

Ammonium Neutralization Effect on Rainwater Chemistry in the Basins of the Eastern Carpathians - Romania

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A study of precipitation chemistry was conducted from 2006 January to 2016 November in the Ciuc and Giurgeu basin, Eastern Carpathians, Romania. The results show that the natural precipitation in these areas is alkaline, with a volume weighted mean (VWM) of 6.49 and 6.88 in Ciuc and Giurgeu basin, respectively. NH_4^+ is the most potential species to completely neutralize the rainwater over the Miercurea Ciuc (Ciuc basin) and Toplita (Giurgeu basin) area. However, in the case of Miercurea Ciuc, Ca^{2+} is also a potential neutralizer. Annual mean percentage concentration of NH_4^+ within the total principal cations is also proof that ammonium dominates the rainwater chemistry in the atmosphere of the studied basins. A comparison between the annual mean deposition fluxes showed that in the Giurgeu basin concentrations of NH_4^+ are higher than in the Ciuc basin. Calculations of the neutralization factors (NFs) show that at both sampling sites NH_4^+ contributed the most to the neutralization process. Ammonium availability index (AAI) has a value of 156.44% and 179.11% for Miercurea Ciuc and Toplita, respectively, indicating excess ammonium over the neutralization value. Fractional acidity (FA) was calculated, indicating that in Miercurea Ciuc 98.74% and in Toplita 99.28% of the rainwater acidity was neutralized. Calculation of the original and measured acidity also showed the neutralization capability of NH_4^+ . Contributions of the marine and non-marine salts and enrichment factors were estimated, helping to identify the possible sources of the major ions in the atmosphere.

Keywords: ammonium neutralization effect, alkalinity, eutrophication, rainwater chemistry, ionic species

Acidic precipitation is the term used to describe rainfall that has a pH level of less than 5.6, and currently is a subject of great controversy because of the damage it does to the environment and property worldwide, being intensely studied. Increased industrialization and urbanization lead to the atmospheric acidity which causes acid rain.

However, in the Ciuc and Giurgeu basins, Eastern Carpathians, Romania, the nature of rainwater has been observed to be alkaline. Natural rains are generally considered as weakly acidic [1]. The buffering acidity by soil-derived species which are rich in Ca, coming from dissolution of calcareous and dolomite rocks in the studied area, and also the ammonia emanations from fertilizers and animal manure are the main cause for the alkaline nature of rainwater. Rainwater collected in Toplita, Giurgeu basin is more alkaline than the rainwater collected in Miercurea Ciuc, Ciuc basin. The weaker neutralizing capacity in Miercurea Ciuc, may be due to the higher industrialization, with higher values of acidic compounds such as emissions of SO_2 and NO_x . The precipitation acidity is controlled by the acidic and basic ionic concentrations. In the atmosphere, the main acids are H_2SO_4 and HNO_3 ; the main bases are NH_3 and CaCO_3 [2]. NH_3 is the most abundant gas-phase alkaline species in the atmosphere [3], and can produce NH_4NO_3 , NH_4HSO_4 , and $[\text{NH}_4]_2\text{SO}_4$ through a series of complex multi-phase interactions with SO_2 and NO_x [2]. Another frequently discussed problem is the eutrophication of terrestrial and aquatic ecosystems, mainly caused by gaseous ammonia and ammonium

compounds, which can be deposited from the air by wet and dry depositions, increasing the nitrogen input [4]. The use of N based fertilizers and livestock breeding also contributes to higher concentrations of NH_4^+ in rainwater. In soil, NH_4^+ contributes to acidification of ecosystems by nitrification. According to Erisman (1993) 1 mol of NH_4^+ can release of 2 mol of H^+ [5]. A study conducted by Behera et al. in 2013 showed that Europe is one of the regions with the highest ammonia emanations beside the Indian subcontinent, China and South America [24]. It is estimated, that over 80% of the global ammonia emissions are from agricultural activities, 11% from biomass burning and 8.3% from industries and traffic [24].

Ammonium has a great influence on rainwater acidity and the ecosystems. In this paper, the wet flux deposition values of ammonium, neutralization, the ammonium availability index and correlation coefficients between NH_4^+ and other ionic species are analyzed, to show the influences of ammonium on the rainwater chemistry in the Ciuc and Giurgeu basin.

Experimental part

Materials and methods

Sampling site

Rainwater samples were collected at two locations, Miercurea Ciuc and Toplita, Eastern Carpathians, Romania, Harghita county, on an event basis, for eleven years.

