

FIȘĂ DE AUTOEVALUARE

privind standardele minime pe domenii ale Universității, pentru funcțiile de cercetare

ANEXA 2

Facultatea de Chimie ASISTENT DE CERCETARE	
Standarde minime:	2 articole științifice publicate în <i>extenso</i> în reviste internaționale, din care 1 în reviste cotate <i>Web of Science</i> cu factor de impact
Rezultat autoevaluare:	4 articole științifice publicate în <i>extenso</i> în reviste internaționale, din care 4 în reviste cotate <i>Web of Science</i> cu factor de impact

Articole științifice publicate în *extenso* în reviste internaționale, cotate *Web of Science* cu factor de impact:

1. Amarandei, C., [Negru, A.G.](#), Soroaga, L.V., Cucu-Man, S.M., Olariu, R.I., Arsene, C.; Assessment of surface water quality in the Podu Iloaiei dam lake (north-eastern Romania): Potential implications for aquaculture activities in the area, *Water*, 13, 2395, **2021**.
Factor de impact: **3,103**
2. [Galon \(Negru\), A.G.](#), Olariu, R.I., Arsene, C.; Size-resolved measurements of PM2.5 water-soluble elements in Iasi, north-eastern Romania: Seasonality, source apportionment and potential implications for human health, *Science of the Total Environment*, 695, 133839, **2019**.
Factor de impact: **6,551**
3. [Galon \(Negru\), A.G.](#), Olariu, R.I., Arsene, C., Chemical characteristics of size resolved atmospheric aerosols in Iasi, north-eastern Romania. Nitrogen-containing inorganic compounds controlling aerosols chemistry in the area, *Atmospheric Chemistry and Physics*, 18, 5879-5904, **2018**.
Factor de impact: **5,668**
4. [Negru, A.G.](#), Arsene, C., Zbancioc, A.M., Mangalagiu, I., Olariu, R.I., Physico-chemical behaviour of newly synthesized macrocyclic compounds. A reality between expectations and experimental evidences, *Revista de Chimie Bucharest*, 66, 9, 1339-1342, **2015**.
Factor de impact: **0,956**

Notă: Factori de impact raportați de *Clarivate* în *Journal Citation Reports* pentru anul de publicare al articolului. Pentru articolul din 2021 a fost luat în considerare factorul de impact al jurnalului pentru anul 2020.

Data,

Dr. Alina-Giorgiana NEGRU

Article

Assessment of Surface Water Quality in the Podu Iloaiei Dam Lake (North-Eastern Romania): Potential Implications for Aquaculture Activities in the Area

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Abstract: The Podu Iloaiei Dam Lake located on the Bahluiet River from Bahlui hydrographic basin, north-eastern Romania, is one of the most important water resources used for aquaculture activities in the region of interest. In the present study, the chemical composition related to water-soluble ions and elements was assessed in both water and sediment samples collected from the area of interest during July 2017 and October 2017, representative months for warm and cold seasons, respectively. Water-soluble ions ($\text{H}_3\text{C}_2\text{O}_2^-$, HCO_2^- , $\text{C}_2\text{O}_4^{2-}$, F^- , Cl^- , NO_2^- , Br^- , NO_3^- , SO_4^{2-} , Li^+ , Na^+ , NH_4^+ , K^+ , and Ca^{2+}) were analyzed by ion chromatography, while inductively coupled plasma mass spectrometry was used to quantify water-soluble fractions of elements (Be, B, Mg, Al, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, Rb, Sr, Mo, Ru, Pd, Ag, Cd, Sn, Sb, Te, Ba, Ir, Tl, Pb, Bi, and U). Evidence was obtained on the contributions of both anthropogenic and natural (pedologic) related sources in controlling the chemical composition of the water and sediment samples in the area. Analysis of Piper diagrams revealed the existence of $\text{CO}_3^{2-}/\text{HCO}_3^-$ and $\text{Ca}^{2+}/\text{Mg}^{2+}$ as dominant species for the sediment samples. The interest water pool was found to be oligotrophic over the warm period and eutrophic over the cold period. Overall, abundances and the association of chemical species in the area seemed to be controlled by a complex interplay between the water body’s main characteristics, meteorological factors, and anthropogenic activities. Moreover, the present results suggest that precautions should be taken for physicochemical parameter monitoring and prevention acts for surface water quality assurance in order to control the potential negative influence of some chemical parameters on fish productivity. Reported data also have a high potential to be used by experts in the field of developing lake water management policies for a sustainable exploitation of various aquatic systems.

