Source identification and exposure assessment to PM₁₀ in the Eastern Carpathians, Romania

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Abstract

Observations of particulate matter less than 10 µm (PM₁₀) were conducted from January to December in 2015 in the Ciuc basin, Eastern Carpathians, Romania. Daily concentrations of PM₁₀ ranged from 10.90 to 167.70 µg/m³, with an annual mean concentration of 46.31 µg/m³, which is higher than the European Union limit of 40 µg/m³. Samples were analyzed for a total of 21 elements. O, C and Si were the most abundant elements accounting for about 85% of the PM₁₀ mass. Source identification showed that the elemental composition of PM₁₀ is represented by post volcanic activity, crustal origin, and anthropogenic sources, caused by the resuspension of crustal material, sea salt and soil dust. The average PM₁₀ composition was 72.10% soil, 20.92% smoke K, 13.84% salt, 1.53% sulfate and 1.02% organic matter. The back-trajectory analysis showed that the majority of PM₁₀ pollution comes from the West, Southwest and South.

Keywords PM₁₀ · Scanning electron microscope · Chemical composition · Source apportionment · Air mass back-trajectories

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1 Introduction

Air pollution is one of the biggest challenges of the twenty-first century due to the highly mobile characteristics of atmospheric pollutants. Fast industrialization, economic growth and high population density resulted in the increase of pollutants and atmospheric particulate matter (PM) (Cao et al. 2009). Particulate matter has solid and liquid particles in its composition, incorporating organic and inorganic components formed by diverse mechanisms (Di Vaio et al. 2016). The inhalable fractions, which are coarse particles with a diameter $\leq 10 \mu\text{m}$ are known as PM_{10} (Naimabadi et al. 2016; Di Vaio et al. 2016). The main sources of PM are natural and anthropogenic, mainly being associated with wind suspended components, sea salt spray, surface soils, as well as with components originating from industrial activities, biomass burning and traffic emissions (Police et al. 2016). Beside its negative influence on the environment, PM also affects human health, contributing to cardiovascular and cerebrovascular diseases (Grahame and Schlesinger 2010; Bodor et al. 2021). Numerous epidemiological studies have shown the relationship between the composition of PM_{10} and adverse respiratory effects (Röösli et al. 2001; Di Vaio et al. 2016). According to Schwarze et al., (2006), a longer exposure to PM can cause lung cancer, while a shorter exposure to airborne coarse particles, bronchitis. Due to its various origins and to the ever changing air quality, PM can have diverse chemical and biological characteristics (Pope and Dockery 2006; Naimabadi et al. 2016), therefore, it is very important to study the chemical and elemental composition of atmospheric particulate matter. Moreover, the elemental composition and characterization of atmospheric PM_{10} can lead to important information on their sources (Cohen et al. 2010). Numerous studies have shown that Al, Ca, Mg, K, Fe and Ti are mainly terrestrial elements, being found in significant concentrations in the Earth's crust (Zalakeviciute et al. 2020; Negrál et al. 2020). However, Mg can be attributed to marine sources too, along with Cl and Na, being present in great concentrations in sea spray (Szép et al. 2018), while Fe, along with Zn can originate from anthropogenic sources too, such as the manufacturing of fuel tanks (Zalakeviciute et al. 2020). According to Du et al. (1997) and Zalakeviciute et al. (2020), Si, Mn, Cu and W can be used in the refinement process or as additives to enhance fuel properties. Ba may be present in PM fractions from coke production (Koniecznyński et al. 2012), while the presence of O and C suggests post volcanic activity.

The present study examines the elemental composition of PM_{10} in the Ciuc basin, Eastern Carpathians, Romania, during January 1st and December 31st, 2015, taking under consideration the meteorological conditions and air mass back-trajectories. To determine the elemental composition of PM_{10} , scanning electron microscopy (SEM) was used combined with energy dispersive X-ray (EDX). The main objective of this study is to assess the sources of 20 elements present in PM_{10} and their effects on human health, by performing various geochemical methods and health risk indices. The De La Roche diagram indicates the transformation mechanisms and the mixing of pollutants, while the analyses on health risk indices shows that even in small concentrations PM_{10} greatly affects the vulnerable age groups. As far as the authors know this is the first study that examines the elemental composition of PM_{10} performed in the Ciuc basin, taking under consideration air mass back-trajectories too, that can significantly influence the elemental composition of particulate matter. Due to its specific microclimate, pollutants tend to accumulate in the studied area, therefore is imperative to address the issue of PM control, and to improve current legislation, hence results of this research may be of great use to local and regional decision makers in order to take preventive measures regarding the exposure to air pollutants.

2 Material and methods

The Ciuc basin (46°30' to 46°10' lat. N and 25°40' to 26°00' long. E) is located in the central part of the Eastern Carpathians (Fig. 1), having an altitude of 600 to 700 m, a length of ~60 km and a maximum width of 10 km, covering an area of ~680 km² (Kristó 1994; Szép et al. 2017a). The basin is characterized by the formation of mesoclimate and microclimate due to the division of the relief (Kristó 1994). The Ciuc basin's climate is influenced by the surrounded dolomitic, calcareous (eastern border) and volcanic mountains (western border of the basin).

Drainage works had a significant impact on the evapotranspiration amount. As a result, these changes brought the growth of the atmospheric static stability conditions in the basin, inducing frequent thermal inversion phenomena and causing the accumulation of atmospheric pollutants (Szép and Mátyás 2014; Szép et al. 2017b; Boga et al. 2021).