Miercurea Ciuc (46°22'N, 25°44'E, elevation ~600 m) is situated in the Ciuc basin, which has tectonic-erosive origin,

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located in the central part of the Eastern Carpathians. It is an intra-Carpathian enclosed basin, which lies between the Harghita Mountains (1800m) and the Ciucului Mountains (1300 – 1400 m), being drained by the Upper Olt. The Ciuc basin has specific topographical and climate conditions, such as persisting atmospheric static stability and nocturnal thermal inversions, especially during winter period [6].

Toplita (46°55' N, 25°22' E, elevation 687 m) is located in eastern Transylvania on the upper reaches of the Mures, more precisely in the northwestern corner of Harghita County. It is situated in the Giurgiu basin flanked by the mountains of Giurgiu, Gurghiu and Călimani. Due to its geographical position, Toplita's climate is humid and cold. As in the case of the Ciuc basin, nocturnal thermal inversions are frequent and persisting.

In areas characterized by a mountain climate, summers are chilly, with abundant precipitations, and cold winters with snow for long periods. In intra-mountain depressions, the specific topo climate with frequent nocturnal thermal inversions, which can be characterized by low temperatures, high relative humidity and stable air circulations [31], make these areas the coldest in Romania.

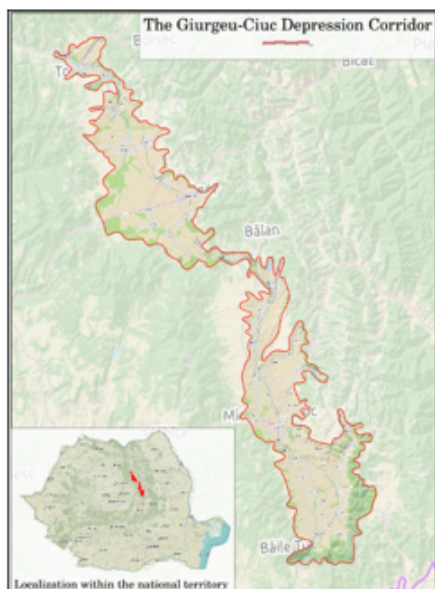


Fig 1. Sampling site locations, Ciuc and Giurgiu basin, Eastern Carpathians, Romania

Lower evapotranspiration, due to groundwater drainage works conducted during the 60's and 70's, increased the static stability of the atmosphere, which caused longer thermal inversion episodes [27-29]. During these periods, the lack of vertical and/or horizontal mixing of air masses, can cause them to persist for days, limiting the dilution process of air pollutants in the basin, hence the accumulation of pollutants occurs [33, 34]. Drainage works and the soil water decrease has led to the degradation of peaty and acidophilic soils, leading to changes in ecosystems, such as the appearance of invasive allochthone species [30]. During thermal inversion periods, the concentrations of ozone and particulate matter suspension increases in many cases above the limit accepted by the European Directives [30]. An increase in the ozone concentrations can seriously affect the vegetation and human health [35]. These above-mentioned facts in the past few years led to a constantly growing concern regarding the inversion phenomenon in areas such as the Ciuc and Giurgiu basins [32].

Miercurea Ciuc is the county seat with ~38.000 inhabitants, pollution is mainly caused by emissions from small scales industries, road traffic, biomass burning, agricultural activities and livestock breeding. Toplita is a small city, with only ~13.000 inhabitants, it is not very

industrialized. The area around the sampling sites is dominated by agricultural activities and livestock breeding, explaining the emissions from N-fertilizers applied to the agricultural fields [7] and from the deposits of natural animal manure, used as fertilizers. Biomass burning is also an important source of NH_4^+ in the rainwater, and it is due to the process of heating with wood-based dwellings. Both studied basins have numerous peat bogs and deposits. In period of drought, their ignition causes peat fires, emitting large concentrations of NH_4^+ to the atmosphere.

Rainwater collection and chemical analysis

The collection of rainwater was conducted between January 2006 and November 2016. During the eleven years, 362 and 118 samples were collected at Miercurea Ciuc and Toplita, respectively, using wet-only collectors containing 24 h integrated samples, being replaced daily. After each collection, pH was immediately measured, using digital pH meters. The biological degradation of the samples was avoided by adding a small amount of thymol to all the samples. After removing the insoluble particles by filtering the samples, they were refrigerated at 4°C. Ion composition analysis (SO_4^{2-} , NO_3^- , NO_2^- , Cl^- , NH_4^+ , Ca^{2+} , Na^+ , K^+ , Mg^{2+}) was then conducted, using atomic absorption (AAS, Perkin Emler, model 2380, Air/C₂H₂, 422.7 nm) and atomic emission techniques (AAS, Perkin Emler, model 2380, Air/C₂H₂, 589 nm), to quantitatively determine the anions and cations in the rainwater. The Cl^- and NH_4^+ were measured by U-VIS spectrometer method (Nicolet Evolution 100, 463 and 440 nm).

