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Chemical characteristics and source apportionment on ionic composition of rainwater in the Romanian Carpathians, Europe, and Conterminous United States

PhD thesis

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1 Introduction

The impacts of climate change are being felt in all geospheres. The effects are visible and inevitable due to the inertia of the climate system, regardless of the result of short- and medium-term emission reduction actions. The quantity and composition of emissions are found not only in air quality but also in atmospheric precipitation. This is a sensitive indicator of changes in the natural and anthropogenic environment.

Intramountain depressions are no different from this phenomenon either. They have a specific microclimate where certain mathematical models can be developed, and which will be extrapolated to the regional and even continental scale in the present thesis. The specificity of intramountain basins from the Romanian Carpathians consists in the distinct microclimate conditions, characterized by periods of accentuated static stability, and the installation of persistent local anticyclonic systems (Szép et al., 2018, 2017). The basins concave shapes favor the thermal stratification of the air (Whiteman et al., 2001). Thus, the cold air descends and accumulates on the bottom of these depressions causing thermal inversions, extremely common in the cold season (Panday et al., 2009; Wekker and Kossmann, 2015). Moreover, due to the sheltering character of the mountains, the wind frequency decreases inside the basins, while the relative humidity of the air is higher, increasing fog frequency (Kossmann et al., 2002). The above-mentioned phenomena are also characteristic to the basins of the Romanian Carpathians, such as the Ciuc basin, Giurgeu basin and Maramures basin. These basins are characterized by unevolved and organic soils, with acidophilic vegetation and ascending mineral springs, developed on tectonic fault lines, their chemistry being imposed by the host rocks (volcanic and magmatic on the eastern frame and sedimentation on the western one) (Szép et al., 2017).

The agricultural policies applied between the years of 1960-1980 led to drastic changes in land use. Thus, the transition to extensive agriculture caused the drainage of these basins, followed by significant evapotranspiration losses. The loss of evapotranspiration, the decrease of the relative humidity and of the precipitations favors the development of heavy drought phenomena and the accumulation of the pollutants and the particles derived from them (Szép and Mátyás, 2014). Lately, the occurrence of heavy drought led to the ignition of the natural peat deposits, either through auto combustion, or through stubble burnout in the Ciuc and Giurgeu basins (Szép et al., 2017).

Air pollution affects everyone, being a permanent risk factor for all regions, and to fight against its negative and harmful effects environmental policies must be adapted to local specificities. The relationship between air pollution and atmospheric precipitation is one of interest, especially in terms of wet deposition and the impact on the pedosphere, biosphere and built heritage values. The chemical composition of atmospheric precipitation has been intensely studied during the last decades, hence the major ion concentrations in rainwater can indicate air quality, showing the relative sources that contributed to polluting the atmosphere.

2 Research objectives

The main aims of this thesis are:

- to identify the sources of natural and/or anthropogenic contamination/pollution of atmospheric precipitations and the contribution of various sources to their chemical composition.

- to present the relationship of interdependence between geology, geomorphology, climate specificities of the studied areas and precipitation chemistry.

- to examine the atmospheric circulations and the microclimate influences on the rainwater chemistry in the studied areas

- to assess the variation of sea salt concentration depending on the dominant air masses and the specific influences of high relief on the chemical composition of precipitation (Foehn winds in the Southern Carpathians)

- to decipher the pH variation, the neutralizing capacity of different chemical species, the wet deposition, the contribution of marine and non-marine salts and the influence of different pollutant sources on the chemical composition of rainwater, taking under account the spatial-temporal evolution of the European continent to establish the dependent relationship with the environmental policies of the European Union.

- to extrapolate and validate the results obtained at the level of the European continent to the level of the contiguous US during the last four decades, including the major ion concentrations, the variation of pH values, the acidifying and neutralizing capacity of rainwater, the wet deposition, the influence of sea-salts and of different pollutant sources, in order to characterize the spatiotemporal differences and interrelationships between different regions in terms of geographical location, climate and economic development, which may present a significant contribution to environmental specialists and political decision makers, offering a benchmark in order to highlight the effects on the chemical composition of rainwater of the implementation of environmental regulations.

3 Materials and methods

3.1. Sampling site description

To conduct the studies on which the present thesis is based, several basins were selected from the Romanian Carpathians, which can be classified into intra-mountain and extra-mountain areas. Later, the results obtained on a local and regional scale were extrapolated to a continental scale, applying the used mathematical models and estimates to the European continent and to the contiguous United States.

Fig. 1 shows the sampling sites selected at the level of the Romanian Carpathians, analyzing rainwater samples from four different locations in the Northern group of the Eastern Carpathians (Baia Mare - BM, Bozinta - BZ, Seini - SE, Somcuta Mare – SM), three intramountain- and one extramountain basin from the Central group of the Eastern Carpathians (Ciuc basin – CB, Giurgeu basin – GB, Deda-Toplita Pass (DTP) and Odorheiu Secuiesc extramountain basin (OSB). From the Southern Carpathians three sampling locations were chosen: Resita (RS), Baile Herculane (BH) and Moldova Noua (MN).

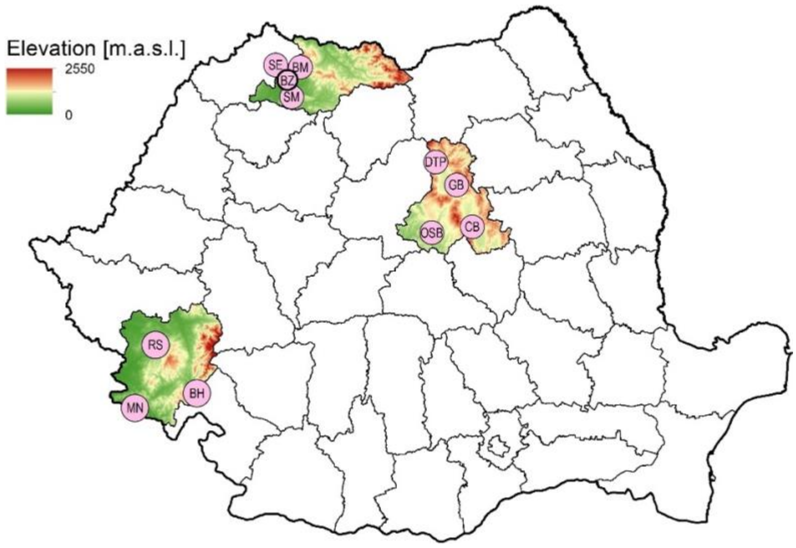

Fig. 1. Sampling site locations from the Central- and Northern- group of the Eastern Carpathians, and Southern Carpathians.