The used PM₁₀ data was detected by the HR 01 regional station. The measurements of PM₁₀ values were carried out by an LSPM10 analyzer following EN12341/98 standards. Sampling took place every two weeks, and a total of 24 samples were analyzed, determining the following elements: O, C, Si, Ca, Al, K, Na, S, Mg, Ti, P, Cl, Mn, Zn, Fe, Sr, N, Ba, W and Cu. To determine the elemental composition of the PM₁₀ the SEM–EDX was used. In order to ensure a good electrical path to the ground, samples were coated with a thin layer of gold under vacuum (1.33×10^{-6} mBar) (to increase electrical conductivity) before introducing the samples in the SEM, therefore improving the imaging quality. This step is essential in order to keep non-conducting specimens and oxides from charging under the electron beam (Ravichandran 2017). After that, the samples were examined by Scanning Jeol JEM 5510 JV SEM, and studied with Oxford Instruments EDS Analysis System Inca 300 (UK) to examine its elemental composition. EDX measurements help to identify the elemental composition (Rápó et al. 2020).

Fig. 1 Sampling site (Ciuc basin, Eastern Carpathians, Romania)

2.1 Source identification

Source apportionment of elemental composition of PM₁₀ was performed using trajectory analysis, enrichment factors (EF), inter-element correlations (Spearman rank-correlation), pollution load index (PLI), geo-accumulation index (I_{geo}), particulate mass reconstructed calculations (RCM) and principal component analysis (PCA). PCA is used in case of large number of variables, summarizing patterns of correlations among them, to be reduced to a smaller number of factors (Santos et al. 2019). To support the PCA results, we used other calculations too, converting the elements into oxides to perform a geochemical analysis.

By using EF, elemental concentrations are normalized to an average total crust value, present in all of the profiles (Lawson and Winchester 1979; Bano et al. 2018):

$$EF(X) = \frac{\left(\frac{X}{Ref}\right)_{aerosol}}{\left(\frac{X}{Ref}\right)_{source}} \quad (1)$$

where X/Ref is the ratio of element X to a reference material, in this case Fe (Yaroshevsky 2006). According to the pollution ranking system proposed by Sutherland (2000), six categories were identified: 1. values of $EF \leq 1$ show the background concentration, 2. values of EF between 1 and 2 show depletion to minimal enrichment, 3. values from 2 to 5 are presenting moderate enrichment, 4. EF values between 5 and 20 show significant enrichment, 5. EF between 20 and 40 very high enrichment, while EF values above 40 present extremely high enrichment.

In order to assess the sediment enrichment, PLI was used, in concordance with the method proposed by Tomlinson et al. (1980):

$$(CF_1 \cdot CF_2 \cdot CF_3 \cdot \dots \dots CF_n)^{\frac{1}{n}} \quad (2)$$

where n is the number of metals and CF is the contamination factor resulted from the calculations between each metal's concentration and its background value. A PLI value greater than 1 shows the presence of pollution, whereas a value < 1 indicates no pollution (Ding et al. 2019). The world average concentration of N, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Mn, Fe, Cu, Zn, Sr and Ba reported for sedimentary rocks by Turekian and Wedepohl (1961) were considered as the background value.

The level of anthropogenic contamination was further assessed by calculating the I_{geo} , using Muller's (1969) formula:

$$I_{geo} = \log_2 \left(\frac{C_n}{1.5B_n} \right) \quad (3)$$

where, C_n represents the measured concentration of heavy metal and B_n is the geochemical background value in average element n.

The common method of Turekian and Wedepohl (1961) has been used for comparing sediment metal concentrations. Generally, the I_{geo} consists of seven grades or classes: I_{geo} value > 5 extremely contaminated (class 6), I_{geo} value between 4–5 strongly to extremely contaminated (class 5), I_{geo} value between 3–4 strongly contaminated (class 4), I_{geo} from 2 to 3 moderately to strongly contaminated (class 3), I_{geo} between 1–2 means moderately contaminated (class 2), I_{geo} between 0–1 is uncontaminated to moderately contaminated (class 1), while an I_{geo} below 0 is uncontaminated (class 0) (Abraham and Parker 2008).

RCM applies multipliers for the several measured species to estimate unmeasured components (Chow et al. 2015), and is calculated by assuming five composite variables. Since black carbon and Pb were not measured in the present study, these factors are left out from the RCM formula. So, the equation for RCM is:

$$RCM = sulfate + salt + soil + smoke\ K + blackcarbon + organic + Zn + Pb \quad (4)$$

where “sulfate” is the ammonium sulfate concentration, “salt” is the sea salt concentration, “soil” is the concentration of soil derived particles, “smoke K” is the concentration of potassium with a source other than soil, and often related to smoke, while “organic” is the concentration of organic matter in the PM_{10} . Using the elemental concentrations of the constituent elements, the sources can be calculated as follows (Siddique and Waheed 2014):

$$sulfate = 4.125S \quad (5)$$

$$salt = 2.54Na \quad (6)$$

Mg, Al, Si, Ca, Ti and Fe oxides, beside many other trace elements, can be found in the composition of soil (Begum et al. 2009):

$$soil = 2.20Al + 2.49Si + 1.63Ca + 1.94Ti + 2.42Fe \quad (7)$$

Other approaches show that the soil dust concentrations in PM_{10} can be computed using the following equation:

$$soil\ dust = 1.15(1.98Al + 2.14Si + 1.2K + 1.4Ca + 1.67Ti + 1.36Fe) \quad (8)$$

