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Assessing the neutralisation, wet deposition and source contributions of the precipitation chemistry over Europe during 2000–2017

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Abstract

Background: The chemical composition of precipitation was assessed in 27 European countries from 2000 to 2017, offering a general point of view on the rainwater chemistry in Europe, contributing to a larger understanding of air pollution and atmospheric chemistry.

Results: The volume-weighted mean concentrations (VWM) were calculated, showing the relative dominance of SO_4^{2-} and Cl^-, explaining the acidic and slightly acidic pH values that ranged from 4.19 to 5.82 over Europe. The VWM concentrations of ionic species measured in rainwater usually followed the $SO_4^{2-} > Cl^- > Na^+ > NH_4^+ > NO_3^- > H^+ > Ca^{2+} > Mg^{2+} > K^+ > HCO_3^-$ downward order, with small exceptions, depending on the industrial activity or legal framework of a particular area. Fractional acidity showed that ∼69% of the inorganic acidity in precipitation is neutralised, whilst neutralisation factors showed that Na^+ and NH_4^+ contributed the most to the neutralising process. The relationship between acidic and neutralising compounds was further examined by calculating the ionic ratios. Wet deposition rates showed the dominance of acidic compounds over neutralising ones, reflecting the climatic influences and the local and regional economic characteristics of different regions from Europe. Origins of major ions in rainwater were examined using the sea salt and non-sea salt fractions, crustal and marine enrichment factors, correlation analysis and the Principal Component Analysis, showing the significant influence of anthropogenic sources (industry, agriculture, traffic). Natural sources (maritime, terrestrial) also play a major role in influencing the precipitation chemistry of the European continent.

Conclusions: The main conclusion of this study regarding the precipitation chemistry of the European continent during the studied period is represented by the relative homogenous distribution of the analysed chemical species, which is most likely due to the unitary economic development and to the implementation of common European policies in the field of environmental protection. Since the pH is still acidic due to the anthropogenic emissions, more attention should be given to the implementation of environmental legislation, especially in non-European Union countries or in countries that joined recently.

Keywords: Rainwater, Chemical composition, Acid rain, Neutralisation, Wet deposition, Source contribution

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Background

The assessment of precipitation chemistry provides important insights on the chemical composition of the atmosphere, taking under account numerous influencing factors, such as the type and distribution of aerosol sources, chemical species, long-range transport of air pollutants and the origin of air masses. Rainwater chemistry was intensely studied worldwide over the past 30 years [1–10], since by determining the chemical composition of precipitation the contributing sources can be identified, understanding the local and regional dispersion of pollutants and their potential effect on the environment through scavenging and deposition processes [11].

The present study assesses the European precipitation chemistry of the last 18 years, during 2000–2017, contributing to better understand some environmental issues, related to air pollution and the chemical composition of the atmosphere. As presented in the study of Vet et al. [8], since 1995 three main studies were published that assessed the global precipitation chemistry, mainly focusing on the wet and dry deposition. In 1996, the World Meteorological Organization released a report [12] that provided a global assessment on the acidic deposition, that was summarised into a publication a year later [13], showing that regions with highest precipitation concentrations and deposition fluxes of sulphate and nitrate coincide with the regions where the highest density of SO_2 and NO_x precursor emissions can be observed. In 2006, Dentener et al. assessed the deposition of nitrogen and sulphur on a regional and global scale, combining measurements with the ensemble mean modelling results of 21 Eulerian (fixed grid) global models used to simulate chemical fate and transport in the atmosphere [14]. The third study [8] is a global assessment of precipitation chemistry and deposition, that has been carried out under the direction of the World Meteorological Organization (WMO) Global Atmosphere Watch (GAW) Scientific Advisory Group for Precipitation Chemistry (SAG-PC), with the objective to characterise the chemical composition of precipitation and deposition (wet, dry, total) for sulphur, nitrogen, acidity, sea salt, mineral base cations, organic acids and phosphorus on global and regional scales, over 2 time-periods: 2000–2002 and 2005–2007 [8]. Regarding acidifying compounds, over the European continent, there have been significant reductions (of the order of 70–90%) in ambient concentrations and deposition of sulphur during the last three decades [8]. Due to the considerable reductions in SO_x emissions, NO_x have become the principal acidifying compounds [15]. As a consequence of declining sulphur emissions in Europe, acidification is slowly declining and some forests and lakes are showing signs

of recovery [15, 16]. According to the European Monitoring and Evaluation Programme (EMEP) in 2017, hotspots of exceedances regarding acidification occurred in the Netherlands and its areas that border Germany and Belgium, as well as in southern Germany. All over the European continent, acidity exceedances occur in about 5.3% of the ecosystem area [17]. It is projected that in 2020 only 4% of the European ecosystem area will exceed the acidification critical loads if current legislation is fully implemented [15].

The objective of the present study is to distinguish the characteristics of the chemical composition of precipitation, including major ions, the variation of pH, sea salts, the neutralising capacity, enrichment factors, wet depositions and source contributions in 27 countries from Europe between 2000 and 2017, including: Austria, Belarus, Croatia, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Netherlands, Norway, Poland, Portugal, Serbia, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and the United Kingdom. The above-mentioned countries were separated into regions as follows: East Central Europe (Belarus, Czech Republic, Hungary, Poland, Slovakia); Northern Europe (Denmark, Estonia, Finland, Iceland, Ireland, Latvia, Norway, Sweden, United Kingdom); Southern Europe (Croatia, Greece, Italy, Portugal, Serbia, Slovenia, Spain, Turkey); and Western Europe including Austria, France, Germany, Netherlands and Switzerland. The study not only reflects on the homogeneity and the differences that can be found between countries and regions, due to different environmental policies, but also takes under consideration the overall characteristics of precipitation chemistry over the European continent. This assessment offers a general point of view of the rainwater chemistry in Europe, and as far as the authors know, such a long-term study summarising the characteristics of chemical composition of rainwater in Europe has not been done yet.

Data and methods

The precipitation chemistry data used in the present study rely on national and regional monitoring methods and networks [8], and were downloaded from the GAW World Data Centre for Precipitation Chemistry, that is publicly available at http://wdcpc.org. The annual data of precipitation amount used in this study were extracted from E-OBS raster dataset (version 19.0). Data have been aggregated on an annual basis, and then extracted using the mean value for each country's polygons. E-OBS data are freely available at http://www.ecad.eu [18].

Regarding major ions, from the downloaded database the following cations and anions were used in further calculations: Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+, Cl^-, SO_4^{2-},

NO_3^-, whilst HCO_3^- and H^+ concentrations were determined based on the empirical relationship between pH, HCO_3^- and H^+, respectively, using the following equations [19–21]:

$$[HCO_3^-] = 10^{-11.24+pH}(eq/l), \tag{1}$$

$$[H^+] = 10^{-pH}(eq/l). \tag{2}$$

For all 27 countries during 2000 and 2017, a total number of 4409 data were processed, having in average from 3 to 48 measurements/year/country in the downloaded database. For each country the mean value was calculated, resulting in one value/year/country and 450 data in total. To ensure the quality and reliability of the data used in the study, collected data were screened and analysed for the entire 18-year period, calculating the ionic balance, which was used as an indicator of the completeness of the measured major constituents [22]. The dataset is considered acceptable if the equivalent ratio of the sum of the anions to the sum of the cations (Σ anions/Σ cations) is within the range of $1 \pm 25\%$ [10, 23].

Assuming that the observed cation/anion deficiency found in the measured samples is due to the presence of H^+ and HCO_3^-, respectively, the ionic balance was recalculated (taking under consideration the concentrations of H^+ and HCO_3^-) showing values that ranged between 0.90 in Estonia and 1.22 in Hungary, with an average of 0.98. Additional ionic imbalances may be due to unmeasured organic acids in rainwater [22], such as $HCOO^-$, CH_3COO^-, $C_2O_4^{2-}$, F^- and PO, which were not been measured and data regarding any organic acids were not available. After rejecting the data that have not met the quality criteria, linear regression analysis was performed

between the grand total anions' concentration and the grand total cations' concentration for Europe and each region, respectively. Strong correlations were obtained between the sum of anions and the sum of cations in each case, the R^2 value being 0.68, 0.75, 0.80, 0.53 and 0.67 for Europe (EU), Central East Europe (CE-EU), Northern Europe (N-EU), Southern Europe (S-EU) and Western Europe (W-EU), respectively (Fig. 1).

