentrations of nitrogen compounds were observed in the cold period (especially NH_4, usually $\sim$0.5–0.8 $mg \cdot dm^{-3}$ depending on the measurement point), particularly in regions with intensive low level emissions from heating systems (Żurek et al., 2013). NO_x and NH_3 have a different effect on pH, as they can acidify or alkalise precipitation respectively. Therefore, it is difficult to estimate the effect of nitrogen compounds on the pH of different types of precipitation.

6.3.3. R3 and S3 factors

The R3 factor indicates a direct proportional correlation between Cu and Pb and reflects the common source of these metals and/or the process shaping their occurrence in rainwater that is difficult to identify. Temperature may also have some influence on the variability of Cu and Pb concentrations (Table 5). However, this effect is most probably episodic in anomalous air temperatures. The S3 factor show the clear influence of an increased PM10 concentration on the reduction of transparency of the atmosphere and the influence of increased wind speed on the reduction of PM10 concentration. This reflects the well-known physical phenomenon of removing atmospheric pollution by wind. However, the PM10 concentration in the atmosphere is not only related to wind speed, and the S3 factor explains only a small percentage (8.8%) of the overall variability of these parameters. It is also important that all these parameters can be characterised by high variability on an hourly scale, their values used for PCA were averaged over 24 h.

6.4. Time variability

The variability of the concentrations of selected chemical constituents (SO_4, HCO_3, Cl, Ca, Na, Zn, Cu, Pb and pH) in rain samples occurring in the years 1996–1998 and 2002–2017 is showed in Figs. 5 and 6. The results of trend analysis using the non-parametric Kendall's