Ion balance technique was used to verify the completeness and correctness of the chemical analysis. The quality of analytical data of water soluble ionic species collected at the sampling sites is shown by the ionic ratio between measured anions and cations. If all the major anions and cations are analyzed, the ratio is expected to be closed to unity [8]. However, according to Keene, data is generally considered acceptable if the ion imbalances that does not exceed $\pm 25\%$ [9]. Missing anions, like HCO_3^- was calculated to lower the deviations from unity. However, the ratio was found to be 0.64 ± 0.42 and 0.69 ± 0.44 for Miercurea Ciuc and Toplita, respectively. This means that there are missing weak organic acids (HCOO^- , CH_3COO^- , $\text{C}_2\text{O}_4^{2-}$) and F^- , PO_4^{3-} , these anions could not be measured directly because of analytical limitations in the present study [8].

Results and discussions

The results of pH measurement for every precipitation event in Miercurea Ciuc and Toplita from 2006 to 2016 indicate that the precipitation in the Eastern Carpathians is alkaline, with a pH volume weighted mean (VWM) of 6.49 and 6.88, and an average of 6.57 and 6.87, respectively. Spearman correlation analysis between the pH of precipitation and its conductivity is not significant for Miercurea Ciuc ($R = 0.282$), while for Toplita the correlation is significant ($R = 0.493$). The statistical analysis of the rainwater compositions, including the volume-weighted mean (VWM), average, minimum, maximum and standard deviation values, showed that among the analyzed ionic species NH_4^+ has the greatest VWM concentration in the case of both sampling sites (Miercurea Ciuc- VWM=158.04 $\mu\text{eq/L}$, range of 1.86-1823.33; Toplita -VWM=407.40 $\mu\text{eq/L}$, range of 11.64-1851.87).

The VWM concentrations of the major ionic species were in the following order for Miercurea Ciuc: $\text{NH}_4^+ > \text{Ca}^{2+} > \text{SO}_4^{2-} > \text{Cl}^- > \text{HCO}_3^- > \text{NO}_3^- > \text{Na}^+ > \text{K}^+ > \text{Mg}^{2+} > \text{NO}_2^- > \text{H}^+$, showing that the two most dominant ions were

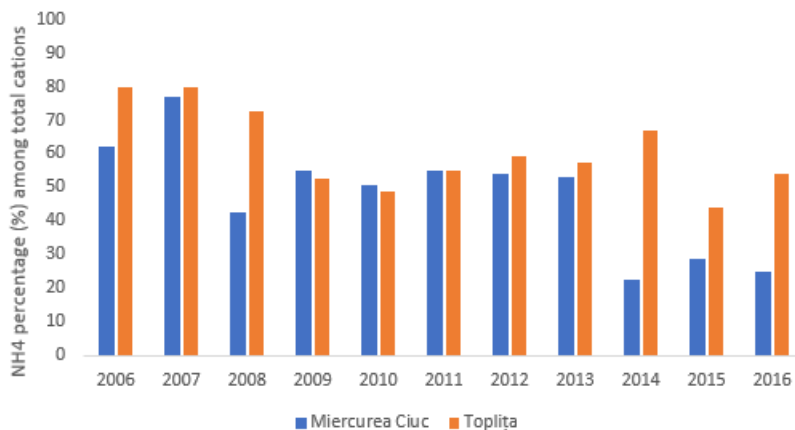


Fig. 2 Annual mean percentage concentration of NH₄⁺ within the total principal cations

NH₄⁺ and Ca²⁺. The NH₄⁺ concentration represented ~54% of the total cations measured. For Toplita, the VWM concentrations of the major ionic species followed the NH₄⁺ > Ca²⁺ > SO₄²⁻ > HCO₃⁻ > Cl⁻ > K⁺ > Na⁺ > NO₃⁻ > Mg²⁺ > NO₂⁻ > H⁺ downward order. The most abundant ion was NH₄⁺, with a concentration accounted for ~66% among total cations. For a more detailed analysis, NH₄⁺ VWM percentage concentrations were calculated within the total principal cations (Na⁺, K⁺, Ca²⁺, Mg²⁺) for the two sampling sites over eleven years. The results are shown in figure 2. The trends indicate higher NH₄⁺ concentration values for Toplita than for Miercurea Ciuc. Most of the years reported values over 50%, notably for the years of 2006, 2007, 2008 and 2014 for Toplita, while for Miercurea Ciuc, the years 2006 and 2007 represented the highest values, in 2014, 2015 and 2016 these values were just slightly above 20%. A decline in the concentration of the NH₄⁺ ion is due to the ~3 times higher Ca²⁺ VWM concentrations measured in the last three years of the studied period.