Results and discussion
Chemical composition of rainwater
To assess the ionic composition of precipitation, the volume-weighted mean (VWM) along with statistical analysis including standard deviation, standard error, mean, minimum and maximum was performed in case of all 27 countries from Europe. Figure 2 shows the spatial variability of the chemical composition of rainwater around Europe for the 2000–2017 period. The volume-weighted means of major ions at each country are represented by a coloured bar chart, on a linear scale. The VWM concentrations of the ionic species measured in rainwater usually followed the $SO_4^{2-} > Cl^- > Na^+ > NH_4^+ > NO_3^- > H^+ > Ca^{2+} > Mg^{2+} > K^+ > HCO_3^-$ downward order, with small exceptions, depending on the industrial activity or legal framework of a particular area. Amongst the analysed cations and anions, SO_4^{2-} presented the highest VWM concentration in all 27 countries, ranging between 40.60 µeq L^{-1} in Spain and 48.38 µeq L^{-1} in Latvia, being followed by Cl^- and Na^+. The average SO_4^{2-} concentration for Europe represented 21.48% and 43.51% of the total ions and anions measured, respectively. In average, amongst the total measured ions Cl^- accounted for 16.24%, whereas amongst anions represented 32.89%.
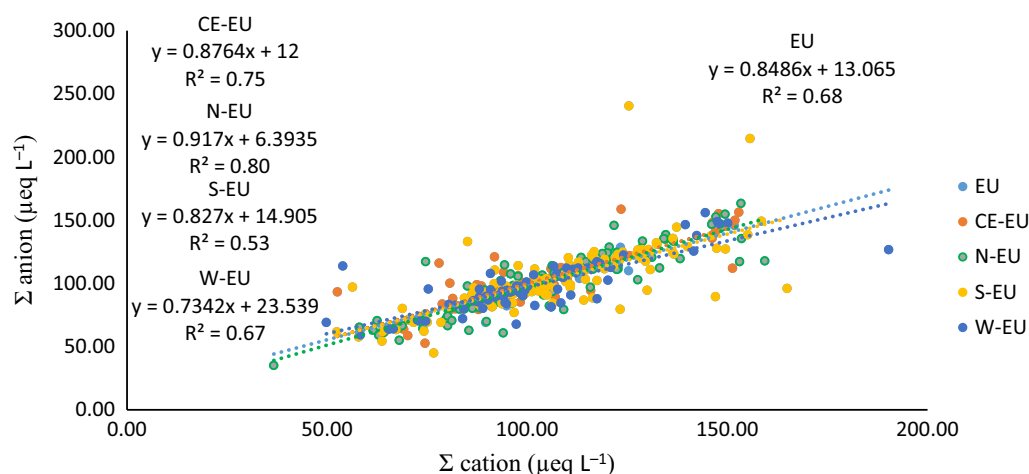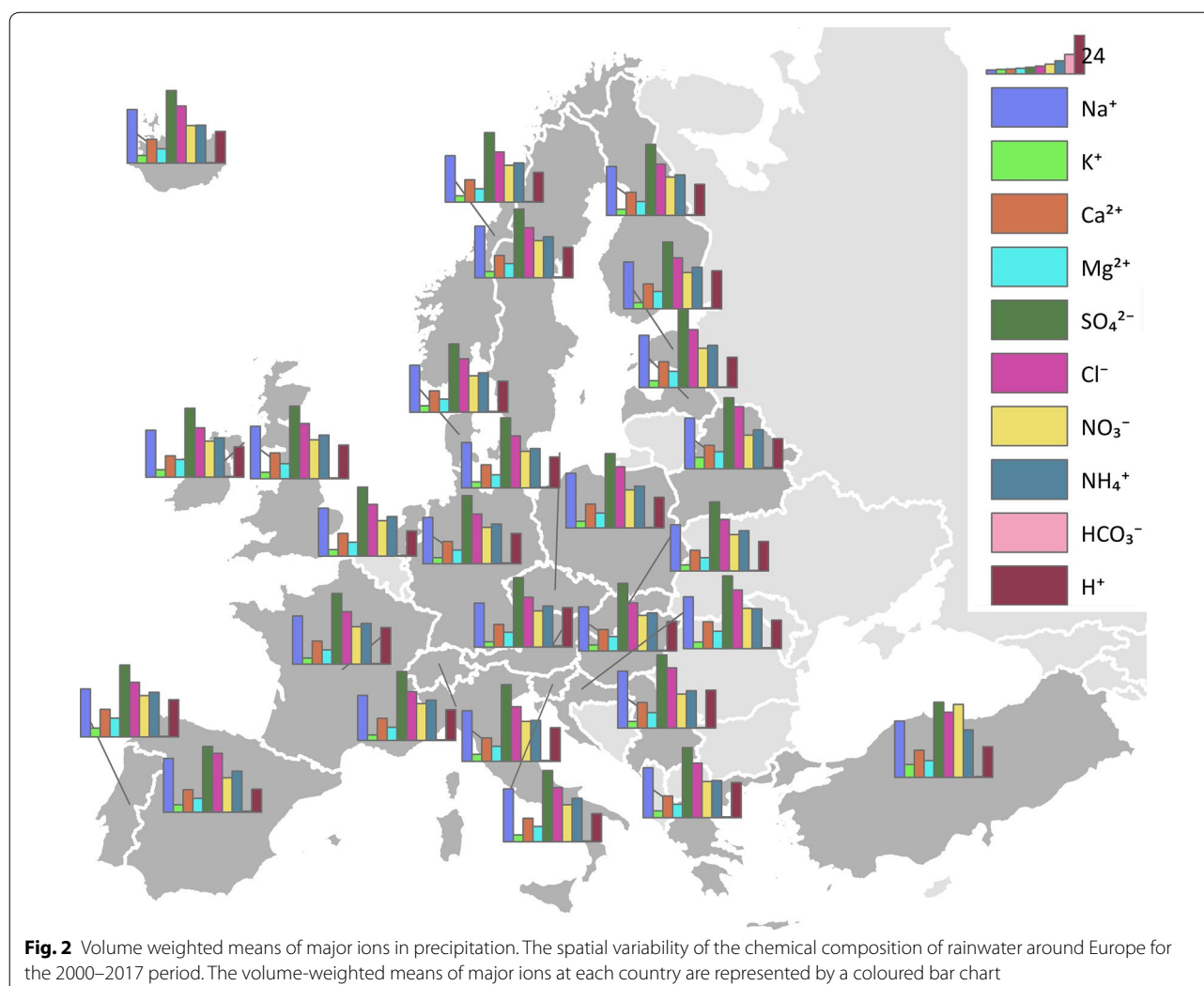

Fig. 1 Relationship between the sum of cations and anions (µeq L^{-1}). Linear regression analysis between the sum of anions and cations for Europe (EU), Central East Europe (CE-EU), Northern Europe (N-EU), Southern Europe (S-EU) and Western Europe (W-EU), respectively

Fig. 2 Volume weighted means of major ions in precipitation. The spatial variability of the chemical composition of rainwater around Europe for the 2000–2017 period. The volume-weighted means of major ions at each country are represented by a coloured bar chart

Na^+ appeared to be the most abundant cation, contributing with 14.95% and 29.54% to the total mass of ions and cations, respectively. In all cases, Na^+ was followed by NH_4^+.

The lack of significant differences between VWM concentrations amongst the studied European countries shows the homogeneity of the analysed data, indicating that the use of common environmental policies and industrial emission regulations resulted in low variability regarding pollutant concentrations at a regional level; additional dissimilarities only occurring at a local level, fact that can be observed in the ionic composition of precipitation.