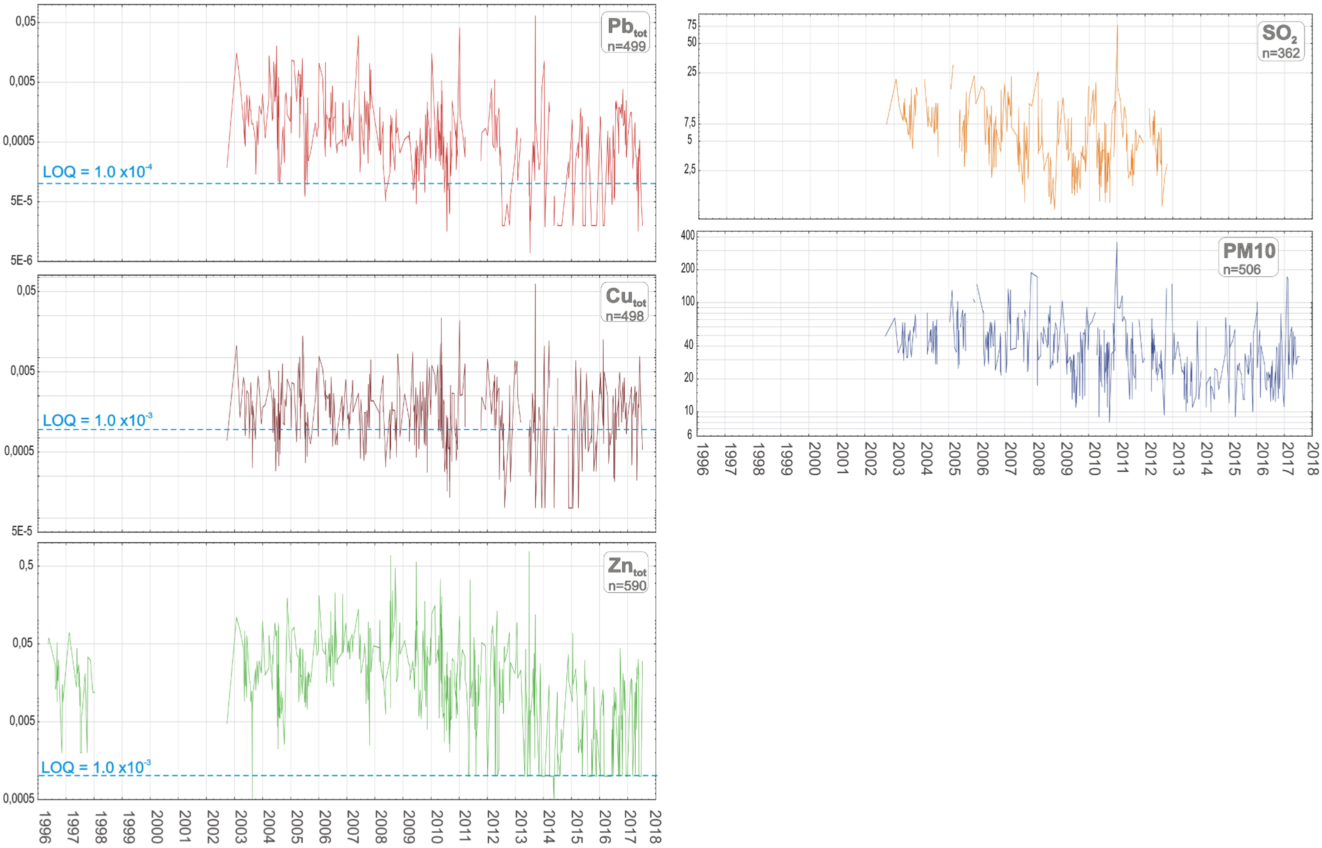

Fig. 6. Time variability of concentrations of trace chemical constituents as well as PM10 and SO_2.

Table 6

The Kendall Tau correlations for selected parameters. * – statistically insignificant result.

	pH	Ca	Na	HCO_3	SO_4	Cl	Zn	Cu	Pb	PM10	SO_2
Kendall Tau Correlations	−0.084	−0.351	0.018*	−0.064	−0.190	−0.087	−0.286	−0.105	−0.279	−0.281	−0.281

tau coefficient (τ) are presented in Table 6. All statistically significant values of τ are negative, which reflects the occurrence of decreasing trends with a probability of 95%. Values of τ are not high, which indicates that there are noticeable but in some cases very weak trends. The strongest trend is for Ca, which may indicate a general decrease in the content of mineral particles (mainly carbonates and aluminosilicates) and/or anthropogenic dusts in the atmosphere of Krakow. These observations are confirmed by a similar, although slightly weaker, correlation for PM10 indicating a trend of decreasing air dustiness on days of precipitation episodes. The analysis of long-term variability of PM10 concentration (regardless of precipitation episodes) also indicates a decrease in the PM10 concentration in Krakow. Similar observations apply to Zn and Pb as well as SO_2. In the case of Pb, the downward trend in concentrations of this element may indicate a connection with the total withdrawal of leaded petrol (which had added lead tetraethyl $(C_2H_5)_4Pb$) from sale in Poland from 2005 onwards. The decrease in SO_2 concentrations, observed independently of the occurrence of precipitation events, is also indicated by other authors (Wilczyńska-Michalik and Michalik, 2017).

A certain regularity of distribution in time is visible for all the parameters analysed. In order to examine this regularity, a factorial ANOVA analysis was performed. Parameters with normal distributions and homogeneous variance were selected for the study. These include: SO_4, Cl, Ca and Na. The first set of independent variables are time criteria: cold and warm periods. The second set of independent variables are two temperature ranges corresponding to the average daily temperature on the day of precipitation: > 10 °C and < 10 °C respectively. In general, the time and temperature ranges adopted reflect periods during which the use of fossil fuels for heating purposes may decrease or increase significantly. The results of the analysis of variance indicate that despite statistically significant results (Table S7), only a negligible part of the variation in concentrations of chemical constituents under analysis is related to the variability of the weather season and/or temperature in the ranges examined. For all the chemical constituents analysed, the parameter ω^2 changes in the range of 0.6–1.4%. Selecting other independent variables, for example other temperature limits (± 0 °C, ± 5 °C, etc.) leads to similar results. There were no interactions found between the independent variables.