Ammonia can directly deposit to the ecosystem, or neutralize acidic components [24]. In addition, ammonia and ammonium species impact nitrogen sensitive landscapes [25] and can harm the ecosystem. In areas such as Ciuc and Giurgeu basins, where acidic soils and acidophilic vegetation is characteristic, excess ammonia and ammonium causes changing in the autochthone vegetation, leading to the disappearance of some species. The NH₃ and NO₂ emissions data measured at the Harghita County Environmental Protection Agency's headquarters are shown in figure 3. A decline in the NO₂ emissions can be observed during the analyzed period. NH₃ emissions are relatively constant, with the exception of 2012, when peat fires in the Ciuc and Giurgeu basin caused a great increase of the NH₃ concentration in the atmosphere. NH₃ can react with acidic SO₄²⁻ and NO₃⁻ to form particulate ammonium sulfate [(NH₄)₂SO₄] and ammonium nitrate (NH₄NO₃) [19]. A decline in the NO_x and SO₂ emission

causes less acidic SO₄²⁻ and NO₃⁻, therefore, a reduction in the reactions with NH₃ will occur [25]. This may be an explanation to the increase in the NH₃ concentrations. Nitrogen can be lost from the soil in the form of ammonia gas. The excessive use of N type fertilizers, such as urea and nitrates, can lead to ammonia volatilization. Soils generated in areas of high rainfall and low temperature, and therefore with low aeration, are generally reducing soils. If the soils are acidic then they will tend to have a greater concentration of ammonia and organic nitrogen than nitrate, and will not readily support nitrifying bacteria, which would oxidize the ammonia [26]. Also, most plants are adapted, through evolutionary processes, to live with very low levels of nitrogen. This means that they are very well adapted to search for and take up nitrogen in different forms. Available nitrogen is often a factor limiting plant production. The increase of available nitrogen in air and precipitation can change the nitrogen conditions, causing over-saturation with nitrogen in plants and trees. This causes a faster growth and formation of larger cells, making them more vulnerable to wind, drought and parasites, and also the inner hormone balance is easily disturbed by this type of nitrogen stress [27].

NH₃ under atmospheric conditions can either be converted to NH₄⁺ or deposited on terrestrial bodies thru dry or wet deposition [10]. The wet deposition can be explained by the reactions that occur both in-cloud and below-cloud between water droplets, gases and aerosols [11]. The in-cloud scavenging mechanism occurs when the pollutant enters cloud droplets or ice crystals, taking part in their formation and growth phases [10]. Thru the collision of cloud droplets containing pollutant, a precipitation event occurs, removing the scavenged pollutants and bringing them to the surface [10, 12]. The process of below cloud scavenging occurs when pollutants adhere directly to falling precipitation. For a more detailed examination of the NH₄⁺ concentrations measured in the

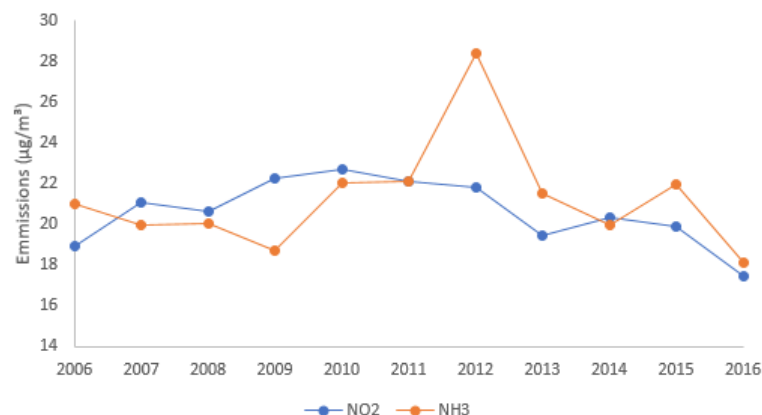


Fig. 3 NO₂ and NH₃ emissions in the Ciuc basin from 2006 to 2016 according to the measurements of the Harghita County Environmental Protection Agency