A more detailed description of the sampling sites discussed in the present thesis can be found in previously published articles (Keresztesi et al., 2020c, 2020a; Szép et al., 2018).

3.2. Sampling and data analysis

3.2.1. Sampling and analytical procedures

During the sampling period, 2006–2017, in the Romanian Carpathians, 2095 rainwater samples were analyzed. Precipitation was collected in all three Carpathian regions by placing rainwater samplers 1.5-2m above ground, from the onset until the end of the rainfall event. The pH values of the samples were immediately measured with digital pH meters standardized with 4.0 and 9.2 pH buffer solutions. Conductivity meters were used to measure the conductivity of each sample. To prevent biological degradation of the sample, thymol was used, followed by the removal of insoluble particles, by filtering the samples through membrane filters. Then, all samples were refrigerated at 4 ºC until further analysis. At all sampling sites from the Romanian Carpathians, anions were measured with Ion Chromatograph (Dionex 2000i/SP) using a CO_3^{2-}/HCO_3^- buffer as eluent (1.7 mM Na_2CO_3/1.8 mM $NaHCO_3$). Cations collected in the central and northern groups of the Eastern Carpathians were analyzed by atomic absorption (AAS, Perkin Emler, model 2380, Air/C_2H_2, 422.7 nm), while in the case of samples gathered in the Southern Carpathians Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES, iCAP 6300 Duo View ICP-AES Spectrometer) was used (Keresztesi et al., 2020a, 2020c). The Cl^- and NH_4^+ were measured by U-VIS spectrometer method (Nicolet Evolution 100, 463 and 440 nm) (Nollet, 2007; Szép et al., 2017).

For a more detailed description of the sampling procedures please check the previously published articles (Keresztesi et al., 2020c, 2020a; Szép et al., 2018).

In the central group of the Eastern Carpathians a total of 362 samples were collected at CB, 114 at GB, 118 samples at DTP and 114 samples at OSB from January 2006 to 2016 November, while in the northern group of the Eastern Carpathians, during a period of 9 years, between January 2009 and December 2017, a total of 1112 rainwater samples were collected: 286 at Baia Mare (BM), 270 at Bozinta (BZ), 280 at Seini (SE) and 276 at Șomcuța Mare (SM). In the sampling sites from the Southern and Carpathians, a total of 275 precipitation samples were collected: 81 at Reșița, 97 at Moldova Nouă, and also 97 samples at Băile Herculane, from January 1st 2014 to December 31st 2017.

The precipitation chemistry data in the case of Europe and the United States (US) of America were downloaded from regional and national monitoring networks (Vet et al., 2014). The ion composition analysis data used in the case for precipitation samples collected in the European Continent were obtained from the GAW World Data Centre for Precipitation Chemistry, that can be accessed at http://wdcpc.org, while data for the conterminous United States were obtained by accessing the National Atmospheric Deposition Program (http://nadp.slh.wisc.edu), through the National Trends Network (NTN). These databases offer a long-term record of rainwater chemistry across the U.S.

3.2.2. Meteorological data and classification methods of atmospheric circulation types

Atmospheric circulation types (CT) were built with the help of the cost733cat v 1.2 classification software (Philipp et al., 2016) and ERA reanalysis (Interim version). In order to do so, mean sea level pressure (MSLP) and the height of 500 hPa geopotential have been chosen. To build the CT, numerous methods were chosen to verify if related synoptic patterns are characteristic for the days with over 10 mm of precipitation, between 1981 and 2016. To construct the CT data were downloaded at a spatial resolution of 0.05 degrees/cell for the period 2005-2014, from CLAAS-2 version of METEOSAT second generation of geostationary satellites; being validated with SYNOP and calibrated with MODIS, moreover the *Liquid water path (LWP)* dataset was also used (Szép et al., 2018). Types that are most related to heavy rainfall were chosen to each classification method, calculating the average of LWP and presenting the possible spreading of LWP values. To assess the interconnection between various synoptic patterns and rainfall in South-eastern Europe, daily classification of CT was used. To derive the classification of weather types cost722class software was used with MSLP data that were extracted from ERA-Interim. Since the predefined thresholds were used to link each day to a certain CT, the Grosswetter-Types (GWT) classification was selected, resulting in 27 weather types during the 1979-2018 period.

3.2.3. Zonal circulations and zonal index construction

To construct the daily zonal index (ZI) ERA Interim MSLP recorded at 12 UTC (Dee et al., 2011) was used, being characterized as the latitudinal difference between MSLP at 56°N and MSLP at 32°N. The meridional index (MI) was built on the same principles, but between 5°E and 45° E longitude, using the method by Kutiel et al., (1996), who used the above-mentioned indices in the Mediterranean area with regard to precipitation. To analyze rainfall that is characteristic to westerly circulations over Romania, the ZI was used, defining the term "strong ZI" as the days with ZI score higher than the 75^{th} % from the overall number of days with ZI greater than 1.

3.3. Methods used in the assessment of chemical composition of rainwater

The acidic and neutralization potential

The fraction of the acidic (AP) and neutralization potential (NP) can be found by applying using the following equation (Keresztesi et al., 2020c, 2019):

$$AP/NP = (NO_3^- + nssSO_4^{2-})/(NH_4^+ + nss\,Ca^{2+} + nssMg^{2+} + nssK^+) \quad (1)$$

where nss stands for the non-sea salt ratio of the cations mentioned above.

