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Influence of peat fires on the rainwater chemistry in intra-mountain basins with specific atmospheric circulations (Eastern Carpathians, Romania)

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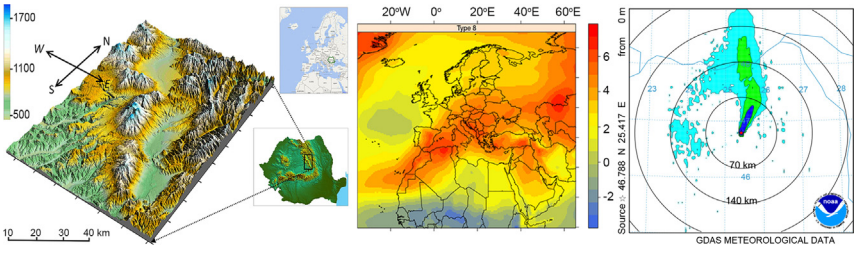
HIGHLIGHTS

- Temperature at 850 hPa for 2012 showed deviations with 2 °C–4 °C greater than for 1981–2016.
- 55% (CB) and 27% (GB) decrease in rainfall amount in 2012 compared to the multiannual mean (2006–2016).
- Acidity of rainwater is mainly neutralized by NH_4^+, soil dust and $CaCO_3$.
- pH increases due to NH_3 in cloud droplets, resulting below-cloud scavenging of SO_2.
- W-NW wind direction had the highest frequency, confirming the westerly anticyclonic circulation.

GRAPHICAL ABSTRACT



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ABSTRACT

A comprehensive study on the chemical composition of precipitation, the influence of peat fires and their relations with atmospheric circulation was conducted in the year of 2012, in two intra-mountain basins, the Ciuc basin (CB) and the Giurgeu basin (GB), Eastern Carpathians, Romania. Atmospheric circulation types showed the presence of a westerly anticyclonic circulation, characterized by a strong development of the Azores High to the northern Atlantic, contributing to the appearance of peat-fires. Using ROCADA daily gridded climatic datasets, the maximum and minimum daily temperatures were extracted, showing deviation from 2 °C to 6 °C in the studied year against the multiannual mean for the 1981–2016 period. Rainwater samples were analyzed for pH, major anions and cations; HCO_3^- concentrations were calculated based on the empirical relationship between pH and HCO_3^-. The results showed that 45.16% and 54.55% of precipitation had pH > 7.0 at CB and GB, respectively. NH_3, NH_4^+ and Ca^{2+} are the main neutralizing agents. The significant correlation between SO_4^{2-} and NH_4^+ ($r = 0.711$ – CB; $r = 0.736$ – GB) indicated neutralization by NH_3 in the forms of $(NH4)_2SO_4$ and NH_4HSO_4. Positive regression coefficient between the sum of ($H^+ + [NH_4^+] + [Ca^{2+}]$) and the sum of ($[nss - SO_4^{2-}] + [NO_3^-]$) ($r = 0.855$ – CB; $r = 0.796$ – GB), showed that acid neutralization was primarily brought by NH_4^+ and/or $CaCO_3$. Using Na as an indicator of marine origin, the proportions of sea salt and non-sea-salt were estimated from elemental ratios. According to correlation analysis and PCA, main acidic ions (SO_4^{2-} and NO_3^-) and NH_4^+ were mainly derived from anthropogenic activities (biomass burning, peat fires, fertilization), while Ca^{2+} and Mg^{2+} originated from terrestrial sources. The behavior of gaseous pollutants and smoke distribution resulted from peat fires were deciphered using the HYSPLIT model in a case study.

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1. Introduction

Rapid economic development, increased energy consumption, anthropogenic activities and industrialization, resulted in severe air pollution problems, causing atmospheric accumulation of various gases and particulate matter, which significantly influence the precipitation chemistry of the atmosphere (Kulshrestha et al., 2003; Zhang et al., 2007). The above-mentioned pollutants, are removed from the atmosphere by wet and dry deposition processes and scavenging mechanisms, such as rain, dew, fog, hail and snow. Precipitation is the most effective process in removing and transporting different ionic compounds, pollutants and soluble gases from the atmosphere to the earth's surface. Contaminants from the atmosphere can be removed in two different mechanisms: the rainout mechanism (in-cloud scavenging) and the washout mechanism (below-cloud scavenging) (Aikawa et al., 2014). During the past three decades, precipitation chemistry and its effects have been widely investigated in many areas worldwide. Although acidic precipitation is more intensively studied, and it's given more importance, alkaline precipitation also has negative effects on the ecosystem, leading to extinction of some species and eutrophication of surface waters.

Basins are known to influence atmospheric motions that extend in scale from the local scale to thousands of kilometers (De Wekker and Kossmann, 2015). Due to the basins concave land form and to no or only a small number of low lying exits, upvalley flows are suppressed or non-existent (De Wekker and Kossmann, 2015). Therefore, cold air drainage from the surrounding slopes accumulates and stagnates in the basin (Whiteman et al., 2001), delaying the convective boundary layer or atmospheric mixing layer growth. During daytime, a basins atmosphere can warm up more than the surrounding plains, promoting a plain to basin flow (De Wekker and Kossmann, 2015). Association of the cold air advection with thermally driven flows have a significant impact on the heat balance of the basin's atmosphere (Kossmann et al., 2002; Whiteman et al., 2000), reducing the atmospheric mixing layer growth (De Wekker and Kossmann, 2015) and also contributing to a greater drought degree. The air quality in basin-like environments may be affected significantly by the plain-to-basin winds, their effect to the thermal structure and convective boundary layer heights (Panday et al., 2009; De Wekker and Kossmann, 2015).