rainwater collected at Miercurea Ciuc and Toplia, wet flux deposition was calculated. As it can be seen in Fig. 4, large discrepancies appear in the wet flux deposition values of NH_4^+ between the two sampling sites. One tendency that can be clearly distinguished, is that NH_4^+ wet deposition values for Toplia are much higher than the values calculated for Miercurea Ciuc. This is true for both seasonal and multi annual means. As in the case of VWM values, the multi annual mean NH_4^+ wet flux deposition value for Toplia (44.22 kg/ha/year) is three times higher than the value measured at Miercurea Ciuc (15.28 kg/ha/year). Regarding the seasonal means, in case of Miercurea Ciuc the values calculated for spring (5.66 kg/ha/year) and summer (5.61 kg/ha/year) are very close, while the values calculated for fall and winter period are smaller, being 2.84 and 1.17 kg/ha/year, respectively. Wet deposition values calculated for Toplia showed a different pattern from Miercurea Ciuc. Here, summer NH_4^+ wet deposition values (23.72 kg/ha/year) were the highest, followed by the multi annual spring (11.45 kg/ha/year) and fall period values (8.25 kg/ha/year). Winter NH_4^+ wet deposition values (0.99 kg/ha/year) were similar to the values calculated for Miercurea Ciuc. The differences between seasons can be due to the amount of precipitation, since NH_4^+ ions are scavenged from the atmosphere through scavenging mechanisms. Although a correlation between the amount of precipitation and seasonal wet deposition values can be found for both Miercurea Ciuc and Toplia, the same cannot be said for the multi annual mean values between the two sampling sites.

In case of Miercurea Ciuc, the multi annual mean precipitation amount is 552.60 mm with a wet deposition multi annual mean value of 15.28 kg/ha/year. For Toplia, the wet deposition multi annual mean is almost three times higher, being 44.21 kg/ha/year, while the multi annual mean of the precipitation amount measured is only 609.44 mm. This shows that the rate of wet flux deposition does not depend on the precipitation amount, showing the in-cloud scavenging process in the case of NH_4^+ . This is also sustained by the weak correlations ($R=0.0006$ - Miercurea Ciuc; $R=0.0532$ - Toplia) between NH_4^+ concentration and the precipitation amount measured at the two sampling sites.

For a more detailed analysis of the relationships between the concentration of ammonium and other acidic ionic species, Spearman correlation analysis was conducted. In Miercurea Ciuc, significant correlations were found between NH_4^+ and SO_4^{2-} ($R = 0.616$), NO_3^- ($R = 0.610$), NO_2^- ($R = 0.527$). The VWM concentrations of SO_4^{2-} , NO_3^- , NO_2^- are as follows: 54.52, 26.46 and 4.76 $\mu\text{eq/L}$, while the VWM concentration of NH_4^+ is 158.04 $\mu\text{eq/L}$, which suggests that a part of the acidic components is neutralized by ammonium. Significant correlation between NH_4^+ and cations like K^+ ($R = 0.605$) and Mg^{2+} ($R = 0.507$) suggests same source origin, such as biomass burning. In case of

Toplia, NH_4^+ correlated well with HCO_3^- ($R = 0.400$) and SO_4^{2-} ($R = 0.371$). The VWM concentrations of HCO_3^- and SO_4^{2-} are 71.42 and 95.03 $\mu\text{eq/L}$, respectively. This means that NH_4^+ plays an important role in the neutralization of these acidic components. Significant correlations between NH_4^+ and other cations such as K^+ , Ca^{2+} and Mg^{2+} suggests the provenience from same sources (crustal and biomass burning). Besides the neutralization of acidic components, NH_4^+ can be deposited directly to the ecosystem with the above-mentioned cations. For both locations correlation with conductivity was significant, being 0.748 and 0.587 for Miercurea Ciuc and Toplia, respectively. By analyzing the correlation coefficients between the NH_4^+ concentration and the rain pH, good correlation was only found at Toplia ($R = 0.326$). For Miercurea Ciuc the correlation coefficient is only 0.088. This result means that despite the neutralization capability of NH_4^+ , the rainwater pH in the Ciuc basin is neutralized by other species as well, such as Ca^{2+} and Mg^{2+} . This is also explained by the smaller difference between the VWM concentrations of Ca^{2+} (78.52 $\mu\text{eq/L}$) and NH_4^+ (158.04 $\mu\text{eq/L}$) in the Ciuc basin, compared to those in the Giurgeu basin (VWM $\text{Ca}^{2+} = 116.13$ $\mu\text{eq/L}$; VWM $\text{NH}_4^+ = 407.40$ $\mu\text{eq/L}$).

The concentrations of NH_4^+ in rainwater are mainly related to ammonia emissions, mostly in areas of intensive agriculture. The largest emissions of ammonia are from N fertilizers, animal manure, fermented feeds such as silage, but biomass burning and peat fires may also have an important role. In the studied area, livestock are kept in large concentrated groupings where animal waste also generates large amounts of ammonia. Over the past decade, agricultural activities had increased in the studied areas, leading to a greater use of N fertilizers.