According to Begum et al. (2009), a reliable smoke indicator from fine K can be obtained by subtracting the fine potassium originated from terrestrial and marine sources, from the total K concentrations:

$$smoke\ K = K_{tot} - 0.036Na - 0.6Fe \quad (9)$$

The hydrogen concentration was calculated by the precipitation pH value, and “organics” was calculated using the following equation:

$$organics = 11(H - 0.25S) \quad (10)$$

2.2 Air mass back-trajectories

During this study, the impact of anthropogenic and natural sources on PM_{10} was investigated in the Ciuc basin, to identify the major particle sources. To identify the air mass trajectories a 24 hr backward trajectory simulation was carried out using the HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) model. Mathematical models are widely used to figure out the relationship between the source and receptor. One of the most important air quality models is the HYSPLIT model. By using HYSPLIT, we can calculate for example the vectors for air pollutants transport using the Lagrangian and Eulerian approach, combined with a three-dimensional grid as a frame of reference (meteorological fields). HYSPLIT is the most popular, widely used model for atmospheric trajectory and dispersion calculations (Draxler and Rolph 2013), is a Lagrangian particle/puff model. The back-trajectory analysis (started from Ciuc basin 46.37°N, 25.80°E) was

carried out for 2 distinct levels: 400 m, to give representative origins of air masses near the surface; and 1500 m, which can serve as a representative height above the boundary layer. The models were used with GDAS (Global Data Assimilation System) meteorological data with 1-degree resolution ($1^\circ \times 1^\circ$ km). To analyze the transport of particles, the source of pollution back trajectories were identified with 24-h long simulation runs. The trajectory calculations were started every six hours for one-year period from January to December 2015, to figure out more precisely the trajectory trends for this period. In this way it was possible to identify the source locations of the pollutant that fall in the track of the back trajectories. Cluster analysis was carried out to classify backward air trajectories obtained during our simulations into different groups of similar history (transport patterns). During cluster analysis the cluster spatial variance (SPVAR) was calculated, while clusters were represented by their mean trajectory by calculating the total spatial variance (TSV) among trajectories using the HYSPLIT platform (Su et al. 2015).

The time scale used was well suited to capture potential short and long-range transport of air pollutants originating from and outside of the basin. It should be also mentioned that most of the pollutants were deposited within a couple of days; hence 24-h could be an important factor, especially in case of PM_{10} .

2.3 Exposure assessment

Exposure of children and adults to PM_{10} were calculated, determining the chemical daily intake (CDI), dermal absorbed dose (DAD) and the exposure concentration (EC):

$$CDI = \frac{C \times \text{IngR} \times EF \times ED \times CF}{BW \times AT} \quad (11)$$

$$DAD = \frac{C \times SA \times AF \times ABS \times EF \times ED \times CF}{BW \times AT} \quad (12)$$

$$EC = \frac{C \times ET \times EF \times ED}{ATn} \quad (13)$$

where, C: metal concentrations in PM_{10} ; IngR: ingestion rate; EF: exposure frequency; ED: exposure duration (6 years for children and 24 years for adults); BW: the average body weight (15 kg for children and 70 kg for adults); AT: averaging time; CF: conversion factor; SA: surface area of the skin that contacts the airborne particulates (3300 cm^2 for adults and 2800 cm^2 for children); AF: skin adherence factor for the airborne particulates; ABS: dermal absorption factor; ET: exposure time; ATn: average time (EPA 2011).

According to Sah et al. (2019) the risk characterization was quantified separately for non-carcinogenic effects. We determined the hazard quotient (HQ), by which we evaluated the non-carcinogenic risk:

$$HQ_{\text{ingest}} = \frac{CDI}{RfDo} \quad (14)$$

$$HQ_{\text{derm}} = \frac{DAD}{RfDo \times GIABS} \quad (15)$$

$$HQ_{inh} = \frac{EC}{RfCi \times 1000 \mu g \text{ mg}^{-1}} \quad (16)$$

where, RfDo: oral reference dose; RfCi: inhalation reference concentrations; GIABS: gastrointestinal absorption factor. The sum of HQ is equal to the hazard index (HI), and if its value is 1, then there is no significant risk of non-carcinogenic effects; with the increase of HI value the risk of non-carcinogenic effects will also grow.

The description of parameters used in non-cancer risk assessment has been given in the Supplementary Material Section (SM) Tables S1 and S2.

2.4 QA/QC

To maintain the quality assurance and quality control during the sampling procedure, forceps was used to handle the filter papers, which were transported in a sealed box and maintained in dust free conditions. During the sampling period, a blank filter paper was collected every month, correcting the results with the blanks (EPA 2002). To determine the mass concentrations, all filter papers have been weighted using a microbalance. Quality assurance procedure was assured by concomitant measurements of three control filter papers, which were kept together with the samples at the temperature of 20 °C and humidity of 50% in a desiccator (EPA 2002).

2.5 Assumptions and uncertainty

All exposure assessment determinations are calculated mathematically, applying widely used unitary procedures. The degree of uncertainty derives from the fact that there are no reports regarding patients, their exact ages, thoracic capacity, and the real degree of exposure.

3 Results and discussion

3.1 Temporal variability of PM₁₀ concentrations

The studied daily concentrations of PM₁₀ ranged from 10.90 to 167.70 µg/m³ (Fig. 2), with an average mass concentration of 46.31 µg/m³. The mean PM₁₀ mass concentration was higher during the cold period (67.24 µg/m³, October–March) than during the warm period

Fig. 2 Temporal variability of daily mean PM₁₀ concentrations (green and red interrupted lines show the days with exceedance values with respect of the daily PM₁₀ limit value; according to the Directive 2008/50/EC)

(25.38 $\mu\text{g}/\text{m}^3$, April–September). During winter, the higher PM_{10} concentrations are correlated with fossil fuel and biomass burning emissions, and enhanced by the meteorological conditions, such as thermal inversions, which favors the accumulation of PM_{10} and other pollutants (Szép and Mátyás 2014; He et al. 2017). The annual mean concentration (46.31 $\mu\text{g}/\text{m}^3$) was higher than the WHO air quality guideline (20 $\mu\text{g}/\text{m}^3$), and the European Union's limit value for PM_{10} (40 $\mu\text{g}/\text{m}^3$).