Neutralization factor (NF)

The neutralizing capacity of precipitation was assessed by applying the following formula (Keresztesi et al., 2019; Szép et al., 2018):

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

where: $[X_i]$ is the concentration of the cations measured in the precipitation samples (Ca^{2+}, NH_4^+, Na^+, K^+, Mg^{2+}) expressed in μeq/L.

Wet deposition flux

Wet deposition fluxes are expressed by multiplying the VWM (mg/L concentration) and the annual rainfall (RF) amount (Szép et al., 2017), according to the following equation:

$$WD\ (kgha^{-1}\ yr^{-1}) = VWM\ (mg\ L^{-1}) * \frac{RF}{100} \quad (3)$$

Marine and crustal enrichment factors

Marine and crustal enrichment factors (EF_{sea}, EF_{crust}) were assessed using the following formula, with Na^+ as the reference element for seawater, and Ca^{2+} as the terrestrial trace ion (Keresztesi et al., 2020b, 2019):

$$EF_{seawater} = [X/Na^+]_{rainwater} / [X/Na^+]_{seawater} \quad (4)$$

$$EF_{crust} = [X/Ca^{2+}]_{rainwater} / [X/Ca^{2+}]_{crust} \quad (5)$$

where X represents the amount of the element of interest in precipitation; X/Na^+ and X/Ca^{2+} of rainwater are the ratios measured in precipitation; X/Na^+ seawater and X/Ca^{2+} crust stand for the ratio of seawater and crustal composition (Keresztesi et al., 2019).

Sea salt and non-sea salt fractions

In order to determine the percentage of seawater and non-seawater sources in rainwater chemistry, the sea salt fractions (SSF) and non-sea salt fractions (NSSF) were calculated, according to the following equations (Das et al., 2005):

$$\%SSF = \frac{100 * (Na)_{rain} * \left(X/Na\right)_{sea}}{(X)_{rain}} \quad (6)$$

$$\%NSSF = 100 - SSF \quad (7)$$

where, X represents the concentration of the respective ion.

In the case of Europe and conterminous US, where the SSF calculated from Na^+ gives values > 100%, and in most rainwater samples the Na^+/Cl^- ratio has similar values compared to the Na^+/Cl^- seawater ratio (0.86), the seawater and non-seawater contributions can be calculated using Cl^- as a reference element (Keresztesi et al., 2020b, 2019):

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

$$\%NSSF = 100 - SSF \quad (9)$$

where X is the concentration of the respective ion.

4 Results

4.1. Atmospheric circulation and effects of the Eastern Carpathians on precipitation

The intra-mountain basins of the Carpathians are characterized by lower amounts of rainfall, imposed by the mountainous orographic barrier. This phenomenon can be observed through the orographic convection, leading to more precipitation on the northwestern slopes, also influenced by the prevalent direction of atmospheric circulations, which has effects on the chemical composition of precipitation too. The rainfall amount, temperature and wind direction are also influenced by the adiabatic conditions, hence on the leeward ramps the air becomes more stable. The orographic convection which implies the link between rainfall and elevation is also causing water vapors to be lifted to the condensation level. The atmospheric circulation type characteristic for Romania is the high extent of the Azores High fronting South and Central Europe; yet this pattern is also correspondent to a meridional circulation in the upper levels of the troposphere, with air masses coming from North-Europe to northwest and southeast, carrying more humidity over the studied areas. The mountainous barrier created by the Eastern Carpathians often stands in the way of these air masses, modifying their trajectory, and the wind direction, which also influences the chemical composition of rainwater.

4.2. General variability and chemical composition of precipitation

Statistical analyses of precipitation chemistry, such as volume-weighted mean (VWM), average, minimum, maximum, standard error and standard deviation values were performed for all studied regions in the present thesis. It was observed that on a more local scale and in general in the Carpathians precipitation chemistry is alkaline, the dominant ions being ammonium, and calcium, while in terms of acidic components, the most relevant are chloride and sulphate. It can be said that the structure of the relief is influencing the rainwater chemistry, hence the association of calcium and magnesium often suggests the dissolution of limestones, the considerable amounts of sulphate, chloride and other acidic components can be a sign of copper smelters, mining activities, industrial activities, and traffic, while the large amount of potassium and ammonium can suggest agricultural works, cattle breeding and cattle waste deposits, but can be a sign of biomass burning or peat fires too. The large concentrations of sea salts, such as sodium and chloride, can indicate marine sources. In the European continent and conterminous United States acidic species had higher concentrations than alkaline ones. For Europe, sulphate was the most abundant, and among cations, sodium. In the US, calcium and magnesium were the most abundant, high values of sulphate were observed in the industrial belts of the US, and high ammonium and potassium concentrations in the agricultural belts.

4.3. Variation of pH

In the studies of Lu et al., (2011); Pu et al., (2017); Tiwari et al., (2016); Xing et al., (2017) and Xu et al., (2015) it is presented that the pH value of precipitation in an unpolluted environment due to the presence of atmospheric CO_2 is around 5.6. In 1982, Charlson and Rhode observed the decreasing trend of this value due to the presence of other naturally occurring acids, stating that the pH values of rainwater in a clean environment can alter between 5 and 5.6 (Charlson and Rodhe, 1982; Hu et al., 2003). According to the above, it can be stated that values below 5.6 indicate acidic rains, while values above 5.6 show the presence of alkaline species in rainwater.

This subchapter presents the multi annual averages and the volume-weighted means for the pH values of rainwater collected in the studied areas from the Romanian Carpathians as well as in Europe and the conterminous US.