In order to determine which cations contribute more to neutralize the free potential acidity, neutralization factors (NFs) were calculated for both sampling sites, using the following equation [12]:

$$NF_{xi} = \frac{[X_i]}{[\text{SO}_4^{2-}] + [\text{NO}_3^-]}$$

where:

$[X_i]$ is the concentration of the alkaline component (Ca^{2+} , NH_4^+ , Na^+ , Mg^{2+} , K^+) expressed in Meq/L^{-1} . The results are shown in table 1. The main neutralizing agent for both locations is ammonium, followed by calcium. For Toplia, the NH_4^+ is responsible for the ~60% of the neutralization, while Ca^{2+} neutralizes ~22% of the rainwaters acidity. Other agents, such as Na^+ , K^+ and Mg^{2+} played a minor role in the neutralization process. In the case of Miercurea Ciuc NH_4^+ and Ca^{2+} neutralized ~48% and ~30%, respectively. Here Ca^{2+} plays a more important role in the neutralization process, which can be explained by the dissolution of limestone and dolomite present in the Ciuc region. Na^+ has also a higher neutralization capacity in comparison with Toplia region, accounting for ~11%.

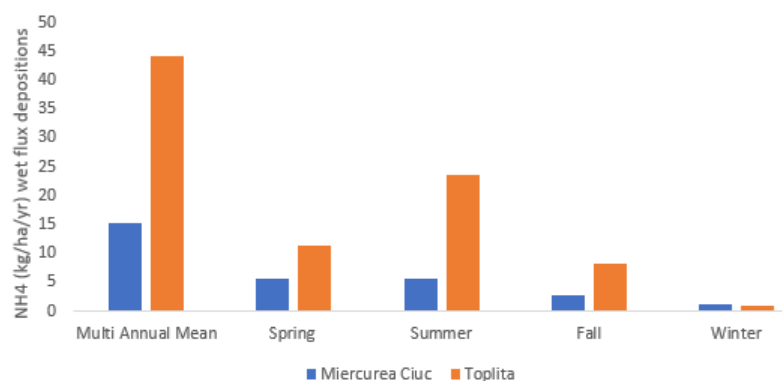


Fig. 4 Multi annual and seasonal means for NH_4^+ wet deposition fluxes (kg/ha/year) for the sampling period

	NF _{NH4}	NFCa	NFNa	NFK	NFMg
Miercurea Ciuc (2006-2016)					
Mean value	2.42	1.47	0.54	0.33	0.25
St. dev.	2.40	1.34	1.03	0.48	0.25
Range	0.03-14.83	0.06-12.47	0.02-8.65	0.02-5.20	0.02-2.64
Toplița (2006-2016)					
Mean value	3.11	1.13	0.47	0.32	0.22
St. dev.	3.46	0.84	0.79	0.31	0.16
Range	0.07-19.54	0.18-4.78	0.04-6.75	0.05-2.13	0.03-0.98

Table 1
NEUTRALIZATION
FACTORS OF THE
MAJOR IONS IN
RAINWATER SAMPLES

Fractional acidity (FA) can also be considered as an indicator of the neutralization process. The main acidifying components of precipitation are SO_4^{2-} and NO_3^- , forming the strong acids (H_2SO_4 ; HNO_3) controlling the acidity of rain. Therefore, FA can be computed as the ratio of

$$[\text{H}^+]/([\text{SO}_4^{2-}] + [\text{NO}_3^-]) \quad [14].$$

If the value of this ratio is one, it is considered that the neutralization process did not occurred at all [15]. This is not the case for the studied areas, in contrary, the values of FA are very low, being 0.01 ± 0.02 and 0.005 ± 0.01 for Miercurea Ciuc and Toplița, respectively. For the studied period, we observed that in Miercurea Ciuc 98.74%, while in Toplița 99.28% of the rainwater acidity was neutralized.

The measured hydrogen ion concentration $[\text{H}^+]$ reflects the acidity of precipitation after neutralization by atmospheric bases, especially NH_4^+ and Ca^{2+} , and is not a measure of the original acidity [16]. Assuming that NH_4^+ and Ca^{2+} in precipitation were originally present as NH_3 and CaCO_3 , the original acidity ($[\text{H}^+] + [\text{NH}_4^+] + [\text{Ca}^{2+}]$) was estimated to compare with the measured acidity (H^+). The results are shown in table 2, reflecting the high concentrations of bases in the atmosphere of both sampling sites. The original acidity is found to be much higher compared to the measured acidity. In case of Miercurea Ciuc the original acidity is 554 times greater than the measured acidity, while in Toplița is 1562 times greater. These values show that in the lack of these neutralizing ions the rainwater would have been very acidic, but is also an explanation for the excess alkaline pH values.