3.2 Elemental composition

Table 1 summarizes the elemental arithmetic means, maximum, minimum, and median of PM_{10} mass. The most abundant PM_{10} elements are O, C and Si, accounting to the 85% of the total PM_{10} mass. During the analyzed days from the cold period (January, February, October, November, December) the O and Si weight percent were lower than in the warm period (March–September). Si has major contributions from sources, such as vegetation, decomposed volcanic rocks, diesel engines, gasoline engines and smoking, while aluminum comes mainly from terrestrial sources, soils and the breakdown of silicates (Cao et al. 2008).

The concentration of C varied during the study period from 13.46 wt% to 56.91 wt% (mean 27.83 wt%). The next higher elemental weight percent's are for Na, Ca, Ti and Al, with 1.20 wt%, 1.18 wt%, 1.07 wt% and 1.00 wt%, respectively, suggesting the common mineralogical sources, derived from soil, resuspension or other anthropogenic activities (Genga et al. 2012). The presence of Na can be due to sea spray and numerous anthropogenic activities, such as wood/biomass combustion (Cao et al. 2008; NIPHE 2012; Keresztesi et al. 2020).

3.3 Source identification

3.3.1 Elemental ratios

Normally PM_{10} Ca weight percent may indicate the terrestrial sources, but the 0.69 mean Ca/Mg ratio much lower than the Ca/Mg ratios in dolomite (1.65) and in crust (1.78) (Taylor 1964) indicate the significant independent sources of Ca, which can be attributed to secondary

Table 1 Elemental weight percent in Ciuc basin for the studied daily of 2015

	elemental weight percent (wt%)						elemental weight percent (wt%)				
	mean	min	max	st. dev	median		mean	min	max	st. dev	median
O	44.80	26.35	54.88	7.20	49.04	Ti	1.07	0.10	5.73	1.00	0.43
C	27.83	13.46	56.91	11.40	21.65	P	0.88	0.19	2.50	0.60	0.50
Si	27.89	12.40	41.34	6.20	28.27	Cl	0.34	0.11	0.68	0.12	0.31
Ca	1.18	0.20	2.51	0.60	1.00	Mn	0.86	0.20	5.60	0.95	0.30
Al	1.00	0.05	2.68	0.59	0.77	Zn	0.87	0.23	2.20	0.60	0.50
K	0.57	0.28	1.66	0.16	0.52	S	0.54	0.14	1.02	0.18	0.55
Fe	0.58	0.03	2.20	0.38	0.43	Mg	0.71	0.04	2.10	0.54	0.52
Na	1.20	0.28	2.75	0.36	1.26	Sr	0.11	0.00	2.60	0.21	0.00
Ba	0.10	0.00	2.50	0.20	0.00	Cu	0.05	0.00	1.20	0.10	0.00
W	0.0042	0.00	0.10	0.01	0.00	N	0.29	0.00	2.20	0.39	0.00

pollution, such as resuspension. Ti (ranging between 0.10 and 5.73; mean 1.07) has been identified as markers for vehicles emission and resuspension dust (Cheng et al. 2018). The Si/Al ratios were examined and found to range between 4.81 and 82.61 (mean 36.76). In the Earth's crust Si/Al ratios were 3.42 (Taylor 1964). The significant differences between ratios may be due to the variation of periods of drought and rainy seasons. During the dry periods of the year, the concentration of silica is much higher than that of aluminum, mainly due to differences in soil concentration. The differences are also seasonal. In winter, the differences are significantly smaller between the two pollutants, indicating their common source. Most road surfaces (95–99%) are composed of rock material (Samiksha and Sunder Raman 2017). The contents of S, Zn, Mn, Mg, Fe, K and P had values varying from 0.54 to 0.88 wt%. Low Cl, Cu, W, Sr, Ba and N elemental weight percent (0.004–0.34 wt%) were also observed. The emission sources of Sr, Zn and Ba can be vehicle brake wearing and tearing (Cheng et al. 2018; Kalaiarasan et al. 2018), while Mn and Cu may come from industry (Xue et al. 2019). The mean ratios of Cl/Na (0.31) are significantly lower in the samples than that in seawater (1.8) (Chesselet et al. 1972; Xu et al. 2013). This fact is mainly due to continental air mass circulations, without a significant marine influence or to air masses that lost their sea spray content by travelling to the interior of the continent, being loaded with pollutants from anthropogenic sources or components from terrestrial ones. These aspects can also be observed from the Hysplit analysis (Fig. 7). The mean S/Ca ratio was 2.80, also much higher than the 0.80 S/Ca ratio in calcareous rocks (gypsum). The results show that the sources of S can be attributed to fossil fuel combustion and rubber tire wearing and other anthropic activities (Xue et al. 2019).