Keywords: heavy metals; water-soluble ions; spatial distribution; nutrients; Podu Iloaiei Dam Lake



Citation: Amarandei, C.; Negru, A.-G.; Soroaga, L.-V.; Cucu-Man, S.-M.; Olariu, R.-I.; Arsene, C. Assessment of Surface Water Quality in the Podu Iloaiei Dam Lake (North-Eastern Romania): Potential Implications for Aquaculture Activities in the Area. *Water* **2021**, *13*, 2395. <https://doi.org/10.3390/w13172395>

Academic Editor: Aldo Fiori

Received: 30 July 2021

Accepted: 26 August 2021

Published: 31 August 2021

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1. Introduction

Changes in surface water’s quality due to dramatically increased chemicals and nutrient materials threaten aquatic ecosystems and the environmental conditions. Evaluation of water and sediment physicochemical characteristics is highly important for quality control of surface water resources and for identification of potential exploitation. Safe water for fish farming requires water parameters to be in certain ranges [1], with some (e.g., pH, water hardness, etc.) being more difficult to be controlled in natural water reservoirs. Additionally, heavy metal contamination of the aquatic environment has drawn special attention because of the persistence, bioaccumulation, and potential adverse effects on biota [2]. Understanding the physicochemical parameters and evaluation of the anthropogenic impact on surface water and sediment are highly important for water quality

assessments and aquatic environmental protection. The sediment is a major sink of heavy metals due to scavenging of metals from the water column. However, it can also be a potential source of metal contamination into the water column and aquatic biota due to remobilization processes. The behavior of heavy metals in sediments, and therefore their distribution, is affected by changes in sediment grain size, organic content, and the redox regime [3]. The construction of dams on rivers and the loss of water discharge could cause the accumulation of anthropogenic waste in water reservoirs [4].

The water used for aquaculture purposes requires appropriate conditions to ensure fishes' growth (fish seeds, feed, fertilizers), and, along with the fish farming activities, chemical residues and microorganisms are usually produced as wastes [5]. Fertilizers are highly soluble substances frequently used for aquaculture purposes [6]. Most of these chemicals are well known for their potential to release nutrients that can cause eutrophication of natural waters. In aquaculture there are also other substances that are less frequently used. Among them, liming material, oxidants, disinfectants, osmoregulators, algicides, coagulants, herbicides, and probiotics should be mentioned [6]. Moreover, in aquaculture the ionic composition of water is important for fish hatching, feeding, development, larval growth, and survival [7]. The concentrations of Ca^{2+} and Mg^{2+} divalent cations play a very important role in the ionic regulation of freshwater fish, with both ions modulating the branchial permeability [8]. Water contamination with agricultural, industrial, or human waste could result in aquaculture product contamination and food safety concerns. However, nowadays there is an increased concern over the potential harm of aquaculture effluents on receiving water bodies and worries over the contamination of aquatic food products with bioaccumulative and potentially harmful chemicals [5,9]. At the European scale, waters' status and pressures are presented in Report No. 7/2018 of the European Environment Agency (EEA) [10]. The ecological status and potential of surface water bodies are assessed based on biological, physicochemical (nutrients, organic pollution, acidification), and hydromorphological elements. In terms of water quality, five classes, including high, good, moderate, poor, and bad, are usually referred to. When speaking about the chemical status derived from the evaluation of priority substances, waters can be assigned as "good" or "failing to achieve good." The EEA report indicates that, at the European scale, 38% of surface water bodies are in good chemical status, 46% are under the critical thresholds for this status, and 16% have an unknown status. Moreover, at the European level, just 40% of the surface water bodies are in good or high ecological status or potential.