In order to assess the balance between acidity and alkalinity, the ratio of acidifying potential (AP) to Neutralization Potential (NP) was calculated. Used as an indicator of chemical nature of the rainwater, AP is the sum of NO_3^- and nssSO_4^{2-} and NP is the sum of NH_4^+ , nssCa^{2+} , nssMg^{2+} , and nssK^+ . The AP/NP ratios were estimated for the studied locations and given in table 2 [15; 17]. The values are much lower than one for both locations, only 0.88% and 7.45% of the samples showed values greater than one for Miercurea Ciuc and Toplița, respectively. The results indicate the dominance of the neutralization potential over the acidic potential in the studied areas.

	$[\text{H}^+] + [\text{NH}_4^+] + [\text{Ca}^{2+}]$ (original acidity)	$[\text{H}^+]$ (measured acidity)	AP/NP
Miercurea Ciuc (2006-2016)			
Mean value	293.78	0.53	0.34
St. dev.	277.30	0.91	0.36
Range	18.51 – 1990.56	0.01 – 8.41	-0.01-4.73
Toplița (2006-2016)			
Mean value	499.85	0.32	0.42
St. dev.	509.72	0.67	0.38
Range	46 – 2634.81	0.01 – 5.70	0.01-1.98

Table 2
COMPARISON BETWEEN
THE MEASURED AND
ORIGINAL ACIDITY AND
THE RATIO OF ACIDIC
POTENTIAL (AP) TO
NEUTRALIZATION
POTENTIAL (NP) IN
RAINWATER FOR THE
STUDIED AREAS

In order to further analyze the extent to which the major anionic species (SO_4^{2-} , NO_3^-) were neutralized with ammonium ion, Ammonium Availability Index (AAI) was calculated, using the following equation:

$$AAI = \frac{[\text{NH}_4^+]}{2[\text{SO}_4^{2-}] + [\text{NO}_3^-]} * 100$$

A hundred percent neutralization signifies that all SO_4^{2-} and NO_3^- is present as ammonium sulfate and ammonium nitrate, respectively [18]. For both Miercurea Ciuc (AAI = 156.44%) and Toplița (AAI = 179.11%), AAI value is greater than 100%, which indicates an excess over the neutralization value. Concerning to pH of the aerosol, apart from ammonium nitrate and sulfate other various organic acids also contribute to sources of acidity [18, 19].

The impact of increasing ammonium concentrations in the atmosphere accompanied by decreasing sulfate concentrations can be demonstrated by the ammonium to sulfate equivalent ratio. For the analyzed period, ammonium to sulfate ratios exceeding 1 were found in 91.19% of the total samples for Miercurea Ciuc, while for Toplița, 73.40% of the samples had $\text{NH}_4^+/\text{SO}_4^{2-}$ ratio values greater than 1. These results are also proof for the significant ammonium concentration increases in the studied areas.

To estimate the marine and non-marine contributions to the rainwater collected at the studied areas, different ratios of sea-salt fractions (SSF), non-sea-salt fractions (NSSF) and enrichment factors (EF) have been calculated (table 3), using the following equations:

$$\text{Enrichment Factor (X)} = \frac{(X/\text{Na})_{\text{rain}}}{(X/\text{Na})_{\text{sea}}}$$

$$\%SSF = \frac{100 * (\text{Na})_{\text{rain}} * (X/\text{Na})_{\text{sea}}}{(X)_{\text{rain}}}$$

$$\%NSSF = 100 - SSF$$

where, X is the concentration of the respective ion.

The selection of the sea-salt tracer ion was conducted according to the rules of Church et al. (1982) and Keene et al. (1986). The rainwater ratios of Cl/Na^+ , $\text{Mg}^{2+}/\text{Na}^+$, Na^+/Cl^- , $\text{Mg}^{2+}/\text{Cl}^-$, $\text{Na}^+/\text{Mg}^{2+}$ and $\text{Cl}^-/\text{Mg}^{2+}$ were calculated. If the quantity ratios of Cl^-/Na^+ and $\text{Mg}^{2+}/\text{Na}^+$ are equal or greater

	$\frac{Cl^-}{Na^+}$	$\frac{K^+}{Na^+}$	$\frac{Ca^{2+}}{Na^+}$	$\frac{Mg^{2+}}{Na^+}$	$\frac{SO_4^{2-}}{Na^+}$
Seawater	1.16	0.02	0.04	0.22	0.12
Miercurea Ciuc (2006-2016)					
Rainwater	3.24	1.48	5.98	1.23	4.02
%SSF	74.85	2.91	1.47	42.33	6.49
%NSSF	25.15	97.09	98.53	57.67	93.51
%EF	2.79	67.35	135.96	5.42	32.15
Toplita (2006-2016)					
Rainwater	2.20	1.46	4.92	0.99	3.81
%SSF	77.53	2.34	1.58	39.37	5.43
%NSSF	22.47	97.66	98.42	60.63	94.57
%EF	1.90	66.46	111.83	4.35	30.48