Variation of pH

The pH values of precipitation in Europe ranged from 4.19 to 5.82, with an average value of 4.80. The occurrence of such low pH values can be explained by the high concentrations of acidic species derived from SO_4^{2-}, Cl^- and NO_3^-, and the lower concentrations of neutralising cations such as Ca^{2+}, Mg^{2+} and NH_4^+. According to the specialty literature, water in equilibrium with an unpolluted atmosphere containing CO_2, NO_x and SO_2 is slightly acidic with a pH value around 5.6 [22, 24, 25]. Therefore, precipitation with a pH below this value is usually considered acidic, showing the influence of heavy anthropogenic emissions of SO_2 and NO_2, originating mainly from industrial activities, coal burning and the cold start of vehicles [24]. The average percentage distribution of pH values in case of the studied countries indicates a higher level of acidity, about 94.44% of the samples having pH values lower than 5; 5.11% between 5 and 5.6; whilst only 0.44% of the data fall in the range between 5.6 and 6 (Fig. 3). At regional scale, some differences can be observed regarding the variation of pH.
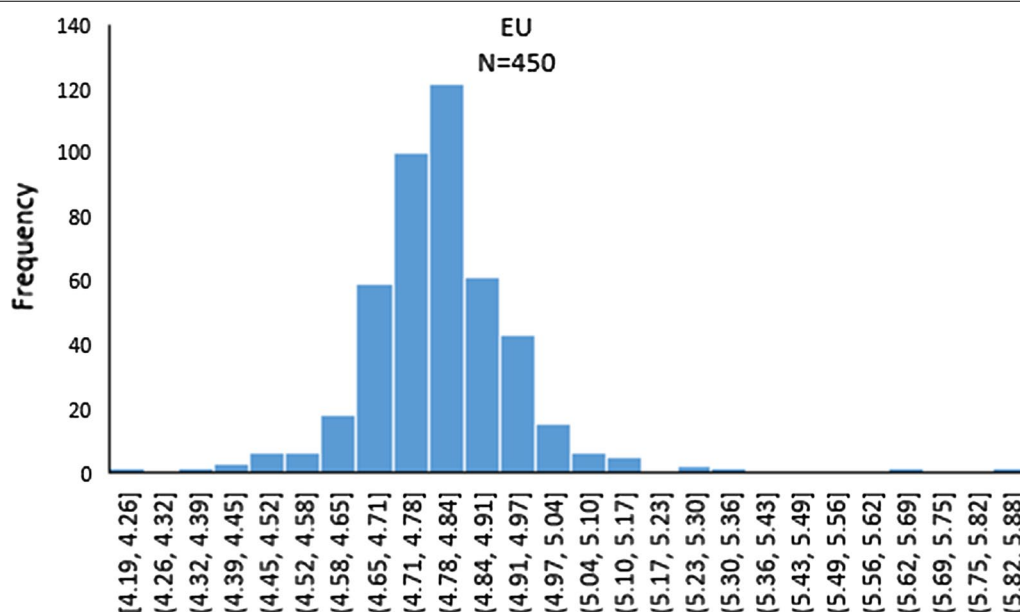
Fig. 3 Frequency distribution of pH for all the studied countries during 2000–2017. The frequency distribution of pH values in case of the studied countries indicates a higher level of acidity, about 94.44% of the samples having pH values lower than 5, 5.11% between 5 and 5.6, whilst only 0.44% of the data fall in the range between 5.6 and 6

In Central East Europe, both the minimum and maximum pH values were recorded at Belarus, being 4.56 and 5.33, respectively, whilst the frequency distribution showed that 93.26% of the values are below 5, and 6.74% between 5 and 5.6. In case of Northern Europe, the precipitation is more acidic, with 96.67% of the pH values being lower than 5 and only 3.33% ranging between 5 and 5.6. The minimum and maximum values were 4.47 and 5.15 recorded in Estonia and in the United Kingdom, respectively.

The southern region of Europe presented a little less acidic pH values, that ranged from 4.39 (Serbia) to 5.17 (Spain), having a normal distribution, with the 91.80% of the values < 5 and 8.20% of the values integrating in the 5–5.6 interval. In the western region, the 95.51% of the rainwater pH values had a frequency of 95.51%, whilst the remaining percentage was equally distributed between the 5–5.6 and 5.6–6 intervals, exhibiting 2.25%.

The frequency distribution of predominantly acidic pH in all the studied countries suggest the significant influence of anthropogenic sources and activities, which correlates with the VWM concentrations of major ions, since such low pH values explain the higher concentrations of acidic ions in comparison with alkaline ones.

Neutralising capacity and alkalisation of rainwater
Previous studies have shown that the acidity of rainwater is usually controlled by the presence of H_2SO_4, HNO_3 and organic acids, whilst the neutralisation of these acidic species occurs mainly in the presence of NH_3 and $CaCO_3$ [10, 22]. Harrison and Pio [26] reported that the abundance of SO_4^{2-} and NO_3^- is relatively constant with altitude, whilst NH_3 and NH_4^+ ions decrease in concentration rapidly with height. According to the above, at cloud level acidic species such as H_2SO_4, HNO_3 and NH_4HSO_4 are more likely to be in majority over neutralised species like $(NH_4)_2SO_4$ and NH_4NO_3 [27]. Hence, at cloud level, the neutralisation process occurs due to the reaction of $Ca(OH)_2$ and $Mg(OH)_2$ with H_2SO_4 and HNO_3 in the cloud condensation nuclei, whilst below cloud level, neutralisation occurs due to ammonia and the adsorption of SO_2 to suspended particulate matter containing Ca^{2+} and Mg^{2+} [27]. The concentration of the H^+ ion reflects the acidity of raindrops after the neutralisation process by Ca^{2+} and NH_4^+ [28]. According to Kaya and Tuncel [29], if the acidity in rainwater is caused by H_2SO_4 and HNO_3 and it is not neutralised, then the $H^+/(SO_4^{2-} + NO_3^-)$ ratio, referred to as fractional acidity (FA) in numerous studies [27, 30], is expected to be unity. FA has a mean value of 0.31, ranging between 0.03 and 1.02, indicating that on average, the 69% of the inorganic acidity in precipitation is neutralised over Europe. Regarding the studied regions, results were similar to the overall FA values, showing an average of 0.29 in Central East Europe and Northern Europe, 0.30 in Southern Europe and 0.31 in Western Europe, respectively. To further investigate the relationship

between neutralisation and rainwater acidity, the FA values were plotted against pH values for Europe and all four regions (Fig. 4).

The results show a positive significant exponential function between FA and pH for Central East Europe ($R^2 = 0.397$), Southern Europe ($R^2 = 0.368$), Western Europe ($R^2 = 0.8114$) and the European continent ($R^2 = 0.4983$), explaining the lower pH values and showing that the main acidic ions that control the precipitations' acidity are sulphate and nitrate, even if the majority of acidic species are neutralised when entering the atmosphere [24]. The lack of significant correlation in case of Norther Europe can be attributed to the influence of different anthropogenic and/or natural sources on the rainwater's pH value.

The neutralising effect of crustal components, ammonium and sodium was determined using the neutralisation factors (NFs) [10, 31]:

$$NF_{xi} = \frac{[X_i]}{[SO_4^{2-}] + [NO_3^-]}, \qquad (3)$$

where $[X_i]$ is the concentration of the alkaline component (Ca^{2+}, NH_4^+, Mg^{2+}, Na^+, K^+). Multiannual mean values of NFs for each country are presented in Fig. 5. The overall results showed that Na^+ has the highest neutralising capacity, with an average value of 0.54, ranging between 0.04 and 0.98, being followed by NH_4^+ that ranged from 0.03 to 1.25, exhibiting a mean value of 0.46. The other cations, such as Ca^{2+}, Mg^{2+} and K^+, did not play such an important role in neutralising the rainwater acidity. In general, values were lower than unity, showing the significant influence of acidic species over the neutralising ones.

Although according to the above-mentioned methods, the neutralisation of rainwater acidity occurs, it is important to note that the neutralising potential (NP) of precipitation is not as dominant as the acidic potential (AP). The acidic potential is the sum of the concentrations of non-sea salt (nss) SO_4^{2-} and NO_3^-, whilst the neutralisation potential is the sum of the concentrations of nns-Ca^{2+}, nss-Mg^{2+}, nss-K^+ and NH_4^+ [32, 33]. The AP/NP ratio was determined for all the studied countries, showing in average higher values than 1, having a minimum value of 1.24 in Portugal and a maximum value of 2.18 in Turkey, explaining the percentage distribution of rainwater pH, that ranges between 5 and 5.6, showing a predominantly acidic character.