The Podu Iloaiei water reservoir, located on the Bahluiet River from the Bahlui River basin in north-eastern Romania, is one of the most important water resources used for aquaculture activities in the region of interest. It has both economic and socio-politic value since the area is considered as one of the most anthropized hydrological basins in the country. Anthropogenic activities have important implications for the formation and evolution of water resources in the Bahlui hydrological basin. Waste from the municipalities and farms located along the Bahluiet River, agricultural runoff, the application of chemical fertilizers in agriculture, and transport routes around the reservoir are the potential pollution sources in the investigated area [11]. Nevertheless, little is known about the chemical parameter levels in the water and sediment of Podu Iloaiei Dam Lake.

Over the years, Directive 2000/60/EC [12] of the European Parliament and of the council establishing the framework for community action in the field of water policy have been implemented in Romania through the Ministry of Waters and Environmental Protection Order No. 161/2006 [13]. According to the norms for classification of surface water quality, the ecological status of water bodies is established on the base of five quality classes for surface waters (I–V) (Table S1 of the Supplementary Material).

For the Bahlui River basin, in terms of required parameters for establishing water quality class, only very few reports can be identified in the literature [14,15]. Both previous studies report measured values for chemical parameters limited to pH, CBO_5 , CCO-Mn , NH_4^+ , NO_2^- , NO_3^- , PO_4^{3-} , and Mg^{2+} [14,15]. There is also one study reporting about

the anthropogenic impact on urban soil properties from the Bahlui Floodplain [16]. The treatment station of the town of Targu Frumos and some livestock farms located along the Bahluiet River are suggested as the main pollution sources of Podu Iloaiei Dam Lake [14]. The impact of anthropogenic activities on water quality parameters of glacial lakes from Rodnei mountains was also reported in a more recent study [17]. Relatively high concentrations of NH_4^+ , NO_2^- , Ca, Mg, Fe, and Cu were identified even in this water representative for a more pristine environment.

Reports on the photochemistry induced either by hydroxyl or nitrite radicals in natural water samples collected from wells in the Letcani area (north-eastern Romania, Bahlui River basin) [18–21] or from selected Romanian lakes [22] are present in the literature. In some studies, the authors also report on experimental evidence for aromatic nitration upon irradiation of natural water samples since, in the interest zones, very high nitrate levels were identified [20,22,23]. However, other representative studies in Europe highlight fairly well the importance of surface water investigations [24].

In Romania, the governmental summary report from 2018 of the National Agency for Environmental Protection classifies the Podu Iloaiei Dam Lake water as moderate (class III) in terms of general physicochemical parameters, but no results are presented for specific pollutants and the chemical status [25]. In the present work, accurate concentrations of water-soluble ions and water-soluble elements in water and sediment samples from Podu Iloaiei Dam Lake were reported. The main objectives of the performed investigations were: (1) to determine the level of heavy metal and ion concentrations for evaluation of water quality status by seasonal change, (2) to investigate the spatial distributions of chemical parameters in water and sediment, (3) to identify their potential sources using the multivariate statistical analysis, and (4) to indicate the suitability of water quality for intensive fish farming purposes. Moreover, the work reported in the present study may be considered as a key reference point for further investigation on potential degradation processes of photolabile organic compounds or in identifying the role played by some elements, e.g., Fe, in the photoproduction of OH radicals under specific conditions.

2. Materials and Methods

2.1. Study Area and Sampling Strategy

The Podu Iloaiei Dam Lake is located in the north-eastern part of Romania (Figure 1) on the Bahluiet River at a distance of 2.5 km upstream of the confluence with the Bahlui River, at 400 m upstream from the town of Podu Iloaiei, Iasi County. The Bahluiet River is an affluent of the Bahlui River located in the area between the Moldavian Plain and the Central Moldavian Plateau. The average altitude of the hydrological basin is 159 m above sea level, and the multiannual average flow rate of Bahluiet River is 1.06 m s^{-1} [26]. The main water input for Podu Iloaiei Dam Lake is Bahluiet River, and other sources include snow melting and natural springs. The Bahluiet River basin has a total surface of 550 km^2 , a length of 50 km, an average slope of 13%, and a sinuosity coefficient of 1.23 [27].