4.4. Acid neutralization

The acidity and alkalinity of precipitation is controlled by various factors and chemical compounds, such as H_2SO_4, HNO_3, organic acids and the existence of NH_3 and $CaCO_3$ (Wu et al., 2016; Xu et al., 2015). According to the specialty literature, the concentration of sulfate and nitrate remains constant in the atmosphere regardless of altitude, while the abundance of ammonia and ammonium may decrease fast with height (Harrison and Pio, 1983). Therefore, at cloud level, acidic compounds such as H_2SO_4, HNO_3, NH_4HSO_4 are more abundant than alkaline compounds such as $(NH_4)_2SO_4$ and NH_4NO_3 (Balasubramanian et al., 2001). Neutralization Factors (NF) and the proportions of Acidic Potential (AP) to Neutralization Potential (NP) were assessed at all studied regions from the Romanian Carpathians, Europe, and conterminous US to examine the rate of neutralizing process in rainwater. The results showed that neutralization of rainwaters acidity occurs at almost 100% in all sampling sites from the Eastern and Southern Carpathians, excepting the OSB sampling site from the Central group of the Eastern Carpathians, where this difference may be due to the orographic barrier effect of the Eastern Carpathians, and to the differences between intra and extra mountain basins. The results of acid neutralization are coinciding with the one of pH variation, hence the acidity of rainwater was only neutralized in ~69% in Europe and ~61% in conterminous US.

4.5. Spatial and temporal variability of Wet Deposition fluxes

Wet deposition may change the rainwater's effect on the ecosystem, also providing information of locally emitted or long-range transported pollutants, due to its dissolved ionic concentrations. Central group in the Eastern Carpathians - WD for NH_4^+, Ca^{2+} and SO_4^{2-} were higher than for other ions. The highest multi annual average WD flux for SO_4^{2-} (36 kg $ha^{-1}yr^{-1}$) was measured at OSB. Here, long-range transported pollutants can be more easily deposited at OSB, than at the other sampling sites, which are protected by the mountain chain from the air masses transporting pollutants. Northern group of the Eastern Carpathians - Among alkaline species, calcium had the highest values at all sampling sites, while amidst acidic species sulfate exhibited the most elevated WD fluxes. Southern Carpathians - WD fluxes for both alkaline and acidic species were the highest in BH, significant values for sulfate and chloride. Amongst cations, calcium had the highest WD rates, values accounting for 97.95 kg/ha/yr at BH, 50.33 kg/ha/yr at MN, and 14.63 kg/ha/yr at RS. Europe - The highest deposition fluxes were obtained for SO_4^{2-}, excepting the value for Turkey, where NO_3^- exhibited the highest WD fluxes. The mean WD value for SO_4^{2-} in Europe was 15.88 kg/ha/yr. Greece has the lowest acidic WD rates, while Slovenia the highest, which can be explained by the climate conditions. Another factor may be the pollutant dispersing conditions, which in Greece can cause lower deposition rates, whereas in Slovenia the pollutant accumulation phenomenon is more significant. US - the most elevated WD fluxes were observed in the case of Cl^-, yielding values of ~35 kg/ha/year in areas where chloride is used in the production process. For cations, WD rates for calcium were the highest, mainly in the desert areas and in the central region.

4.6. Origins of major ions in rainwater

Spearman's rank correlation analysis, Principal Component Analysis, marine and crustal enrichment factors, sea salt fractions and non-sea salt fractions are useful tools to decipher and to assess the the origins of pollutants and to decipher the interactions and relationships amongst gases, particles, and ionic compounds. The significant correlation coefficients between certain ions can indicate their sources in general, but in most cases the local specificities can also be explained. The results of all above-mentioned methods were similar. In most cases, a significant correlation between Na^+ and K^+, Ca^{2+}, and Mg^{2+} indicates the presence of alkali plagioclase feldspars, that are rich in sodium and potassium, phyllosilicates and amphiboles, which can be frequently found in the Eastern Carpathians, showing the volcanic origins of these mountains (Szép et al., 2018). Another significant correlation coefficient can be found between Na^+ and Cl^-, which usually indicates the marine influence in rainwater, moreover, sodium is often used as a marine tracer element, due to its content in seawater, silicate and halite rocks (Szép et al., 2018). In the Eastern Carpathians this correlation coefficient may also indicate the presence of moffette gas, salt mines and mineral springs. According to Rao et al., (2017), chloride can be found in enriched form in seawater, halite rocks and pollutants originated from anthropogenic activities. A good correlation between Cl^- and SO_4^-, NO_3^-, and NO_2^- can indicate the presence of anthropogenic sources (coal combustion, refuse incineration, biomass burning) (Rao et al., 2017). If SO_4^{2-} and Cl^- correlates well in areas where non sea-salt chloride has high values, it may indicate emissions from the metallurgic industry, known for coal combustion and use of Cl^- (Xu et al., 2009). Alkaline ions, such as Ca^{2+}, K^+ and Mg^{2+}, which are known as essential soil components, are very effective neutralizing agents. A significant correlation between calcium and magnesium implies their common origin, such as the dissolution/weathering of calcite, dolomite and limestone, the presence of open quarries, and/or cement factories (Niu et al., 2014; Rao et al., 2017; Szép et al., 2018; Xiao, 2016). Significant correlations between major cations and anions indicate that acid pollutants can be absorbed by the particulate matter and react with alkaline compounds (Pu et al., 2017). Positive correlation between Ca^{2+} and SO_4^{2-} and Na^+ and SO_4^{2-} may be an indicator to the weathering process of gypsum or to the presence of other evaporitic salts, such as mirabilite and thernadite (Stoiber and Rose, 1974; Wu et al., 2014). The above-mentioned compounds are an indicator of volcanic fumaroles and post volcanic activity. Also, a positive correlation coefficient between cations like calcium, magnesium and potassium may suggest their common origin from terrestrial/ crustal sources (Mouli et al., 2005).