To further examine the relationship between acidic species and neutralising compounds, and to understand the relative contributions of sulphuric and nitric acid to the total acidity of rainwater [25, 28], ionic ratios such as $(NO_3^- + Cl^-)/SO_4^{2-}$, SO_4^{2-}/NO_3^-, NH_4^+/NO_3^-, NH_4^+/SO_4^{2-}, $(Ca^{2+} + Mg^{2+} + NH_4^+)/(NO_3^- + SO_4^{2-})$ and $(NO_3^- + SO_4^{2-})/(Ca^{2+} + Mg^{2+})$ were calculated. In Europe, the average $(NO_3^- + Cl^-)/SO_4^{2-}$ ratio was 1.31, ranging from 0.87 (Estonia) to 9.72 (Turkey), exhibiting in average at all countries higher ratios than unity. These results indicate that nitric and hydrochloric acid had a significant contribution to the acidity of precipitation, whereas a ratio below one shows the influence of sulphuric acid [34]. The average ratios of SO_4^{2-}/NO_3^- ranged from 1.78 (Portugal) to 2.83 (Serbia) having a mean value of 1.96, showing that sulphuric acid had a more substantial effect on the acidity of rainwater than nitric acid. Analysing the concentrations of NH_4^+ reported to the concentrations of NO_3^-, it can be said that ammonium neutralises nitrous species, since this
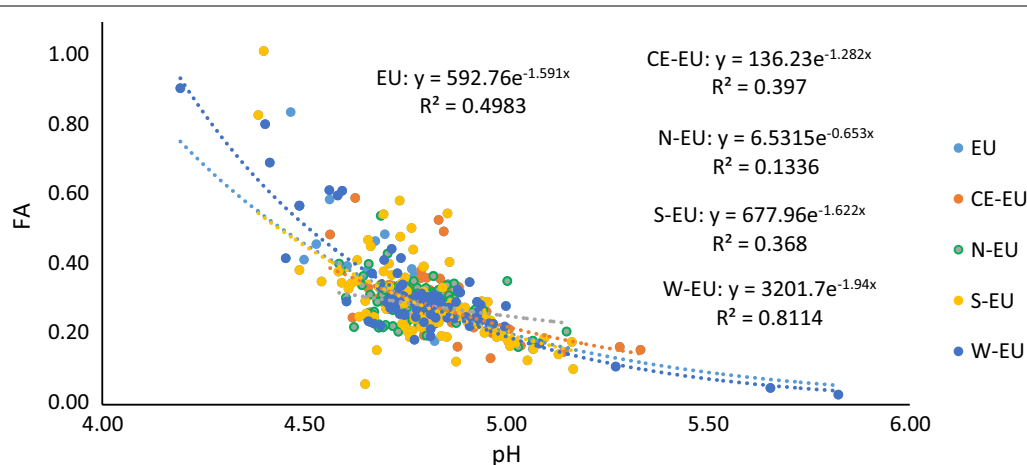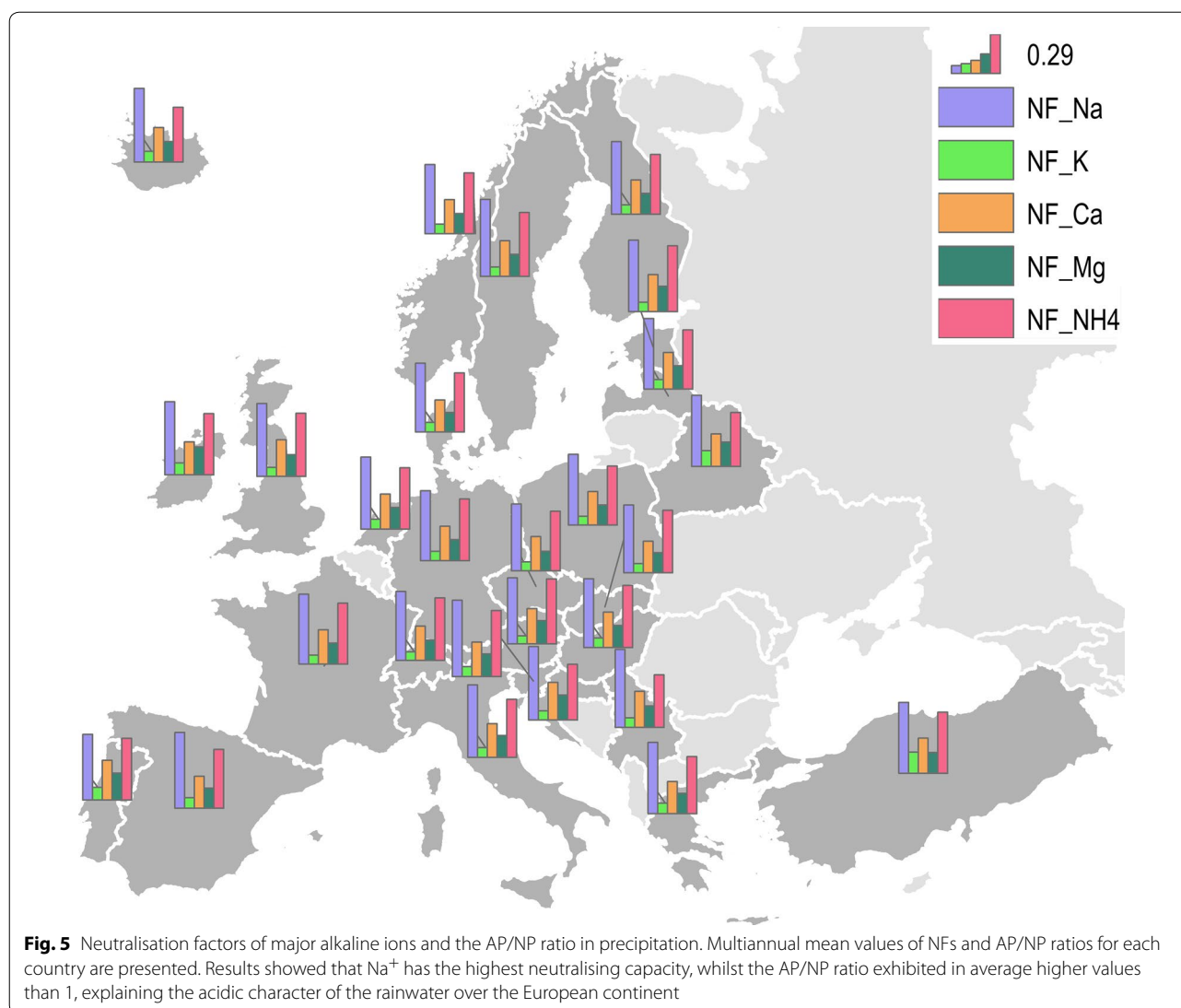

Fig. 4 Relationship between FA and pH in rainwater samples over Europe and the studied regions. Linear regression analysis between FA and pH values showed a positive significant exponential function for the European continent and its regions, respectively

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Fig. 5 Neutralisation factors of major alkaline ions and the AP/NP ratio in precipitation. Multiannual mean values of NFs and AP/NP ratios for each country are presented. Results showed that Na$^+$ has the highest neutralising capacity, whilst the AP/NP ratio exhibited in average higher values than 1, explaining the acidic character of the rainwater over the European continent

ratio exhibited higher values than unity (avg. 1.12), possibly forming NH_4NO_3 in the atmosphere [35]. The NH_4^+/SO_4^{2-} ratio can be used to indicate the relationship between different ions in the atmosphere. According to [36], if this ratio is lower than unity sulphates such as $CaSO_4$ and $(NH_4)_2SO_4 \cdot CaSO_4 \cdot 2H_2O$ are formed, if the molar ratio of NH_4^+/SO_4^{2-} is closer to one, it means that both NH_4HSO_4 and $(NH_4)_2SO_4$ are present in the atmosphere. For Europe, the results showed a ratio that ranged between 0.50 (Serbia) and 0.64 (Turkey), with an average value of 0.58, meaning that sulphates such as $CaSO_4$ and $(NH_4)_2SO_4 \cdot CaSO_4 \cdot 2H_2O$ are often formed the atmosphere. The average ratio of $(Ca^{2+} + Mg^{2+} + NH_4^+)/(NO_3^- + SO_4^{2-})$ is 0.73, which is below one, and the average ratio of $(NO_3^- + SO_4^{2-})/(Ca^{2+} + Mg^{2+})$ that exhibited a mean value of 2.94 indicate the acidic nature of rainwater and the significant

influence of NO_3^- and SO_4^{2-} compounds in the atmosphere over Europe.

To assess the availability of ammonia for neutralisation of acidic species (H_2SO_4, HNO_3) in the atmosphere, the ammonium availability index (AAI) was determined. AAI is expressed by the molar ratio of the ammonium concentration to the amount needed to fully neutralise sulphuric and nitric acids [37, 38]:

$$AAI = \frac{[NH_4^+]}{2 \times [SO_4^{2-}] + [NO_3^-]} \times 100\%. \quad (4)$$

If AAI < 100%, there is an ammonium deficit, suggesting that sulphate and nitrate are acidic; if AAI = 100%, then the precise neutralisation of sulphate and nitrate occurs, whilst if the value of AAI exceeds 100%, then there is sufficient

ammonium to fully neutralise sulphuric and nitric acids. In general, significant differences between the studied regions were not observed; the mean value of AAI during the studied period for Europe was 22.86%, with values ranging between 3.07% (Turkey) and 60.02% (Slovenia), indicating that there is no enough ammonium present to fully neutralise sulphuric and nitric acids. AAI is only an indicator of the neutralising capacity of NH_4^+ over sulphuric and nitric acids and its value did not correspond to the pH value of the rainwater, since there are other neutralising compounds such as calcium, magnesium or sodium, that could contribute to the pH value of precipitation [37].