The Podu Iloaiei Dam Lake was made to regulate the Bahluiet River water flow rate, and it is used for fish farming and irrigation. Podu Iloaiei Dam Lake has a water surface of 251 ha and a dam of 14.1 m in elevation and 640 m in width [28]. The area and volume of Podu Iloaiei Lake can vary considerably throughout the year. The water level is usually lower during the summer (June, July, and August) and higher during major rainfall events in the autumn (September, October, and November). The lake water is evacuated for the winter time.

The hydrographic basin is characterized by alluvial soils, carbonated alluviums, soils rich in sodium sulphates, meadow chernozem (formed on clayey and maroon substrates), and gray soils. Surface deposits are represented by monotonous succession of marches, clays, and sands with some intercalations of limestone sandstone, which is disposed monoclinaly [11]. Bessarabia deposits (clay marls with intrusions of sand) from the Sarmatian age dominate the basin. Quaternary deposits from the Pleistocene age and Holocene deposits are also located in the Bahluiet River area [27].

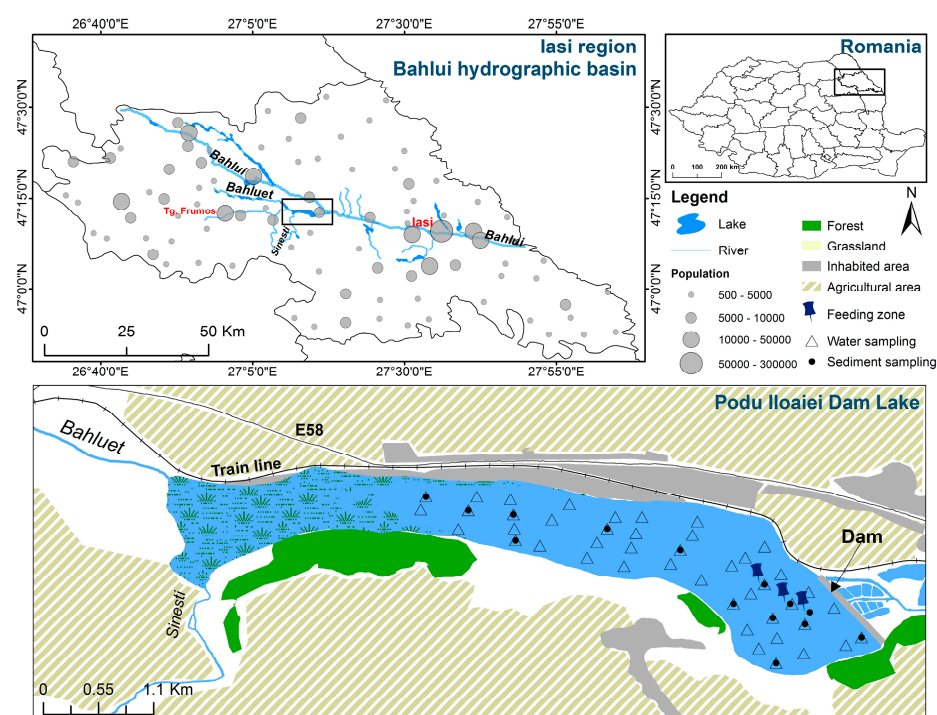


Figure 1. Location of the study area, water, and sediment sampling points.

The climate of the area is temperate–continental, with warm summers and cold winters. During the year, the temperature typically ranges from -5°C to 28°C , rarely reaching below -14°C or above 33°C , and the annual rainfall average is 589 mm. In the year the sampling was undertaken, May and June 2017 recorded the highest average precipitation values of 44 and 54 mm, respectively, and October 2017 was the month with the lowest rainfall, with an average of 27 mm.

According to the National Institute of Statistics, in the Prut–Barlad hydrographic area, including the Bahlui hydrographic area, about 71% of the surface is used for agriculture, 14% is covered by forests, 12% is occupied by construction, and 3% is occupied by surface waters [29]. The Podu Iloaiei Dam Lake is used for fish farming and is an important source of water for fishponds downstream of the dam [26].