3.3.2 Enrichment factor, pollution load index and geo-accumulation index

According to Espitia-Pérez et al. (2018), to identify the impact of emission sources, the crustal EFs of the trace elements can be compared to the Earth's crust. The results regarding the EF values are following the downward order $S > N > Cl > Si > Zn > Sr > K > Ca > P > W > Ba > Mg > Al > Cu > Na > Ti > Mn$, suggesting an origin dominated by anthropogenic sources (Table 2). The results of EFs showed that S, N, Cl and Si were enriched in PM_{10} . S had the highest EF values among the studied elements, having a remarkably high enrichment (average value 203.99), indicating the substantial contribution from anthropogenic emissions, such as fossil fuel combustion or rubber tire wearing. The EFs of Na, Ti, Cu, Mn (< 1), Al, Mg, Ba (1–2) and Ca, K, P, W (2–5) showed lower values than 10, indicating the elements mainly had terrestrial origins (Li et al. 2018). Sr and Zn (ranging between 5 and 20) were medially enriched and were probably under the impact of motor vehicle and brake wearing emissions (Xue et al. 2019).

The EF values suggest that Al, Ca, and Si have an anthropogenic component from the total mass composition, K originates from biomass burning and agriculture, while Mn and Cu can be attributed to industrial activities. Fossil fuel burning and industry is the main generator for S, while Zn can be originated from motor vehicle emissions and also industry (Yan et al. 2017; Yu et al. 2018; Xue et al. 2019). In Table 3 the Si, S, Cl and Zn show PLI values greater than 1, which may be due to the influence of anthropogenic sources, such as industrial processes, abrasion of metallic materials and traffic-related sources and construction works (Cheng et al. 2018; Casares et al. 2019).

The calculated I_{geo} values (Table 3) indicate that only Si, S and Cl have high positive values ($I_{geo} = 0.18, 0.48$ and 0.35) which are ranked in class 1. Other elements (Na, Mg, Al, P, K, Ca, Ti, Mn, Fe, Cu, Ba, Sr, W and Zn) have negative I_{geo} values. The contents of S, Si and Cl increase as a result of some anthropogenic activities in the Ciuc basin, indicating

Table 2 EF average crustal and PM₁₀ compositions

	Earth's crust	EF		Earth's crust	EF
Al/Fe	1.73	1.08	Na/Fe	0.54	0.90
Ba/Fe	0.014	1.35	P/Fe	0.02	2.77
Ca/Fe	0.64	4.33	S/Fe	0.01	203.99
Cl/Fe	0.004	37.68	Si/Fe	6.34	21.02
Cu/Fe	0.001	0.92	Sr/Fe	0.0073	6.18
K/Fe	0.54	4.67	Ti/Fe	0.097	0.51
Mg/Fe	0.4	1.31	W/Fe	0.000028	2.36
Mn/Fe	0.022	0.35	Zn/Fe	0.0018	6.25
N/Fe	0.00041	60.20			

the presence of mixed sources, such as household wood combustion, traffic, industrial activities, and construction works (Wang 2015). S can be attributed to vehicle fuel combustion, biomass burning and industrial activities, while Cl can be originated from biomass burning and marine sources. Si can be emitted from biomass burning, coal combustion and soil resuspension (Xie et al. 2009; Casares et al. 2019).

3.3.3 Particle mass reconstruction

Based on the determination of the amount of resuspended soil particles in particulate matter (Eq. 7), they are present in 72.10% of the average composition of the analyzed samples. The elements used in the formula are Al, Si, Ca, Fe and Ti, of which Si is present in significant amounts. We also used Eq. 8 in order to verify the percentage of resuspended soil particles. This resulted in 68.79% which supports the correctness of Eq. 7. During winter, in the Ciuc basin the main heating sources are biomass combustion and natural gas, which are major contributors to air pollution in the studied area (Szép et al. 2019).

The RCM elementary analysis estimates that the average PM₁₀ composition is 72.10% soil, 20.92% smoke K, 13.84% salt, 1.53% sulfate and 1.02% organic matter. The average RCM calculated for the dataset was about 95.71% as compared to the PM₁₀ concentration. The missing 4.29% of mass could be water vapor, which was not measured in this study. The comparison of RCM and gravimetric mass is presented in Fig. 3. The significant correlation coefficient (0.88) between the RCM and gravimetric mass suggests a good agreement between the methods.

Table 3 *PLI* and *I*_{geo} values

	<i>PLI</i>	<i>I</i> _{geo}		<i>PLI</i>	<i>I</i> _{geo}
Na	0.19	-2.95	K	0.20	-2.90
Mg	0.05	-4.97	Ca	0.05	-5.00
Al	0.12	-3.62	Ti	0.08	-5.09
Si	1.70	0.18	Mn	0.04	-5.19
P	0.32	-2.47	Fe	0.13	-3.54
Ba	0.00	-2.18	Sr	0.00	-0.13
Cu	0.00	-0.87	W	0.00	-1.33
S	2.09	0.48	Zn	1.19	-0.33
Cl	1.92	0.35	N	0.00	0.00

Fig. 3 Comparison between RCM and Gravimetric mass during the studied period

3.3.4 Correlation analysis

Several different techniques have been used in our study to define the various emission sources and the observed pollutant concentrations: first from the correlation coefficients of each of these pollutants with each other, and then applying PCA. In Fig. 4 the correlation matrix coefficients can be observed.