Intra-mountain basins in the Eastern Carpathians are characterized by local anticyclonic conditions, with long episodes of static stability of the atmosphere, often involving thermal inversions. The Ciuc basin (CB) and Giurgeu basin (GB) are also called as “the Carpathians cold pole”. Under these conditions, the accumulation of particulate matter and pollutants is more favored (Szép and Mátyás, 2014), greatly influencing these basins precipitation chemistry.

The CB and the GB, formed thru tectonic erosion in volcanic dams have a unique ecosystem, being developed on peaty soils and peat bogs, which can occupy a space of >10 m deep, hosting acidophilic vegetation (Szép et al., 2017). Lately, the CB and GB have been confronting with heavy drought phenomena, leading to the ignition of the natural peat deposits, either through auto combustion, or through stubble burn-out (Szép et al., 2017). Combustion of vegetation recently has been recognized as a major source of atmospheric pollution, releasing large amounts of gases and particles in the atmosphere (Balasubramanian et al., 1999). Primary smoke particles and secondary organic aerosols can affect the number of cloud condensation nuclei, cloud droplet size and precipitation (Godoy-Silva et al., 2017; Kanakidou et al., 2012). Fine particles are efficient dispersers of solar radiation, and usually have a large impact on local and regional visibility, affecting the local and regional climate (Crutzen and Andreae, 1990). Particulate matter is a heterogeneous mixture of particles differing in size, origin and chemical composition, and has not been defined by chemical nature, structure or source (Grantz et al., 2003).

The most aggressive and important peat fire in the past 20 years was studied, when the peat deposits burned for a month and a half, intensely contributing to the already increased ammonia concentration in the atmosphere. As a primary gaseous pollutant, ammonia is the major neutralizing agent in the atmosphere and has a significant role in the atmospheric chemistry (Hassan et al., 2013). Biomass is the main household combustion in both basins, and stubble burnings are intensely used during spring and fall for land clearance and removal of dry vegetation to improve productivity. This unfortunate habit of local farmers, thru which they clear the ploughlands, often results in the accidental ignition of the peat deposits. The aim of this study is to present the effects of peat fires, stubble and biomass burning on the precipitation chemistry, reporting the chemical composition of rainwater collected during 2012, the most extreme year from the last two decades, with low amounts of precipitation, long episodes of drought, accentuated static stability conditions and thermal inversion phenomena, which also contributed to more increased pollutant concentrations in the atmosphere. We first present and discuss the chemical characteristics and the alkaline nature of rainwater in the studied intra-mountain basins from the central part of Eastern Carpathians, regarding their specific geomorphological, meteorological and climatic conditions. Then, the effects of peat fires, stubble and biomass burning are presented thru a case study. This study shows the negative effects of peat fires and stubble burnings on the atmosphere and rainwater, in intra-mountain basin areas with the most specific climate from the Eastern Carpathians.

2. Materials and methods

2.1. Sampling site

The CB and GB are intra-mountain depressions, situated in the central part of the Eastern Carpathians, Romania (Fig. 1) having characteristic and specific climatological, meteorological and topographical conditions, where atmospheric static stability and thermal inversions are a daily phenomenon, which can persist from a few hours a day to several weeks.

CB is flanked to the west by Harghita Mountains (1800 m) and to the East by Ciucului Mountains (1300–1400 m), drained by the Upper Olt (Szép et al., 2017). The average annual temperature is 6.51 °C, with a relative humidity of 81.18%, while the mean annual rainfall during the last decade was 596.3 mm (Szép et al., 2017). GB is flanked by the Gurghiu Mountains to the west, and Giurgeu Mountains to the east. It is connected to the Ciuc basin through Izvorul Muresului.

The enclosed character of the CB and GB has a decisive influence on the climate, with almost constant thermal inversions, atmospheric static stability, frequent fog and late springtime. These basins are known to be the “cold poles” of the Eastern Carpathians, where temperatures below −30 °C have been measured repeatedly. The air pollution in these regions is mainly caused by peat fires, biomass and stubble burning, livestock breeding and the use of natural and chemical fertilizers in agricultural activities.

2.2. Sampling and analysis

Rainwater samples were collected over the year of 2012 in the CB (46′22′N, 25′44′E, elevation ~600 m) and in the GB (46′42′N, 25′40′E, elevation 750 m) in order to analyze the chemical composition of rainwater and the effects of peat fires on the concentrations of major ions in the rainwater. In both cases, wet-only collectors containing 24-hour integrated samplers were used, being replaced daily. Ion chromatograph and atomic absorption techniques were used to determine quantitatively the anions and cations. The anions (SO_4^{2-}, NO_3^-, NO_2^-) were analyzed by Ion Chromatograph (Dionex 2000i/SP) using a CO_3^{2-}/HCO_3^- buffer as eluent (1.7 mM Na_2CO_3/1.8 mM $NaHCO_3$), used in isocratic analysis, and 25 mM H_2SO_4 as regenerant. 100 ppm stock solutions of sodium salts of each of the ions were prepared. The concentrations were calculated based on the peak area of the above-mentioned standards. After every five samples, peak response was checked, by running