Wet deposition rates of major ions

Wet deposition is an important pathway of pollutant removal from the atmosphere, giving further insights on the chemical composition of precipitation and providing information on long-range transported pollutants. The multiannual wet deposition (WD) fluxes for all studied regions were estimated according to the following equation [21]:

$$\text{WD}\left(\text{kg ha}^{-1}\,\text{year}^{-1}\right) = \text{VWM}\left(\text{mg L}^{-1}\right) \times \frac{\text{RF}}{100} \tag{5}$$

where WD is expressed in kg ha^{-1} year^{-1}, VWM is the volume-weighted mean expressed in mg L^{-1}, whilst RF is the annual rainfall amount.

The multiannual wet deposition fluxes for the 2000–2017 period for Europe are displayed in Fig. 6, varying from site to site due to different rainwater amounts. Regarding at the results, large differences in the annual deposition rates of anions to cations were obtained. The highest deposition fluxes were obtained for sulphate, with the exception of Turkey, where nitrate had higher deposition rates. The average SO_4^{2-} for Europe

Fig. 6 Average multiannual wet deposition rates (kg ha^{-1} year^{-1}) of major ions. The multiannual wet deposition fluxes for the 2000–2017 period for Europe varied from site to site due to different rainwater amounts, establishing large differences in the annual deposition rates of anions to cations

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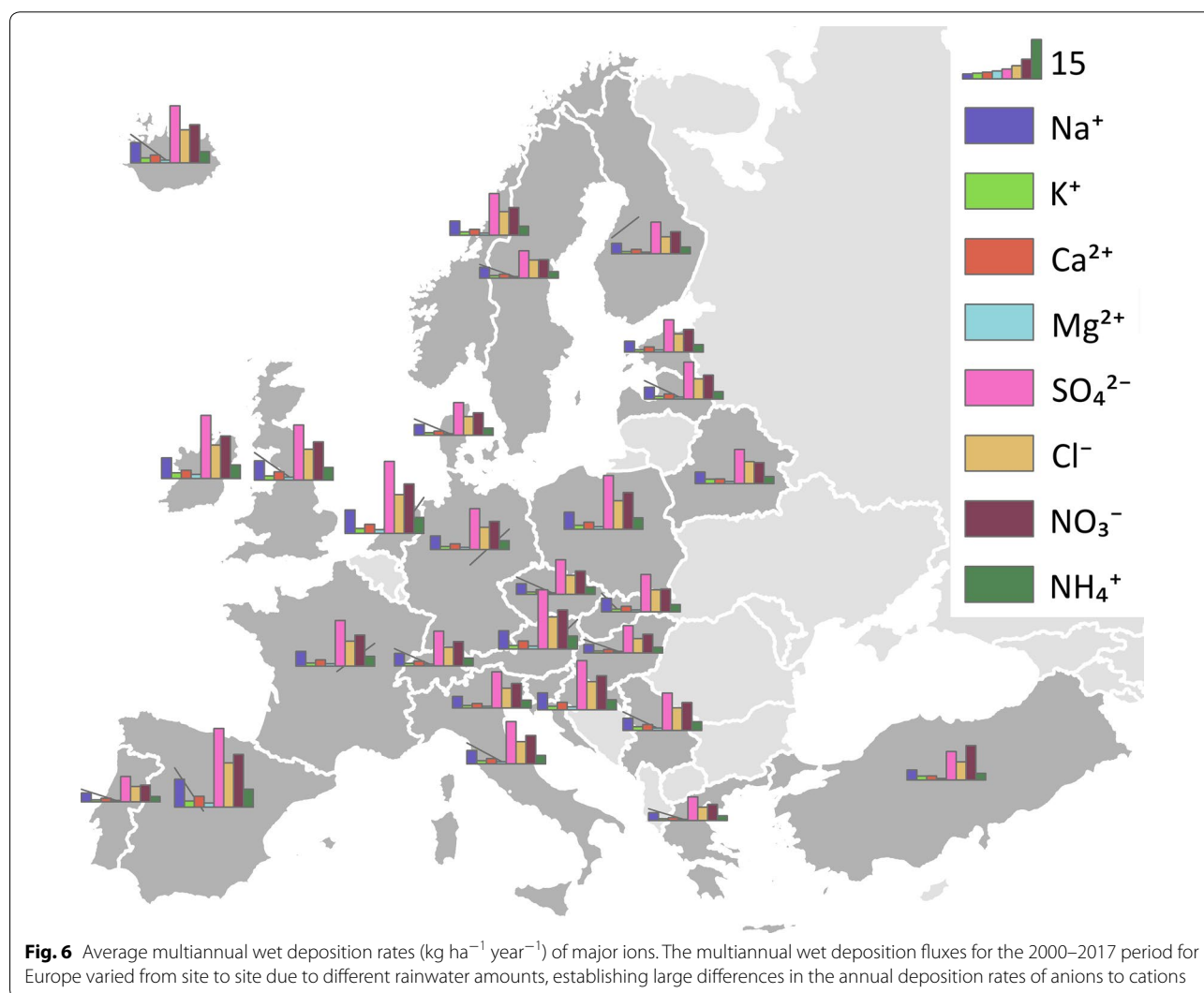
was 15.88 kg ha^{-1} year^{-1}, ranging between 8.87 kg ha^{-1} year^{-1} (Greece) and 29.64 kg ha^{-1} year^{-1} (Slovenia). The total quantity of sulphate deposited on the surface of the studied European countries was 428.86 kg ha^{-1} year^{-1}. Nitrate and chloride also presented high WD values, with an average of 10.96 kg ha^{-1} year^{-1} (min. 6.05 kg ha^{-1} year^{-1} – Greece; max. 20.14 kg ha^{-1} year^{-1}—Slovenia) and 8.93 kg ha^{-1} year^{-1} (min. 5.05 kg ha^{-1} year^{-1}—Greece; max. 16.66 kg ha^{-1} year^{-1}—Slovenia), respectively.

Regarding the results, it can be said that in case of acidic species, the lowest depositions can be found in Greece, whilst the highest in Slovenia. This is probably due to the Mediterranean climate in Greece, with less amounts of precipitation versus the moderate continental climate of Slovenia, with abundant precipitation in the western part of the country. The good pollutant dispersion conditions, mainly in the insular regions of Greece, may also be a cause for lower deposition rates, whereas in Slovenia the effect of continental pollutant accumulation can be felt more intensely. In case of cations, the maximum WD fluxes were estimated for sodium (10.55 kg ha^{-1} year^{-1}) and ammonium (6.78 kg ha^{-1} year^{-1}), both being registered in Slovenia. The average deposition fluxes for Na$^+$ and NH$_4^+$ were 5.32 and 3.43 kg ha^{-1} year^{-1}, whilst the total amount of WD in case of these cations was 143.71 and 92.57 kg ha^{-1} year^{-1}, respectively. Overall, these results correlate with the values of pH, neutralisation factors, ionic ratios and the ammonium availability indexes, explaining the greater concentration of acidic compounds in precipitation, that may be caused by the anthropogenic and industrial activities, coal combustion and traffic.

Origins of major ions in precipitation
Marine and crustal enrichment factors
The chemical composition of rainwater is mainly influenced by anthropogenic sources, sea spray, volcanic activity, biogenic material and terrestrial dust from weathering [9, 39, 40].

Marine and crustal enrichment factors (EFs) were applied to identify and examine the sources and contributions of major ions in rainwater [41, 42]. Enrichment factors are based on the elemental ratio found between ions measured in rainwater compared to a similar ratio for a reference material [40]. In general, Na$^+$ is used as a reference element for seawater, since it is assumed to be originating only from marine sources [21, 43], whilst to characterise the ions deriving from the continental crust Ca^{2+} can be used as the reference ion [44]. Marine and crustal EFs can be expressed as

$$EF_{seawater} = [X/Na^+]_{rainwater}/[X/Na^+]_{seawater}, \quad (6)$$

$$EF_{crust} = [X/Ca^{2+}]_{rainwater}/[X/Ca^{2+}]_{crust}, \quad (7)$$

where X is the concentration of the element of interest in rainwater, X/Na$^+$ and X/Ca^{2+} of rainwater represent the ratio from rainwater composition, whilst X/Na$^+$ seawater and X/Ca^{2+} crust are the ratio of seawater and crustal composition, respectively [2, 45].

The mean values of marine and crustal enrichment factors are shown in Table 1. An element is considered to be enriched or diluted relative to the reference source if the EF value is much higher or much smaller than unity, respectively [10, 30, 39]. The values of marine EFs for Cl$^-$ ranged between 0.86 in Sweden and 1.29 in Austria, whilst the EF$_{Crust}$ values for the same element ranged from 682.75 (Portugal) to 1090.18 (Belarus). These results suggest that Cl$^-$ has marine origins, since the EF$_{Marine}$ values are close to the seawater reference ratio (1.16), whilst the EF values for continental crust are much higher than one, indicating a significant enrichment.