A positive correlation between Ca/Fe (0.611) would be indicative of the presence of ferromagnesian silicates and other common terrestrial sources. The significant correlation between Ca and Mg (0.810) suggests the same source origin (Valdés et al. 2005), such as dolomite, calcite and limestone, showing that Ca and Mg mainly comes from the weathering of calcareous, dolomitic rocks (Keresztesi et al. 2017). Silicate minerals are presumed to be present in this fraction as evidenced by the high Mg/Fe (0.903) elemental ratio. The origin of silicates are volcanic, metamorphic rocks, common in the Ciuc basin, containing Mg, Fe and Al. This also explains the presence of the significant positive correlations between Mg/Al (0.573) and Fe/Al (0.903). On the other hand, the presence of the mineral fractions in the PM₁₀ can also support the significant correlations between Ca/Na (0.439), Si/Mg (0.483), Ti/Mn (0.725), Al/K (0.903), Na/P (0.479) and S/Mg (0.435), confirming again the crustal origin of these elements in PM₁₀ (Avino et al. 2014). Another part of the PM₁₀ fraction, as mentioned in the determinations of pollution indices, derives from emission sources and resuspension. The major components of coarse PM₁₀ could be aluminosilicates and other oxides from crust (Pfeiffer 2005). This explains the presence

Fig. 4 Spearman's rank correlation between the elements in Ciuc basin (statistically significant correlation coefficients $p < 0.05$)

of the correlations between Na/O (0.643), Ca/O (0.557), Al/O (0.569), Si/O (0.819), Si/Ca (0.532), O/S (0.457) and O/P (0.692). The positive correlation values between Si/Cl (0.508), Si/Na (0.608), Si/S (0.489), Ca/K (0.611) and S/Fe (0.435) indicates the common sources, such as biomass burning. S and Fe take part in the neutralization of the PM₁₀ layers as synergistic elements and they have high geochemical affinities, if they meet each other in any medium they start to react to the other element (Roy et al. 2015). The correlation coefficients between Si/Cl, Si/Na, Si/S and Ca/Al (0.563) can also be an indicator for industrial activities. Na/Cl correlation (0.485) indicates the possible presence of sea-spray contribution to PM₁₀ and other common sources.

3.3.5 Principal component analysis

According to Malandrino et al. (2013) the chemometric treatment of the experimental data was carried out through the application of principal component analysis (PCA). Table 4 presents the Varimax rotated factor loadings with eigenvalues > 1, explaining 91.99% of the total variance. The first factor (F1) explaining most of the total variance (35.87%) has high loadings of O, C, Si, K, S and Cl. The association of these elements can suggest post volcanic activity, but high loadings of Cl and S are also a tracer of anthropogenic emissions, such as biomass burning or fuel combustion (Johansen et al. 2011).

Representing 22.72% of the total variance with high loadings of Al, K, Fe, Na and P the second factor is considered to have mixed sources. The correlation between Al, K, Fe and Na can be related to the resuspension of these elements, in the form of crustal material and soil dust (Koçak et al. 2011; Ramírez et al. 2018). According to Malandrino et al. (2013) the correlation of Fe and P is more difficult to explain, but P in the aqueous form in correlation with sodium can form Na₃PO₄, which in the industry is used as a cleaning agent, lubricant, food additive, stain remover and degreaser. The association of K and P can be

Table 4 Analysis Source apportionment using Principal Component Analysis

	<i>F1</i>	<i>F2</i>	<i>F3</i>	<i>F4</i>	<i>F5</i>
O	0.930	0.226	0.259	-0.044	0.081
C	0.953	0.175	0.090	-0.117	0.105
Si	0.940	-0.027	0.179	-0.038	0.162
Ca	0.159	0.052	0.897	0.164	0.101
Al	0.022	0.698	0.538	0.294	-0.035
K	0.837	0.519	0.010	-0.073	0.080
Fe	0.196	0.865	0.393	0.069	-0.085
Na	0.425	0.870	0.064	-0.076	0.036
S	0.895	0.317	0.149	-0.091	0.000
Mg	0.157	0.307	0.842	-0.030	-0.128
Ti	-0.140	-0.012	0.259	0.881	-0.036
P	0.386	0.887	0.000	-0.063	-0.129
Cl	0.867	0.259	-0.074	-0.027	-0.054
Mn	-0.058	0.038	-0.055	0.922	0.000
Zn	0.170	-0.098	-0.019	-0.030	0.973
% Total variance	35.87	22.72	14.44	11.93	7.03

found in N type chemical fertilizers. The third factor (F3) is related to terrestrial sources, accounting for 14.44% of the total variance with high loadings of Ca and Mg. These two elements are a common tracer of crustal material and can be associated with the dissolution of calcareous and dolomite rocks, or resuspended or long-range transported road dust (Keresztesi et al. 2017). Factor 4 (F4) explained 11.93% of the total variance, showing high loadings of Ti and Mn, which are usually associated with mineral aerosols or industry (Allen et al. 2001). The fifth factor represented only 7.03% of the total variance with a significant proportion of Zn, which is a representative for vehicle sources. Zn is associated with tire wear and brake abrasion (Ramírez et al. 2018), being a vulcanizing agent in tire manufacturing (Tanner et al. 2008).

Overall, it can be said that at the studied area the major source of aerosol components is represented by post volcanic activity and crustal origin, caused by the resuspension of crustal material and soil dust.

3.3.6 Geochemical analysis

The Ciuc basin consists of partly volcanic, metamorphic, and partly sedimentary rocks: andesites, dolomites and crystalline slates. Analyzing Fig. 5, one can observe mixed sources: high Si concentrations, higher than those of andesites, suggesting that most of them originate from secondary, anthropogenic sources, such as resuspension of the abandoned materials. In the particulate matter samples, the Si concentration does not follow the original rock composition, suggesting that particulate matter tends to accumulate based on element affinity and charge neutralization.