In their study, Jiang and Yan, (2010), suggested that a strong correlation coefficient between conductivity and calcium and bicarbonate indicates the interrelationship among water and rocks, resulting in limestone and dolomite dissolution. The presence of sylvite (KCl) is indicated by the strong correlation between potassium and chloride, which may be present in soil minerals, blown into the atmosphere, and dissolved in rainwater (Rao et al., 2017). Positive correlations between NH_4^+ and SO_4^{2-} may occur due to the chemical reactions in the atmosphere (Zhang et al., 2007). In general, ammonia is present in the atmosphere under the form of $(NH_4)_2SO_4$, NH_4HSO_4 and NH_4NO_3, being the result of chemical reactions with H_2SO_4 and HNO_3 (Gong et al., 2013). In general, a positive correlation between NH_4^+ and K^+ can be attributed to the excessive use of N type fertilizers, cattle waste deposits, agricultural activities and biomass burning. Another tracer of agricultural activities is the significant correlation between NH_4^+ and NO_3^-. Significant correlations between SO_4^{2-} and NO_3^- are indicators of industrial activities, traffic and coal combustion (Y. Z. Cao et al., 2009). A significant negative correlation coefficient among pH values, sulfate and nitrate may indicate the effects of acidic compounds on pH value and rainwaters acidity.

4.7. The Foehn effect in the Southern Carpathians

By analyzing the sea salt factors and non-sea salt factors in the Southern Carpathians, the lack of marine salts were observed in the rainwater samples collected in this area. The highest Cl^- SSF value was calculated for RS, being only 35%, while at BH and MN its values were even smaller, exhibiting 20.23% and 26.77%. This may be occurring due to the presence of Foehn winds. The precipitation amounts and their distribution upon the Balkan peninsula were analyzed, considering the cyclonic circulations too in the eastern Mediterranean basin during the 1979-2018 period. Air masses travelling from N-Europe to the Mediterranean Sea in the Gulf of Genova lead to cyclogenesis, enhancing baroclinic conditions (the dominant mechanism shaping cyclones and anticyclones). The cyclones born in this area usually travel from W to E, crossing the Dinaric Alps, towards the Balkans. As they travel towards the east, their humidity content is constantly decreasing due to the orographic barrier imposed by the high elevated terrain in this area. In terms of absolute frequency, these synoptic types are more frequent in the winter, spring and autumn and less in the summertime, when anticyclonic conditions are usually prevalent upon Europe. As a result of the orographic lifting the sea salts concentration in the precipitation is affected due to the adiabatic processes on the windward slopes of Dinaric Alps. This also has effects upon the temperature in the airmass since the descending air on the leeward side will be warmer and subsequently drier due to the adiabatic compression.

4.8. Zonal circulations, zonal index, and chemical composition of air masses

The influence of airmasses travelling from NW, NE, SW and SE Europe, and the contribution of long-range transported pollutants on rainwater collected in the Northern group of the Eastern Carpathians, is assessed using ZI and MI daily values, which are subsided in 8 groups depending on their direction. In general, trajectories such as N-S or W-E are given by the positive or negative phases of ZI and MI, while for directions such as NE, NW, SE, and SW, secondary directions are observed. For example, the NW direction is characterized by a positive ZI and a negative MI, while SE direction can be recognized by a negative ZI and a positive MI. Rainwater chemistry data collected at BM was examined using this technique. Rainfall events were grouped into four groups, depending on their ZI and MI value. Therefore, 82 rainwater events were counted to be originating from NW, 12 as originating from NE, 51 as originating from SW and 56 as coming from SE, while 85 events were catalogued as of mixed/uncertain origin, accounting to the total of 286 rainfall events recorded at BM. To assess the imprint of long-range transported pollutants, the volume weighted means of major ions measured under each above-mentioned direction were compared to the VWMs of major ions measured for the entire database. The VWMs of sulfate registered in case of SE and NE directions exhibited 184.38 μeq l^{-1} and 155.76 μeq l^{-1}, respectively, which are significantly higher than the VWM for the entire studied period (142.66 μeq l^{-1}). The NW and SW advection types presented more similar sulfate VWM values to the overall VWM, measuring 132.66 μeq l^{-1} and 135.82 μeq l^{-1}, respectively, showing that although SE and NE advection types are the least dominant. Air masses coming from these directions transport more acidifying pollutants than the NW and SW directions. A possible explanation to these differences may be the industrial activities in non-EU member countries (Ukraine, Russia), which operate under different environmental laws and regulations, while the air-masses originating from the Balkan Peninsula and southwestern Romania can be loaded with higher concentrations of acidic compounds due to the presence of unmodernized industrial sites. Spearman correlation analysis was also applied to the data extracted with the use of MI and ZI values. Strong correlation coefficient (r=0.56) was observed between chloride and sodium for NW advection type, sustaining the air masses that originate from the Atlantic Ocean. Marine and non-marine fractions were also assessed, sustaining that chloride is originated from sea spray, having the following values for NW, SW, SE and NE directions: 93.54%, 91.49%, 65.90% and 84.30%. As it can be observed, lower values of SSF were registered for SE and NE directions, which may be due to the continental influences, such as the Siberian Anticyclone, hence the variability of rainwater chemistry is largely controlled by the magnitude of dominant air masses.

Thesis statements

The thesis presents a comprehensive analysis on the chemical composition of precipitation, performed in the Romanian Carpathians, Europe, and the contiguous U.S.

1. Analyzing the data, the orographic barrier and atmospheric circulations can be easily observed. The drainage works, the loss of evapotranspiration, and the local anticyclonic conditions led to the decrease of precipitation amount in the last decades. Very stable local anticyclonic systems and the orographic barrier of the Eastern Carpathians may lead to the occurrence of long drought periods.

2. In the northern group of the Eastern Carpathians data shows the influence of long-range transported pollutants, by applying a meteorological technique (the zonal and meridional index) in the field of precipitation chemistry. This can be useful to show the effect of different polluting sources in countries outside the European Union, that have different environmental legislation and regulations.

3. In the Southern Carpathians, the assessment of rainwater chemistry showed that in some relief conditions, atmospheric circulations and the main air mass transport routes may be influenced by meteorological phenomena, as in this case the Foehn effect. This can be frequently observed on the leeward slopes of the Dinaric Alps, when air masses travelling thru the mountainous chain and Balkan Peninsula are desiccated of their humidity, fact that is also felt in the chemical composition of precipitation.