Table 3
SSF: SEA SALT FRACTION; NSSF: NON-SEA SALT FRACTION; EF: ENRICHMENT FACTOR

than the corresponding values of standard seawater ($Cl^-/Na^+ = 1.16$, $Mg^{2+}/Na^+ = 0.23$), Na^+ is the sea-salt tracer ion. If the quantity ratios of Na^+/Cl^- and $Mg^{2+}/Cl^- \geq$ corresponding values of standard sea-water ($Na^+/Cl^- = 0.86$, $Mg^{2+}/Cl^- = 0.20$), Cl^- is the sea-salt tracer ion, and if the quantity ratios of Na^+/Mg^{2+} and $Cl^-/Mg^{2+} \geq$ corresponding values of standard sea-water ($Na^+/Mg^{2+} = 4.40$, $Cl^-/Mg^{2+} = 5.13$), Mg^{2+} is the sea-salt tracer ion [9-21].

The results for the studied locations showed that Na^+ should be used as the reference element in both cases, although the rainwater ratio is three times higher for Miercurea Ciuc, and two times higher for Toplita. These high ratios may be due to the contribution of Cl^- from other anthropogenic or crustal sources [22]. The ratios of SO_4^{2-} , Mg^{2+} , K^+ and Ca^{2+} are also elevated in comparison with the sea water ratios, suggesting the provenience from other sources than marine for these elements. Higher values of EF than one also indicates the absence of marine influence at Miercurea Ciuc and Toplita.

Conclusions

This study attempts to present a more detailed analysis on the NH_4^+ concentration in the atmosphere over the Ciuc and Giurgeu basins, collected at Miercurea Ciuc and Toplita, providing insights on the influence of ammonium to the rainwaters alkalinity. The statistical analysis of the rainwater compositions, showed that among the analyzed ionic species NH_4^+ has the greatest VWM concentration in the case of both sampling sites (Miercurea Ciuc - VWM=158.04 $\mu eq/L$, range of 1.86-1823.33; Toplita - VWM=407.40 $\mu eq/L$, range of 11.64-1851.87). The NH_4^+ concentration represented ~54% and ~66% of the total cations measured for Miercurea Ciuc and Toplita, respectively. Multi annual mean NH_4^+ wet flux deposition value for Toplita (44.22 kg/ha/year) is three times higher than the value measured at Miercurea Ciuc (15.28 kg/ha/year). The rate of wet flux deposition does not depend on the precipitation amount, showing the in-cloud scavenging process in the case of NH_4^+ . This is also sustained by the weak correlations ($R=0.0006$ -Miercurea Ciuc; $R=0.0532$ -Toplita) between NH_4^+ concentration and the precipitation amount measured at the two sampling sites. NH_4^+ contributes the most to the neutralization process, having the highest NF values (2.42- Miercurea Ciuc; 3.11 -Toplita). For Toplita, NH_4^+ is responsible for the ~60% of the neutralization, while in the case of Miercurea Ciuc NH_4^+ neutralized ~48%. Here Ca^{2+} plays a more important role in the neutralization process, neutralizing ~30% of the rainwaters acidity, which can be explained by the dissolution of limestone and dolomite present in the Ciuc

region. The values of FA are very low, being 0.01 ± 0.02 and 0.005 ± 0.01 for Miercurea Ciuc and Toplita, respectively. In Miercurea Ciuc 98.74%, while in Toplita 99.28% of the rainwater acidity was neutralized. The original acidity is 554 and 1562 times greater than the measured acidity in Miercurea Ciuc and Toplita, respectively. In the lack of these neutralizing ions the rainwater would have been very acidic. The assessment of the AP/NP showed the dominance of the neutralization potential over the acidic potential in the studied areas. The large capacity of ammonium to neutralize rainwaters acidity is proved by the AAI results, which showed an excess over the neutralization value in both locations (Miercurea Ciuc - AAI = 156.44%; Toplita - AAI = 179.11%). Estimating the SSF, NSSF and EF the sources of the ionic species were analyzed. NH_4^+ mainly originates from agricultural activities, livestock breeding and biomass burning. Peat soils, deposits and bogs are characteristic for the studied areas. Being very flammable, these peat deposits often ignite, especially in periods of drought, emitting large quantities of ammonia to the atmosphere. A higher concentration in NH_4^+ in the Giurgeu basin, Toplita area is probably due to the larger peat bogs and deposits. Short term localized weather patterns, which are characteristic in basin areas, may also impact fertilizer and manure volatilization and the NH_3 , NH_4^+ emission rates. NH_3 from excessive use of fertilizers, human and animal waste discharge, and traffic emissions leads to an increased level of reactive N in the natural system, having a great impact on the ecosystem, leading to N stress and eutrophication.

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