The major oxides of the studied samples have a large variation in SiO_2 (85.74–97.91 wt %), K_2O (0.17–5.96 wt %), Al_2O_3 (0.26–3.62 wt %), MgO (0.17–3.19 wt %), CaO (0.56–3.06 wt %), Fe_2O_3 (0.09–2.15 wt %), Na_2O (0.02–1.61 wt %), P_2O_5 (0.01–0.53 wt %), TiO_2 (0.001–0.37 wt %). The above-mentioned oxides are the common oxides of the soil, in addition to water and carbonates (Malm et al. 1994; Motallebi et al. 2003), they appear in the atmosphere through resuspension (Gietl et al. 2010). Moreover, the De La Roche diagram shows that the concentrations of Ca, Mg and Al do not reach the composition of the rocks, showing the accumulation of Si.

Fig. 5 Total alkali versus silica (TAS) diagram and De La Roche diagram

3.3.7 Back-trajectory analysis

Long-range simulations were carried out with HYSPLIT Lagrangian model to analyze the possible pollution sources in the Ciuc basin. The main aim of the HYSPLIT simulation was to determine the origin of PM_{10} arriving from different regions during the selected period. The optimum number of clusters were selected based on the TSV change against the number of iteration graph (Fig. 6) for 400 m and y for 1500 m, respectively (Su et al. 2015). As a result, the numbers of selected clusters are 5 and 4, where sharp decreases were observed. In order to decipher the air mass movements during the 1-year period the clusters (average trajectories) for both altitudes were analyzed and are presented in Fig. 7.

More than 70% of the simulated wind flow pattern shows south westerly circulation origin, which is indicating a high-pressure system. On the other hand, the model-simulated wind flow shows strong north, north-east flow. The significant difference between 400 and 1500 m altitude is that the origins of air parcels are higher in case of 1500 m (higher with at least 500 m for each cluster). As stated earlier the optimal number of clusters for 1500 m was 4. Comparing the 4 and 5 cluster solutions (1500 m) the main difference was that the air masses paths originated over Croatia, Hungary and western part of Romania in 4-cluster solution were separated into sub-systems (clusters), however in 5 cluster solutions the contribution percentages were the same. The air systems obtained for 400 m and the contribution percentage of each cluster (5-cluster solution) was as follows: cluster 5 originated from the north-eastern part and passed through Ukraine, Moldova and then reached the Ciuc basin. The followed trajectory is a few hundred kilometers long and represents 11% of all the trajectories obtained for the one-year period. On the other hand, two clusters of westerly and south-easterly inflow, (clusters 1 and 4), have mainly local or regional characteristics, with shortest travel distance and represent more than 60% of all the clusters. Clusters 2 and 3 seem to have the longest trajectories, which can transport pollutants from long distances from countries like Hungary and Ukraine. Both clusters have a contribution of ~10% and are characterized by fast movements. Analyzing and comparing the results obtained for 1500 m, it is obvious that important similarities are between the two solutions. The dominating clusters were as follows: 1, 3 and 4, with a contribution of 22%, 37% and 35%, respectively. The remaining 5% (cluster 2) -distinctive system- was characterized by the fastest transport pattern (longest in length) among all the clusters (400 and 1500 m).

Fig. 6 TSV changes, obtained for 400 m and 1500 m agl, based on number of clusters

Fig. 7 Mean trajectory solutions for five clusters at 400 m and four clusters at 1500 m

Originated from Netherlands and transported over Western and Central Europe (Germany, Czech Republic, Slovakia, eastern part of Hungary) has the potential to be loaded with pollutants generated by anthropogenic activities. This can be attributed to the highly industrialized countries; however, this system has the minimum contribution, only 5%.

On the other hand, we must mention that the impact of natural sources may also be significant under certain meteorological conditions. The study demonstrated that PM concentrations in Ciuc basin may be influenced by winds arriving in the region from and outside Romania. The results show that significant amount of PM₁₀ may arriving to the studied area, while the most frequent air masses entering Ciuc basin and hence influencing PM₁₀ concentrations come from the West and South, specifically the SW directions. In case of 400 m solutions 77% of the trajectories were originated from these directions and similar tendency was observed at 1500 m with 72%. The proposed methodology used through the study e.g. long-range trajectory and cluster analysis were satisfactory to identify the source regions of the trajectories arriving to the study area and carrying anthropogenic and natural sources pollutants. As a conclusion we can say that the source regions were identified using long-range simulations and it is a reliable tool to understand the contribution of pollutants transported from the source regions to the studied area.

3.4 Health risks of metals in PM₁₀

The cumulative risk (HQ and HI) values of non-carcinogenic substances of Al, Ba, Cl, Cu, Fe, Mn, P, Sr, Ti, W and Zn for both children and adult are shown in Table 5. These values are for the three exposure pathways of ingestion, inhalation, and dermal contact (Sah et al. 2019). Although estimated HIs for all the studied chemical compounds/elements were below the safe level (i.e. < 1) for both adults and children, several HIs were found to be higher than others, indicating the necessity to carefully monitor their concentration. The HQ values of Cu (2.90E-03 and 1.24E-03), Mn (2.20E-02 and 6.74E-03) for both children and adults via inhalation, P (1.41E-03 and 1.51E-04), Fe (2.39E-03 and 2.57E-04) via ingestion and Al (1.60E-02 and 8.80E-02), Cl (9.42E-03 and 5.18E-02), Fe (1.51E-02 and

8.30E-02), Mn (6.61E-03 and 3.63E-02), Ti (5.49E-03 and 3.02E-02), Zn (2.29E-04 and 1.26E-03) for children and adults via dermal contact were almost reaching the safe level, while in the case of other elements the HQ values were lower than the safe level. In the case of HI results the elements almost reached the level of safety, except the values of Ba (7.88E-07 and 8.88E-08) Sr (6.52E-08 and 7.25E-09), W (5.28E-08 and 5.50E-09). Some of the aforesaid metals are key components of human homeostasis, but in increased concentration they become toxic causing pathologic states and diseases. For example, the vital role of Fe is widely acknowledged, Fe being involved in fundamental biological activities such as oxygen transportation, cellular metabolism, mitochondrial respiration, DNA synthesis, cellular growth and differentiation (Ganz 2013; Paul et al. 2017).