Both EF$_{Marine}$ and EF$_{Crust}$ values have shown that K$^+$ is mainly derived from terrestrial sources, since EFs are enriched compared to seawater and slightly diluted or exhibiting values that are close to the K$^+$/Ca^{2+} (0.504) reference crustal ratio. Regarding crustal enrichment factors for K$^+$, in average values ranged between 0.46 (Austria) and 0.71 (Ireland), excepting Belarus (1.13) and Turkey (1.24), where EF values greater than one are suggesting the influence of other sources too, since fine particulate potassium is a result of biomass combustion [9] and also can be found in some types of chemical fertilisers [46]. EF ratios for Mg^{2+}/Ca^{2+} are ranging between 1.03 (Czech Republic) and 1.58 (Belarus), showing a slight enrichment relative to the reference Mg^{2+}/Ca^{2+} (0.561) ratio. This suggests that a small fraction of Mg^{2+} ions in rainwater may originate from sources other than terrestrial, such as marine. EF seawater values for Ca^{2+} showed crustal origins, from soil-derived components and terrestrial dust or limestone/dolomite weathering [30]. As expected, both marine and crustal EF values for SO$_4^{2-}$ are present in highly enriched form, showing the significant influence of anthropogenic activities and the minimal contribution from soil dust and sea salts [39, 44].

Sea salt and non-sea salt contributions
To estimate the marine and non-marine contribution of different ionic species in precipitation, sea salt fractions (SSF) and non-sea salt fractions (NSSF) were calculated, using Cl$^-$ as a reference element. Since in most of the rains, the Na$^+$/Cl$^-$ ratio showed approximate results with the Na$^+$/Cl$^-$ marine ratio (0.86), the use of chloride as a sea salt tracer was found valid [47]. The contributions of sea salt fractions (SSF) and non-sea salt fractions (NSSF)

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Table 1 Enrichment factors for sea salt and soil components relative to rainwater

	EF$_{seawater}$					EF$_{crust}$				
	$\frac{Cl^-}{Na^+}$	$\frac{K^+}{Na^+}$	$\frac{Ca^{2+}}{Na^+}$	$\frac{Mg^{2+}}{Na^+}$	$\frac{SO_4^{2-}}{Na^+}$	$\frac{Cl^-}{Ca^{2+}}$	$\frac{K^+}{Ca^{2+}}$	$\frac{Na^+}{Ca^{2+}}$	$\frac{Mg^{2+}}{Ca^{2+}}$	$\frac{SO_4^{2-}}{Ca^{2+}}$
Austria	1.29	5.79	14.85	1.77	18.06	738.01	0.46	3.33	1.23	172.22
Belarus	1.11	10.81	11.54	1.55	11.68	1090.18	1.13	4.84	1.58	199.88
Croatia	1.02	5.87	12.17	1.51	11.67	722.55	0.50	3.52	1.20	148.49
Czech Rep.	1.04	6.25	12.12	1.33	13.66	764.52	0.53	3.52	1.03	170.94
Denmark	1.08	6.66	11.06	1.33	13.49	858.23	0.62	3.87	1.12	183.65
Estonia	0.94	6.09	12.17	1.66	12.07	741.85	0.55	3.73	1.37	162.47
Finland	0.91	5.86	11.20	1.29	12.11	727.14	0.54	3.78	1.08	164.61
France	0.95	5.93	11.62	1.37	12.48	740.59	0.53	3.69	1.11	164.43
Germany	0.93	6.13	11.64	1.37	12.52	716.60	0.54	3.64	1.10	163.60
Greece	1.00	7.33	11.14	1.34	14.20	802.12	0.66	3.98	1.13	190.45
Hungary	0.94	6.40	12.00	1.45	13.02	714.80	0.55	3.55	1.17	167.17
Iceland	0.90	6.56	11.33	1.27	12.05	754.74	0.64	3.92	1.08	162.83
Ireland	0.91	7.65	10.57	1.75	12.08	769.16	0.71	3.98	1.50	174.15
Italy	0.94	6.35	11.41	1.40	12.44	778.61	0.61	4.01	1.19	175.54
Latvia	0.96	6.32	12.34	1.53	12.74	716.91	0.54	3.55	1.14	160.32
Norway	0.94	6.53	11.74	1.32	12.88	726.41	0.58	3.65	1.07	167.90
Poland	0.95	5.75	11.01	1.27	11.96	763.16	0.53	3.76	1.08	164.90
Portugal	0.99	9.04	14.26	1.89	12.58	682.75	0.67	3.23	1.27	144.30
Serbia	0.94	5.68	10.88	1.25	11.13	784.42	0.54	3.92	1.09	157.94
Slovakia	0.97	6.27	11.05	1.35	13.02	797.72	0.59	3.88	1.15	180.18
Slovenia	0.88	6.03	10.73	1.33	11.43	747.90	0.58	4.00	1.17	161.96
Spain	1.01	6.67	10.25	1.23	10.69	853.01	0.66	4.18	1.12	157.65
Sweden	0.86	5.81	12.59	1.42	12.96	714.06	0.55	4.03	1.15	165.51
Switzerland	0.94	5.82	11.81	1.33	12.90	711.91	0.51	3.59	1.06	166.21
Netherlands	0.92	6.37	11.32	1.34	11.96	727.58	0.57	3.70	1.10	161.74
Turkey	0.99	13.55	12.02	1.50	11.72	773.77	1.24	3.70	1.18	151.19
UK	0.91	5.69	11.87	1.33	12.00	715.31	0.51	3.68	1.08	155.88

Marine and crustal enrichment factors (EFs) were applied to identify and examine the sources and contributions of major ions in rainwater

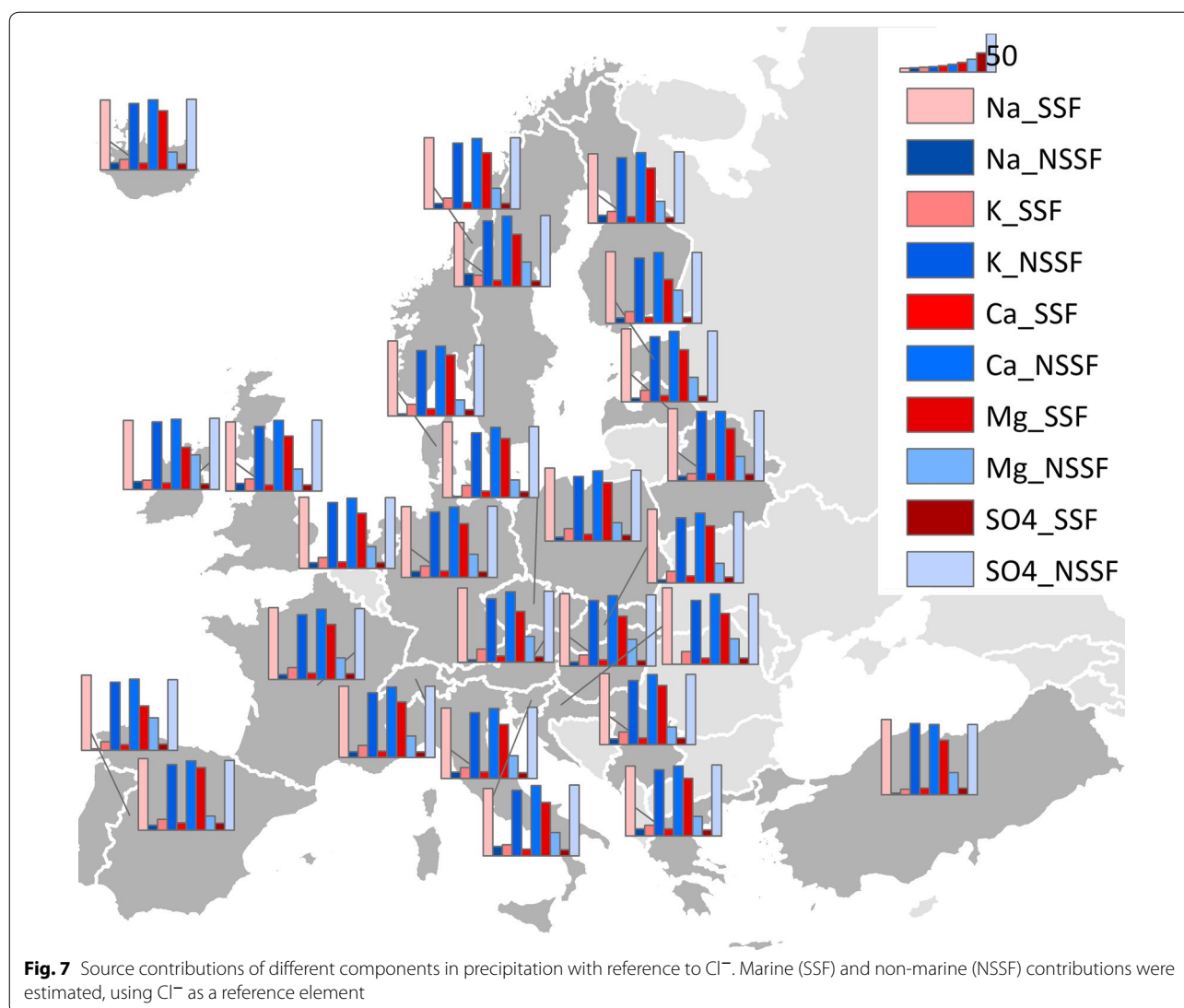can be defined by comparing the Na^+/Cl^- ratio in rainwater to that of seawater, using the following equations:

$$\% \text{ SSF} = \frac{100 * (Cl)_{rain} * \left(\frac{X}{Cl} \right)_{sea}}{(X)_{rain}}, \tag{8}$$

$$\% \text{ NSSF} = 100 - \text{SSF}, \tag{9}$$

where X is the concentration of the respective ion.

Results presented in Fig. 7 are in concordance with that found in case of enrichment factors, suggesting that Ca^{2+}, K^+ and SO_4^{2-} appear to be of non-marine origin over the studied countries, whilst Mg^{2+} beside crustal origin can also be attributed to sea salt influences. In average, over the studied countries, 91.42% Ca^{2+}, 85.60% K^+ and 92.13% SO_4^{2-} in precipitation came from non-sea salt sources. The high percentage of nss-SO_4^{2-} shows the influence of rapid industrialisation, which comes along with considerable energy consumption, such as coal combustion and SO_2 emission by thermal power plants [10]. Almost all of Ca^{2+} in all the studied countries can not only be attributed to terrestrial sources, namely the dissolution of dolomites and limestone [21, 40], the remote transport of soil dust from arid and semi-arid areas, which contains large amounts of Ca^{2+} [10], but also be attributed to anthropogenic activities too, such as quarries or cement factories [5]. Potassium can have various non-marine sources, since it can be found as coarse particles in soil, whilst fine particulate K^+ from biomass burning and agricultural activities can be present in the atmosphere [9, 30]. As found in some previous studies, Mg^{2+} can be attributed to marine sources too. Furthermore, Xiao et al. [48] found that in some remote ocean areas, magnesium had higher concentrations than calcium, which explains the average of 70.43% of Mg^{2+} that can be attributed to sea salts, and only 29.57% to other sources. Cl^- in rainwater at all sampling sites mainly

Fig. 7 Source contributions of different components in precipitation with reference to Cl⁻. Marine (SSF) and non-marine (NSSF) contributions were estimated, using Cl⁻ as a reference element
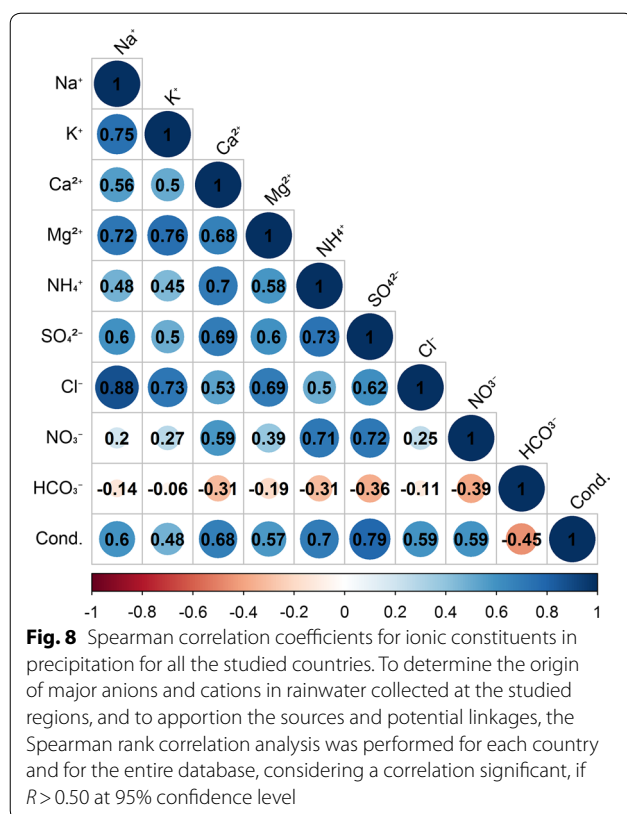
originated from sea salt, having an average SSF value of 93.26%, ranging between 83.22% (Sweden) and 99.63% (Croatia). The non-sea salt fraction of Cl⁻ from rainwater can be attributed to various anthropogenic activities, such as automobile exhaust [49] or iron and steel production [50].

Spearman's rank correlation analysis

To determine the origin of major anions and cations in rainwater collected at the studied regions, and to apportion the sources and potential linkages, the Spearman rank correlation analysis was performed for each country and for the entire database, considering a correlation significant, if $R > 0.50$ at 95% confidence level (Fig. 8).

SO_4^{2-} and NO_3^- are significantly correlated ($R = 0.72$ for the entire database), showing the similarity of their chemical behaviour in precipitation, as well as the common source (fossil fuel combustion, industrial activities) [10] and co-emission of their precursors (SO_2 and NO_x) [44]. Regarding the correlations between these ions over each studied region, the coefficients were 0.75, 0.70, 0.70 and 0.67 for Northern Europe, Western Europe, Southern Europe and Central East Europe, respectively. Similarly, significant correlation values were found between SO_4^{2-} and Cl⁻ ($R = 0.62$) for all countries, R exhibiting the same value in Northern Europe, 0.66 in Western Europe, 0.56 in Southern Europe and 0.63 in Central East Europe. The SO_4^{2-}, Cl⁻ pair exhibited higher correlation values in the regions where the contribution of NSS chloride was higher, which indicates anthropogenic origin, such as the metallurgic industry, known for coal combustion and use of Cl⁻ [50]. The coexistence of Ca^{2+} and Mg^{2+}, Ca^{2+} and Na^+, Mg^{2+} and K^+, and Na^+ and K^+ was observed, indicating the common terrestrial origin in soil and dust.

Fig. 8 Spearman correlation coefficients for ionic constituents in precipitation for all the studied countries. To determine the origin of major anions and cations in rainwater collected at the studied regions, and to apportion the sources and potential linkages, the Spearman rank correlation analysis was performed for each country and for the entire database, considering a correlation significant, if $R > 0.50$ at 95% confidence level

Table 2 Varimax rotated factor loadings, total variance and possible sources over Europe

Europe	F1	F2	F3	F4	F5
Na^+	0.26	*0.87*	0.27	− 0.07	0.12
K^+	0.14	0.14	0.09	0.02	*0.98*
Ca^{2+}	*0.70*	0.22	*0.52*	0.20	0.04
Mg^{2+}	0.29	0.39	*0.82*	0.11	0.13
SO_4^{2-}	*0.76*	0.51	0.10	0.17	0.07
Cl^-	0.27	*0.89*	0.20	0.07	0.11
NO_3^-	0.09	0.01	0.07	*0.99*	0.02
NH_4^+	*0.89*	0.19	0.17	0.05	0.15
% Total variance	26.47	25.71	13.70	12.92	12.84
Possible source	Anthropogenic and mixed	Marine	Terrestrial	Traffic	Biomass burning and fertilisation

Principal Component Analysis (PCA) has been applied to precipitation chemistry data, in order to identify possible sources of pollutants and to reveal the important relationships amongst variables