In order to evaluate the chemical parameters of the investigated environment, water and sediment samples were collected from Podu Iloaiei Dam Lake in 50 mL polypropylene bottles in two sessions. The entire set of samples comprised 88 water samples and 28 sediment samples collected on 16 July 2017 and 5 October 2017, respectively. The sampling strategy was designed so as to obtain a significant number of data points for an accurate statistical treatment or for high-resolution distribution maps. The availability of technical resources was the limitative factor in increasing the sampling frequency or the number of the samples for each matrix. The distribution of the water and sediment sampling points is presented in Figure 1.

Water samples were collected from a ~ 10 cm depth (from the water surface layer), and sediment samples were collected from a ~ 20 cm depth (from the water–soil interface). The samples were stored at -4°C until the analysis, which was performed within a maximum of 72 h after sampling.

2.2. Materials and Methods

2.2.1. Water-Soluble Ions Analysis by Ion Chromatography

The following inorganic anions: chloride (Cl^-), fluoride (F^-), bromide (Br^-), nitrite (NO_2^-), nitrate (NO_3^-), phosphate (PO_4^{3-}) and sulphate (SO_4^{2-}); organic anions: acetate ($\text{H}_3\text{C}_2\text{O}_2^-$), formate (HCO_2^-), and oxalate ($\text{C}_2\text{O}_4^{2-}$); and inorganic cations: sodium (Na^+),

potassium (K^+), lithium (Li^+), ammonium (NH_4^+), magnesium (Mg^{2+}), and calcium (Ca^{2+}) were quantified by ion chromatography.

The sediment samples were dried at 50 °C for 72 h in a ventilated oven (Ecocell), and 0.1–0.2 g of dry sediments were weighted and subjected to extraction with deionized water by ultrasound-assisted extraction (ultrasonic bath Elmasonic S70H, Elma, Singen, Germany) for 45 min at room temperature. The water samples and the aqueous extract of the sediment samples were filtered before analysis using cellulose acetate filters (ADVANTEC) with a pore diameter of 0.20 μm .

The ion determination was performed by the DIONEX ICS-5000+ DP system (Thermo Scientific, Waltham, MA, USA). In the case of anion determination, a 4.5/1.4 mM CO_3^{2-}/HCO_3^- solution was used for elution at a flow rate of 1.2 mL min^{-1} , using an AS22 column (4 $\times$ 250 mm) and an AERS 500 suppressor (4 mm). A 20 mM methanesulfonic acid solution was used as mobile phase at a flow rate of 1.0 mL min^{-1} for cation separation. In this case, a CS12A column (4 $\times$ 250 mm) and a CSRS 300 suppressor (4 mm) were used.

The external standard method was used to quantify water-soluble ions in both water and sediment samples. Calibration curves were performed in the concentration range of 50–3000 $\mu g L^{-1}$ for anions and 50–2500 $\mu g L^{-1}$ for cations. For the calibration curves, the required standard solutions were prepared by appropriate dilutions of seven anions-II and six cations-II Dionex standards. Calibration curves of water-soluble organic anions (acetate, formate, and oxalate) were acquired using solutions prepared with sodium salts of the anions (sodium acetate, $\geq 99\%$, from Merck, Darmstadt, Germany; sodium formate, 99%, and sodium oxalate, 99.9%, from AnalAR NORMAPUR, Leuven, Belgium).

The water samples' dilutions, the extraction of soluble ions from the sediment samples, and the preparation of the mobile phases and standard solutions were performed with deionized water (resistivity of 18.2 $M\Omega \cdot cm$) provided by the Milli-Q Advantage A10 system (Millipore, Burlington, MA, USA).

HCO_3^- is one of the major anions present in the water samples but cannot be determined by ion chromatography while using CO_3^{2-}/HCO_3^- as eluent. In an attempt to supplement the ionic balance, its estimation was used according to the method proposed by Arsene and co-workers [30]. The statistically significant correlation between the sum of the Ca^{2+} and Mg^{2+} concentrations and the anion deficit estimated from the ionic balance were taken into account. For both the sampling sessions, the linear regressions obtained between these variables are shown in Figure S1 of the Supplementary Material (SM).