Excessive Fe accumulation may result in augmented oxidative stress and successive dysfunction of various organs and systems such as liver, spleen, heart, bone marrow, pancreas and central nervous system (Gujja et al. 2010). According to Chen et al. (2018), Mn is known as a cofactor for several enzymes implicated in antioxidant protection, energy production, immune response, and regulation of neuronal activities. The brain is the critical target of Mn intoxication, which has been associated with cognitive, motor, and behavior deficits through amplified oxidative stress and apoptosis, mitochondrial dysfunction, protein misfolding, autophagy dysregulation, and impairment of other metal homeostasis (Holley et al. 2011; Chen et al. 2018). Mn exposure is a public health concern especially in young age when the brain is still developing (Bjørklund et al. 2017). The summary regarding the relationship between health effects and measured contaminants in the studied area via the inhalation exposure pathway is shown in Table 6 (IEC 2009). The elements which were studied and analyzed during the present study are not carcinogens, but they can cause several other diseases.

Being the third most abundant element on Earth, Al is easily distributed and frequently present in the environment, being toxic for the human organism, especially to bones, bone marrow and the nervous system (Saiyed and Yokel 2005). According to Oskarsson (2015) acute or chronic exposure to barium salts can cause several disorders, such as renal intoxication, hypertension, cardiac malfunction, and hearing loss at experimental animals.

Table 5 HQ and HI for metals in PM₁₀

	Ingestion		Dermal		Inhalation		HI	
	Children	Adults	Children	Adults	Children	Adults	Children	Adults
Al	2.54E-06	2.72E-07	1.60E-02	8.80E-02			1.60E-02	8.80E-02
Ba	7.58E-07	8.12E-08	3.03E-08	7.65E-09			7.88E-07	8.88E-08
Cl	1.50E-06	1.60E-07	9.42E-03	5.18E-02			9.42E-03	5.18E-02
Cu	1.93E-08	2.07E-09	5.40E-07	4.55E-15	2.90E-03	1.24E-03	2.90E-03	1.24E-03
Fe	2.39E-03	2.57E-04	1.51E-02	8.30E-02			1.75E-02	8.32E-02
Mn	1.05E-04	1.12E-05	6.61E-03	3.63E-02	2.20E-02	9.44E-03	2.87E-02	4.58E-02
P	1.41E-03	1.51E-04	2.38E-03	3.32E-13			3.79E-03	1.51E-04
Sr	6.35E-08	6.80E-09	1.78E-09	4.49E-10			6.52E-08	7.25E-09
Ti	2.61E-05	1.20E-05	5.49E-03	3.02E-02			5.51E-03	3.02E-02
W	5.14E-08	5.50E-09	1.44E-09	1.21E-17			5.28E-08	5.50E-09
Zn	3.64E-05	3.90E-06	2.29E-04	1.26E-03			2.66E-04	1.26E-03

Table 6 Hazard identification summery table according to (IEC 2009)

	Al	Ba	Cl	Cu	Fe	Mn	P	Sr	Ti	W	Zn
Respiratory		C	A	A, C	C	C			U		
Cardiovascular		C									
Dermatological			A							A	C
Gastrointestinal		C					U				
Hematological							U				C
Immune								C*			
Neurological	U					S, C					
Musculoskeletal		C									
Reproductive						C					

A Acute (1 h to 14 days of exposure), C Chronic (Over one year of exposure), S Subchronic (14 to 364 days of exposure, or repeated 8-h exposures), U Uncertain

*for Radiostrontium, ⁹⁰Sr

4 Conclusions

PM₁₀ concentrations were studied during the year of 2015 in the Ciuc basin, Eastern Carpathians in order to determine the elemental composition and the sources of atmospheric particulate matter. Results showed that daily concentrations of PM₁₀ range from 10.90 to 167.70 µg/m³, with an annual mean concentration of 46.31 µg/m³, being higher than the European Union's limit value for PM₁₀. It was observed that the highest concentrations of PM₁₀ occur during the cold period (October–March), exhibiting a mean value of 67.24 µg/m³. According to the SEM/EDX data, five principal components can be distinguished, suggesting that PM₁₀ can originate from five different sources such as post volcanic activity, crustal origin and anthropogenic sources, caused by the resuspension of crustal material, sea salt and soil dust. The C-rich particles identified in particulate matter by physical and chemical characterization showed that vehicular traffic and biomass burning are one of the most important sources of PM₁₀. The determination of HQ and HI contributed in the evaluation of non-carcinogenic risk, resulting that HQ values of Cu, Mn for both children and adults via inhalation, P, Fe via ingestion and Al, Cl, Fe, Mn, Ti for children and adults via dermal contact almost reached the level of safety while for other elements, the HQ values were lower than the safe level. In the case of HI results, the elements almost reached the safe level, except the values of Cu, Sr and W. The back-trajectory analysis showed that the most frequent air masses entering the Ciuc Basin influencing PM₁₀ concentrations came from the SW. The results of this study may be of great use to local and regional decision makers, to take preventive measures regarding the exposure to air pollutants.

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Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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