The italic values indicate the significant loadings in case of each factor

The significant correlations between Ca^{2+} and Mg^{2+} ($R = 0.65$) for the entire database, as well as for all four regions (0.65—Northern Europe, 0.69—Western Europe, 0.75—Southern Europe and 0.59—Central East Europe) imply the presence of calcite, dolomite and limestone in the studied areas, and also being an indicator of quarries or cement factories [30, 51–53]. Good correlation coefficients between Na^+ and K^+ (0.75—Europe and Northern Europe, 0.84—Western Europe, 0.64—Southern Europe, 0.68—Central East Europe) are an indicator of alkali feldspars [30]. The Ca^{2+}, Na^+ and Mg^{2+}, K^+ pairs are usually found in silicates; therefore, the significant positive correlation coefficients between Ca^{2+}, Na^+ ($R = 0.56$) and Mg^{2+}, K^+ ($R = 0.76$) are an indicator of the variety of igneous, metamorphic and sedimentary rocks in the studied regions. The very good correlation coefficients between Ca^{2+} and SO_4^{2-} ($R = 0.69$), Ca^{2+} and Cl^- ($R = 0.53$), Ca^{2+} and NO_3^- ($R = 0.59$), Mg^{2+} and SO_4^{2-} ($R = 0.60$), Mg^{2+} and Cl^- ($R = 0.69$) are an indicator of the neutralising capacity of cations over acidic compounds, and according to Lu et al. [44] are probably the result from the reaction of alkaline species rich in Ca^{2+} and Mg^{2+} with H_2SO_4, HNO_3 and HCl acids. In the atmosphere, ammonia is usually present in the form of $(NH_4)_2SO_4$, NH_4HSO_4 and NH_4NO_3, being the product of its reaction with H_2SO_4 and HNO_3 [9]. Since the correlation coefficient of NH_4^+,

SO_4^{2-} ($R = 0.73$) and NH_4^+, NO_3 ($R = 0.71$) presented similar values, it can be said that $(NH_4)_2SO_4$, NH_4HSO_4 and NH_4NO_3 have equal contributions [44] to the overall precipitation chemistry of the studied European countries. The ratio between the above-mentioned species can differ from region to region. The significantly positive correlation between Na^+ and Cl^- ($R = 0.88$—Europe and Northern Europe, $R = 0.94$—Western Europe, $R = 0.82$—Southern Europe, $R = 0.89$—Central East Europe) indicates that probably not only the major part of these ions originated from sea salt, but chloride may also be present in precipitation from mofette emanations, mineral springs and salt mines [30].

Principal Component Analysis

Principal Component Analysis (PCA) has been applied to precipitation chemistry data, in order to identify the possible sources of pollutants and to reveal the important relationships amongst variables [54], summarising the patterns of correlations amongst variables and reducing a large number of variables to a smaller number of factors [27].

The rainwater air pollutants may have natural, anthropogenic or mixed origins, depending on their sources or the sources of their precursors [55]. Table 2 presents the Varimax rotated factor loading patterns, with five major components that were extracted accounting for 91.64% of the total variance.

The first factor explained the 26.47% of the total variance having high loadings on NH_4^+, SO_4^{2-} and Ca^{2+}, indicating the influence of anthropogenic activities, such as industrial emissions or the presence of open quarries, the

use of fertilisers in agriculture [56], and wind-blown soil dust [57]; therefore, it can be attributed to mixed sources with significant anthropogenic impact. The presence of anthropogenic NH_4^+ in rainwater can be attributed to agricultural NH_3 emissions, from cattle waste deposits, natural and chemical fertilisers [41, 58]; to biomass combustion and wildfires [59], having a particularly large contribution across Western and Central East Europe [55]. The increased occurrence and severity of wildfires in the last decades are known as a large contributor to the sources of ammonium in precipitation via PM emissions [60].

The interconnection between NH_4^+ and SO_4^{2-} is derived from acidic pollutants emitted to the atmosphere through industrial activities, enhancing the occurrence of aerosols containing $(NH_4)_2SO_4$ and NH_4HSO_4 [27]. The association of Ca^{2+} and SO_4^{2-} can be accounted to the presence of $CaSO_4$. The sources of dissolved $CaSO_4$ in rainwater can be due to the neutralisation reactions between carbonate minerals and sulphuric acid, to the dissolution of gypsum or anhydrite, and to the crystallisation of gypsum in the atmosphere [61].

The second factor is attributed to maritime sources, presenting high loads of Na^+ and Cl^- and explaining the 25.71% of the total variance. The influence of sea salts is significant due to the position of the European continent, being surrounded by seas and oceans.

The third factor is represented by the 13.70% of the total variance, being largely influenced by high loadings on Ca^{2+} and Mg^{2+}, showing the contribution of crustal sources. The above-mentioned ions originate from the dissolution of dolomites and limestone, taking part in the neutralisation process as suspended $CaCO_3$ and $MgCO_3$ [30]. Also, chemical weathering of silicates can produce sodium ions that have a significant contribution to the neutralisation process.

Traffic is a major source of NO_3 [55, 62]; therefore, the fourth factor that exhibited a high loading of nitrate and the 12.92% of the total variance is attributed to vehicular emission.

The high loading of K^+ explaining 12.84% of the total variance in case of the fifth factor indicates biomass burning as a possible source of potassium [63, 64]. According to Khare et al [65], potassium may be considered as a chemical signature of biomass burning, and is also present in complex chemical fertilisers, such as NPK [41, 46].

Conclusions

The chemical compositions of rainwater, pH variations, acidifying and neutralising processes, wet deposition rates and source contributions were determined in 27 European countries over a period of 18 years. The main conclusion of this study regarding the precipitation chemistry of the European continent during the studied period is represented by the relative homogenous distribution of the analysed chemical species, which is most likely due to the unitary economic development and to the implementation of common European policies in the field of environmental protection. Results showed the local characteristics, that are often diminished or enhanced by the dominant atmospheric circulations, loaded with different pollutants originating from neighbouring regions. Wet deposition rates also reflect the climatic influences and the local and regional economic characteristics of different regions from Europe. Enrichment factors, Spearman's rank correlation coefficients and the Principal Component Analysis highlighted that the precipitation chemistry of Europe is mainly controlled by anthropogenic influences. Sulphate and nitrate, that largely contribute to the rainwater's acidity, originate from industrial activities and traffic; ammonium and potassium can be attributed to biomass combustion, wildfires and agricultural activities, such as natural and chemical fertilisers. Magnesium and calcium are tracers of terrestrial sources, whilst chloride and potassium represent the maritime influence. The interconnection between rainwaters, slightly acidic and acidic pH, and the ionic concentrations of neutralising compounds in precipitation leads to the conclusion that acidic species are more predominant in the atmosphere of the European continent than neutralising ones. The results showed that the main acidifying agents are sulphur and nitrogen compounds that originate from different industrial and agricultural activities, including traffic emissions and farming. Exposure to air pollutants and to precipitation containing sulphur and nitrogen compounds greatly affects the ecosystem and the environment, also damaging vegetation and fauna, leading to several environmental impacts, heavily influencing the quality of water and soil. Ammonia and nitrogen oxides are considered as the most harmful air pollutants in terms of damage to ecosystems [15]. The above-mentioned compounds (NH_3 and NO_x) introduce large amounts of nutrient nitrogen into terrestrial and aquatic ecosystems, leading to eutrophication that may cause changes in species diversity and invasion of new species [15]. Nitrogen oxides along with sulphur dioxide also contribute to the acidification process of soil, lakes and rivers, causing biodiversity loss. According to the 2018 Report of the European Environmental Agency, the annual limit value for nitrogen dioxide continues to be widely exceeded over Europe. Whilst in case of sulphur dioxide, even if over the past three decades SO_x emissions considerably reduced, due to their higher acidifying potential in comparison with NO_x, sulphur oxides still have a significant contribution

to acidification. Therefore, we consider that it is of great importance for policy and decision makers to pay attention to the pollutant concentrations of these acidifying compounds, and which dissolved in rainwater may have more immediate effects of the environment.

Abbreviations
EU: Europe; CE-EU: Central East Europe; N-EU: Northern Europe; S-EU: Southern Europe; W-EU: Western Europe; VWM: volume-weighted mean; FA: fractional acidity; NF: neutralising factor; NFs: neutralising factors; NP: neutralising potential; AP: acidic potential; AAI: ammonium availability index; WD: wet deposition; EFs: enrichment factors; EF: enrichment factor; SSF: sea salt fraction; NSSF: non-sea salt fraction; PCA: Principal Component Analysis; NPK: a complex fertiliser composed from nitrogen, phosphorus and potassium; EMEP: European Monitoring and Evaluation Programme; EEA: European Environment Agency.

Authors' contributions
Conceptualisation: RS; methodology: ÁK, RS, MVB, IAN, ZsB; writing: ÁK; supervision: RS, MVB. All authors read and approved the final manuscript.

Availability of data and materials
The precipitation chemistry data used in the present study were downloaded from the GAW World Data Centre for Precipitation Chemistry, that is publicly available at http://wdcpc.org. The annual data of precipitation amount used in this study were extracted from E-OBS raster dataset (version 19.0). E-OBS data are freely available at http://www.ecad.eu.

Ethics approval and consent to participate
Not applicable.

Consent for publication
Not applicable.

Competing interests
The authors declare that they have no competing interests.

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