4. The comprehensive assessment targeting 27 European countries highlighted the importance of environmental protection and the unitary appliance of environmental legislation.

5. The analysis made on the data collected in the contiguous US over a period of 40 years, highlighted the interconnections and differences between the studied areas, The results that were obtained may provide an overview to environmental specialists and political decision makers of the current situation and may be of great help in further analyses or studies, that evaluate the effects of the implementation of environmental regulations on the chemical composition of the atmosphere.

Publications related to the thesis

N°	Article	IF	AIS
1	Szép R, Mateescu E, Nechifor AC, **Keresztesi Á** (2017) Chemical characteristics and source analysis on ionic composition of rainwater collected in the Carpathians "Cold Pole," Ciuc basin, Eastern Carpathians, Romania. *Environmental Science and Pollution Research* **24**: 27288–27302. https://doi.org/10.1007/s11356-017-0318-2	4.223	0.520
2	**Keresztesi Á**, Petres S, Ghita G, Dumitru FD, Moncea MA, Ozunu A, Szép R (2018) Ammonium neutralization effect on rainwater chemistry in the basins of the Eastern Carpathians-Romania. *Revista de Chimie* **69**: 57–63.	1.755	0.064
3	Szép R, Mateescu E, Niță IA, Birsan MV, Bodor Z, **Keresztesi Á** (2018) Effects of the Eastern Carpathians on atmospheric circulations and precipitation chemistry from 2006 to 2016 at four monitoring stations (Eastern Carpathians, Romania). *Atmospheric Research* **214**: 311–328. https://doi.org/10.1016/j.atmosres.2018.08.009	5.369	1.010
4	Szép R, Bodor Z, Miklóssy I, Niță IA, Oprea OA, **Keresztesi Á** (2019) Influence of peat fires on the rainwater chemistry in intra-mountain basins with specific atmospheric circulations (Eastern Carpathians, Romania). *Science of the Total Environment* **647**: 275–289. https://doi.org/10.1016/j.scitotenv.2018.07.462	7.963	1.119
5	**Keresztesi Á**, Boga R, Bodor Z, Bodor K, Tonk S, Deák G, Nita IA (2019) The Analysis of the Chemical Composition of Precipitation During the Driest Year from the Last Decade. *Present Environment and Sustainable Development* **13**: 19–32. https://doi.org/10.2478/pesd-2019-0002	0	0
6	**Keresztesi Á**, Birsan MV, Nita IA, Bodor Z, Szép R (2019) Assessing the neutralisation, wet deposition and source contributions of the precipitation chemistry over Europe during 2000–2017. *Environmental Sciences Europe* **31**: 50. https://doi.org/10.1186/s12302-019-0234-9	5.893	0
7	Birsan MV, Micu DM, Niță IA, Mateescu E, Szép R, **Keresztesi Á**, (2019) Spatio-temporal changes in annual temperature extremes over Romania (1961–2013). *Romanian Journal of Physics* **64**: 816.	1.888	0.194
8	**Keresztesi Á**, Nita I, Birsan MV, Bodor Z, Szép R, (2020) The risk of cross-border pollution and the influence of regional climate on the rainwater chemistry in the Southern Carpathians, Romania. *Environmental Science and Pollution*	4.223	0.520

N°	Article	IF	AIS
	Research **27**: 9382–9402. https://doi.org/10.1007/s11356-019-07478-9		
9	**Keresztesi Á**, Nita IA, Birsan MV, Bodor Z, Pernyeszi T, Micheu MM, Szép R (2020) Assessing the variations in the chemical composition of rainwater and air masses using the zonal and meridional index. *Atmospheric Research* **237**: 104846. https://doi.org/10.1016/j.atmosres.2020.104846	5.369	1.010
10	Birsan MV, Nita IA, Craciun A, Sfîcă L, Radu C, Szep R, **Keresztesi Á,** Micheu MM (2020) Observed changes in mean and maximum monthly wind speed over Romania since AD 1961. *Romanian Reports in Physics* **72**: 702.	1.785	0.170
11	Nita IA, Sfica L, Apostol L, Radu C, **Keresztesi Á**, Szep R (2020) Changes in cyclone intensity over Romania according to 12 tracking methods. *Romanian Reports in Physics* **72**: 706.	1.785	0.170
12	**Keresztesi Á,** Nita IA, Boga R, Birsan MV, Bodor Z, Szép R (2020). Spatial and long-term analysis of rainwater chemistry over the conterminous United States. *Environmental Research* **188**: 109872. https://doi.org/10.1016/j.envres.2020.109872	6.498	1.218
13	Bodor Z, Bodor K, **Keresztesi Á,** Szép R (2020) Major air pollutants seasonal variation analysis and long-range transport of PM_{10} in an urban environment with specific climate condition in Transylvania (Romania). *Environmental Science and Pollution Research* **27**: 38181–38199. https://doi.org/10.1007/s11356-020-09838-2	4.223	0.520
	Total	**50.974**	**6.515**

ISI Proceedings & Publications in international databases

1. **Keresztesi Á**, Korodi A, Boga R, Ghita G, Ilie M, Petres S (2017) Chemical characteristics of wet precipitation in the Eastern Carpathians, Romania. ECOTERRA - J. Environ. Res. Prot. 14, 52–59.