7. Conclusions

The research completed permitted a better understanding of the processes shaping the chemical composition of different types of precipitation in one of the most polluted cities in Europe. It was found that the concentrations of chemical constituents differed depending on the type of precipitation. This conclusion applies mainly to rain and snow, and is observed primarily for Na and Cl, but is only to a small extent associated with the total variability in concentrations of these chemical constituents. For the remaining chemical constituents analysed, i.e. Al, Fe and SO_4, the variation of concentrations depending on the type of precipitation is even less significant or negligible. The observed variation can be largely attributed to anthropogenic factors such as the use of road salt or brine for de-icing the traffic routes. The main processes affecting the chemical composition of rain and snow are the chemical weathering of suspended dust and the formation of mineral acid aerosols. These processes shape the chemistry of both rain and snow in a similar manner, however, one can observe a different effect of PM10 on the chemical composition of these types of precipitation. Indirectly, this indicates differences in the chemical composition of particulate matter in the atmosphere between the warm period, and the cold period when solid fuels are used for heating on a large scale. The different relationship between pH and the chemical constituents of rain and snow is also derived from the differences in the chemical composition of PM10. It was found that the effectiveness of chemical weathering of particles and dusts suspended in the air, which may buffer the pH of precipitation, has a significant influence on the pH of rain and snow. In other words, high concentrations of dusts in the air of Krakow may, paradoxically, to some extent prevent a decrease in the pH of atmospheric precipitation, especially in the cold period. However, it should be noted that this interpretation does not take into account the effect of gaseous nitrogen compounds on the pH of precipitation, which undoubtedly occurs. Therefore, the description of the factors shaping the variation in the pH of precipitation, although we consider it to be reliable, cannot be treated as complete. The interpretation presented above concerns only a part (about one third or less) of the analysed data set. This interpretation is characterized by high credibility, and refers to processes whose occurrence was determined with a probability of 95% (confidence level of statistical methods used). It is also possible that the same or very similar interpretation is also true for the rest of the analysed data set, however, with a lower probability that is difficult to determine. In addition, it cannot be excluded that the remaining part of the variability of the parameters under analysis may be theoretically related to sources and/or processes different from those presented in our paper. This state of affairs is a result of many factors. One of them is the need to significantly simplify the description of different meteorological conditions. Very large errors, typical for the physical/chemical analyses of precipitation, are also an important factor. It is likely that even a significant increase in the number of cases analysed and/or an extension of the study period will not lead to significantly better results in the studies of the chemical composition of precipitation.

The temporal variability of the study parameters is largely oscillatory (seasonal), however, general directions of variability of these parameters over time can be noticed. In the years 1996–2017, we observed a slight, but noticeable and basically constant decrease in the concentrations of most of the chemical constituents of precipitation as well as in the concentrations of PM10 and SO_2 in the air. To a large extent, this indicates a connection with the closure of industrial plants in or near Krakow and a reduction in emissions of exhaust fumes and industrial dust. A gradual change in the method of heating (mainly using natural gas or fuel oil) and/or the use of better quality coal, which is the result of the economic and social development of the city, may also be important. A very weak but noticeable trend towards a decrease in the pH of rainwater can generally be attributed to a decrease in the amount of particulate matter buffering the pH of rainwater. Most probably, this effect may still be observable for some time, although given the reduced emission of SO_2 from industrial sources and the anti-smog activities carried out in Krakow (a total ban on solid fuels for heating, mainly coal and wood, from 2019), typical acid rains with a pH significantly lower than currently observed should not be expected. Since other factors (gaseous nitrogen compounds) affect the pH of precipitation, a comprehensive description of these relationships seems to pose an important task for the immediate future, particularly in view of the significant development of road traffic and the increase in the number of cars, which are significant, new sources of gaseous nitrogen compounds.

CRediT authorship contribution statement

Tomasz Kotowski: Conceptualization, Formal analysis, Investigation, Methodology, Software, Supervision, Validation, Visualization, Writing - original draft, Writing - review & editing. **Jacek Motyka:** Conceptualization, Data curation, Investigation, Methodology, Project administration, Resources, Writing - original draft. **Wiesław Knap:** Data curation, Investigation, Methodology, Resources, Validation. **Jarosław Bielewski:** Data curation, Investigation, Resources, Software, Writing - original draft.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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