Complementary publications (not related to the topic of the thesis)

N°	**Article**	**IF**	**AIS**
1	Petres S, Lanyi S, Piriianu M, **Keresztesi Á**, Nechifor AC (2018) Evolution of Tropospheric Ozone and Relationship with Temperature and NOx for the 2007-2016 Decade in the Ciuc Depression. *Revista de Chimie* **69**: 601–608.	1.755	0.064
2	Rápó E, Szép R, **Keresztesi Á**, Suciu M, Tonk S (2018) Adsorptive removal of cationic and anionic dyes from aqueous solutions by using eggshell household waste as biosorbent. *Acta Chimica Slovenica* **65**: 709–717. https://doi.org/10.17344/acsi.2018.4401	1.735	0.151
3	Micheu MM, Birsan MV, Szép R, **Keresztesi Á**, Nita IA (2020) From air pollution to cardiovascular diseases: the emerging role of epigenetics. Molecular Biology Reports **47**: 5559–5567. https://doi.org/10.1007/s11033-020-05570-9	2.316	0.40
4	Micheu MM, Birsan MV, Nita IA, Andrei MD, Nebunu D, Acatrinei C, Sfica L, Szép R, **Keresztesi Á**, F-dez. de Arróyabe Hernáez P, Onciul S, Scafa-Udriste A, Dorobantu M (2021) Influence of meteorological variables on people with cardiovascular diseases in Bucharest, Romania (2011-2012). *Romanian Reports in Physics* 73 (707).	1.785	0.170
5	Boga R, **Keresztesi Á**, Bodor Z, et al (2021) Influence of rising air temperature and solar radiation on the tropospheric ozone in the Ciuc Basin, Romania. *Romanian Journal of Physics* 66, 805.	1.888	0.194
6	Boga R, **Keresztesi Á**, Bodor Z, Tonk S, Szép R, Micheu MM (2021) Source identification and exposure assessment to PM10 in the Eastern Carpathians, Romania. *Journal of Atmospheric Chemistry 78 (77-97).*	2.158	0.73
7	Bodor K, Micheu MM, **Keresztesi Á**, Birsan MV, Nita IA, Bodor Z, Petres S, Korodi A, Szép R (2021) Effects of PM10 and Weather on Respiratory and Cardiovascular Diseases in the Ciuc Basin (Romanian Carpathians). Atmosphere 12 (289). https://doi.org/10.3390/atmos12020289	2.686	0
8	Kósa CsA, Nagy K, Szenci O, Baska-Vincze B, Andrásofszky E, Szép R, **Keresztesi Á**, Mircean M, Taulescu M, Kutasi O (2021) The role of selenium and vitamin E in a Transylvanian enzootic equine recurrent rhabdomyolysis syndrome. Acta Veterinaria Hungarica 69 (3).	0.955	0

9	Elena HOLBAN, Gyorgy DEAK, Răzvan MATACHE, Tiberius DĂNĂLACHE, Monica MATEI, Mădălina BOBOC, Marius RAISCHI, Ionuț GHEORGHE, Ágnes KERESZTESI , Ferenc KILÁR, IDENTIFICATION OF STURGEON BEHAVIOR IN DIFFERENT HYDROMORPHODYNAMIC CONDITIONS RESULTING FROM THE IMPLEMENTATION OF HYDROTECHNICAL ARRANGEMENTS, International Journal of Conservation Science, In press, 2022.	0	0
10	György DEÁK, Natalia ENACHE, Lucian LASLO, Anda ROTARU, Monica MATEI, Madalina BOBOC, Cristina SILAGHI, Sorina CALIN, Ágnes KERESZTESI, Ferenc KILÁR, CO2 EFFLUX MEASUREMENTS ON AQUATIC AND TERRESTRIAL ECOSYSTEMS IN THE CONTEXT OF CLIMATE CHANGE, International Journal of Conservation Science, In press, 2022.	0	0
	Total	**15.278**	**1.709**

ISI proceedings & Publications in international databases

1. Korodi A, Petres S, **Keresztesi Á**, Szép R (2017) Sustainable Developement. Theory or Practice? SGEM2017 17th Int. Multidiscip. Sci. GeoConference 54. https://doi.org/10.5593/sgem2017/54/s23.049
2. Ilie M, Deák G, Anghel AM, **Keresztesi Á**, Mărcuș IM (2017) Mathematical modelling of pollutant dispersion in atmosphere resulting from an asphalt mixture preparation plant, in: International Multidisciplinary Scientific GeoConference Surveying Geology and Mining Ecology Management, SGEM. https://doi.org/10.5593/sgem2017H/43/S19.054
3. Petres S, Boga R, **Keresztesi Á,** Ghita G, Ilie M, Deák Gy (2017) Comparative study of air temperature evolution in the Ciuc depression, *ECOTERRA – Journal of Environmental Research and Protection*, 14(2), 60-69.
4. Boga R, Korodi A, **Keresztesi Á,** Ghita G, Ilie M, Deák Gy (2017) Tropospheric ozone temporal variations and relationship to atmospheric oxidation, *ECOTERRA – Journal of Environmental Research and Protection*, 14(2), 44 – 51.
5. Dumitru FD, Panait AM, Olteanu MV, Holban E, Deák Gy, Szép R, **Keresztesi Á** (2017) Assessing the preservation state of a Romanian historic concrete icon – the Constanta Casino, *Ecoterra*, Volume: 14, Issue: 3, pp. 1-7.
6. Raischi SN, Balaceanu CN, Raischi M, Dumitru FD, Moncea A, Laslo L, Deák Gy, **Keresztesi Á** (2018) Air Pollution Analysis in Moldova Noua Waste Dump, *ECOTERRA – Journal of Environmental Research and Protection*, 14(2), 70-77.

Posters and presentations related to this thesis

1. **Keresztesi Á**, Szép R, Boga R, Korodi A, Petres S, Miklóssy I (2017) Precipitation Chemistry in The Ciuc Basin. *International Symposium, Present Environment and Sustainable Development*, Book Of Abstracts, P. 46–47, 2-4 June 2017, Iasi [presentation].
2. Szép R, **Keresztesi Á**, Korodi A, Petres S, Miklóssy I, Boga R (2017) Calitatea Aerului În Depresiunea Ciucului - Realitate Și Percepție. *International Symposium, Present*

Environment and Sustainable Development, Book Of Abstracts, P. 87–88, 2-4 June 2017, Iasi. [presentation]

3. Szép R, **Keresztesi Á**, Boga R, Korodi A, Petres S, Schimbări Cliatice. Realitate Și Percepție. *Conferința Internațională, Fenomene Meteo Extreme Și Sisteme De Avertizare Timpurie În Contextul Managementului Riscului Dezastrelor Naturale*, București, 16-17 October 2017 - [presentation]
4. **Keresztesi Á**., Szép R., Boga R., Korodi A., Petres S., Schimbări Climatice În Depresiunea Ciucului. *Conferința Internațională, Centrul Educațional Privind Adaptarea La Efectele Schimbărilor Climatice Perspective și Cooperare la Nivel Național și European*, Târgu-Mureș, 18-19 October 2017. [presentation]
5. **Keresztesi Á**, Szép R, Boga R, Korodi A, Petres S,(2021) Climate Change effects on ecosystems in the Ciuc Basin..*International Conference on Natural Ecosystems and Climate Change Adaptation Needs*, Brasov, 20-21 October 2017. [presentation]
6. **Keresztesi Á**, Szép R, Boga R, Bodor Zs, Miklóssy I (2012) Precipitation Chemistry And The Influence Of Different Sources On The Ionic Composition Of Rainwater Collected In Harghita County, Romania. *XXIII-th International Conference Of Chemistry*, 25-28 October 2017, Deva, Romania. [presentation]
7. **Keresztesi Á**, Szép R, Bodor Zs, Péter H (2018) Variabilitate în Chimia Precipitațiilor în Depresiunile Intra- și Extra-Montane, *International Symposium, Present Environment and Sustainable Development*, 1 – 3 June 2018, Iasi, Romania [presentation]
8. **Keresztesi Á**, Szép R, Bodor Zs, Boga R, Tonk Sz, Nita IA (2018) The Dinaric Alps Foehn Effect on The Ionic Composition Of Rainwater Collected In Caras-Severin County, Romania. *24th International Conference On Chemistry, Sovata Bai, Romania*, 24-27 October 2018. [presentation]
9. **Keresztesi Á,** Szép R, Birsan MV, Nita IA, Bodor Zs, Assessing The Chemical Composition Of Precipitation Over The European Continent During The Last Two Decades, *21st Edition Of The Scientific Research And Education In The Air Force International Conference (AFASES 2019)*, 28 May – 02 June 2019, Brasov, Romania. [presentation]
10. Bodor Zs, Bodor K, Szep R, **Keresztesi Á** (2019) Seasonal variation and long-range transport of major air pollutants in the Ciuc Basin (Romania) with specific climate condition. *XIX International Multidisciplinary Scientific Geoconference SGEM 2019*, 28 June – 7 July, 2019, Albena, Bulgaria - International Scientific Geoconference SGEM2019 [poster]
11. **Keresztesi Á**, Szép R, Bodor Z, Bodor K, Schmutzer G, Bálint K (2020) Long-term analysis of rainwater chemistry over the European continent, 26th International Conference on Chemistry, October 30th. [presentation]
12. **Keresztesi Á**, Szép R, Bodor Z, Bodor K, Tánczos S (2021) Long-term analysis of rainwater chemistry over the conterminous United States, 27th International Conference on Chemistry, October 29th. [presentation]

Posters and presentations not related to this thesis

1. Boga R, Szép R, Korodi A, **Keresztesi Á** (2017) Tropospheric ozone temporal variations and relationship to atmospheric oxidation. International Symposium. *Present Environment and Sustainable Development*, 2-4 June 2017 Iasi. Book of Abstracts, p. 72-73. [presentation]

2. Bodor K, Bodor Z, Boga R, **Keresztesi Á** (2019) Time series analysis from 2008 to 2018 of PM10 evaluation of Bucharest region, Romania. *The 14th Edition of Present Environment and Sustainable Development International Conference*, Iași, 2019. [presentation]
3. Bodor K, Bodor Z, Szép R, **Keresztesi Á**, Szép A (2020) Characterization of some bottled Romanian mineral waters on the basis of the total mineral content, 26th International Conference on Chemistry, October 30th. [presentation]
4. Bodor K, Bodor Z, Szép A, Szép R, **Keresztesi Á** (2021) Human health impact assessment and time series analysis of lead content of PM10 particulate matter in Copsa Mică Romania, 27th International Conference on Chemistry, October 29th. [presentation]

Awards and merit scholarships

Awards

1. BEST PRESENTATION AWARD: Bodor Zs., Bodor K, Szep R, **Keresztesi Á** (2019) Seasonal variation and long-range transport of major air pollutants in the Ciuc Basin (Romania) with specific climate condition. *XIX International Multidisciplinary Scientific Geoconference SGEM 2019*, 28 June – 7 July 2019, Albena, Bulgaria. [poster]
2. SPECIAL AWARD: **Keresztesi Á**, Szép R, Bodor Z, Bodor K, Schmutzer G, Bálint K (2020) Long-term analysis of rainwater chemistry over the European continent, 26th International Conference on Chemistry, October 30th. [presentation]
3. 2nd PLACE: Bodor K, Bodor Z, Szép R, **Keresztesi Á**, Szép A (2020) Characterization of some bottled Romanian mineral waters on the basis of the total mineral content, 26th International Conference on Chemistry, October 30th. [presentation]

Scholarships

1. Székely Forerunner Fellowship, 2018
2. Collegium Talentum Scholarship for 2020/2021 school year.
3. New National Excellence Program (Új Nemzeti Kiválóság Program) Scholarship for 2020/2021 school year.
4. New National Excellence Program (Új Nemzeti Kiválóság Program) Scholarship for 2021/2022 school year.

Scientific impact

- Cumulative Impact Factor (IF): **66.252**
- Impact Factor / No. of authors: **50.326**
- Cumulative Article Influence Score (AIS): **8.224**
- Hirsch index (Web of Science): **10**
- Citations (Web of Science): **319 total**
- ISI indexed publications: **25 total (12 as first/corresponding author)**
- Total participation to international and national conferences: **13**