2.2.2. Water-Soluble Elements Analyses by Inductively Coupled Plasma Mass Spectrometry

The analysis of water-soluble fractions of the elements in water and sediment samples was performed for Be, B, Mg, Al, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, Rb, Sr, Mo, Ru, Pd, Ag, Cd, Sn, Sb, Te, Ba, Ir, Tl, Pb, Bi, and U by inductively coupled plasma mass spectrometry (ICP-MS) using the ICP-MS 7700X system (Agilent Technologies, Santa Clara, CA, USA). For the analysis, a 1 mL water sample and a 1 mL sediment aqueous extract (solution used for the ion chromatography analysis) were diluted with 8.5 mL 3% HNO_3 . As an internal standard, 0.5 mL of indium (In) solution (1 mg L^{-1}) was added in each sample. Internal standard calibration curves were achieved using the multi-element standard solutions with 30 elements (Li, Be, B, Na, Mg, Al, K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Mo, Ag, Cd, Te, Ba, Tl, Pb, Bi, and U) and 8 elements (Ti, Ge, Mo, Ru, Pd, Sn, Sb, and Ir). Suprapur[®] nitric acid (65%) and all standard solutions used for ICP-MS analysis were purchased from Merck, Darmstadt, Germany.

During the analysis, in order to prevent the possible contributions brought by the contaminations, special emphasis was placed on carefully controlling the entire array of analysis steps. During the analysis sequence, for the quality control assurance, blanks and control samples were frequently analyzed. Tables S2 and S3 in the Supplementary Materials show the limits of detection (LoD) and the limits of quantification (LoQ) for the chemical species investigated in the present study.

2.3. Statistical Analysis of the Data

The mean, the standard deviation, and the median of the water-soluble ions and elements concentrations were calculated to obtain the variation between two different sampling sessions.

Multivariate statistical tools were applied in Origin 2018 to analyze the associations among different chemical species. Pearson's correlation coefficient and hierarchical cluster analysis were used for source apportionment. The Kolmogorov–Smirnov test was performed to check possible differences between the sampling sessions. Significant differences between the ions and the elements concentrations in both sampling sessions were identified with the value of $p < 0.05$ (95% confidence level).

Cluster analysis of the data with the Ward calculation method [31] was applied to identify possible common sources for the chemical species quantified in the water and sediment samples for both sampling sessions. This is a method of assessing the distance between two clusters by minimizing intra-cluster variability. Other studies in the field of water quality using the Ward method for cluster analysis have been identified in the literature [32,33]. Following the data processing, the graphs known as dendrograms show how the elements are grouped into classes according to the similarities between them.

The geostatistical method was implemented to comprehensively describe the variation of chemical species concentration in the surface water and sediment of Podu Iloaiei Dam Lake. In addition to the cluster analysis, the analysis of the geospatial distributions of the quantified species was used in order to discriminate between the potential contributions of the sources of pedological, atmospheric, or anthropogenic origin. In the literature, geostatistical data processing and the multivariate statistic data evaluation approach have been used for the investigation of pollutants in soil, sediment, and natural waters [34,35]. In order to achieve geospatial distributions of water-soluble ionic species quantified in water and sediment samples, the Google Earth Pro and ArcMap programs included in the ArcGIS 10.2 package were used. Kriging Ordinary interpolation methods with a spherical semivariogram and inverse distance weighting (IDW) interpolation were used for data processing. Compared to IDW, the Kriging method uses the theory of regionalized variables, which assumes that the direction and distance between data reflect a spatial correlation that is applied in explaining their variation by determining the semivariogram [36,37]. For this reason, the Kriging method is more complex and is not applicable to databases with a small number of cases. IDW is easier to apply, faster, not very restrictive in terms of the number of cases per variable or in terms of variance, and usually applies to highly variable data. The IDW method was used for sediment database comprised of a reduced number of available samples (14 compared to 44 for water).

3. Results

3.1. Water-Soluble Ions

The major ions quantified by ion chromatography in water and sediment samples were Cl^- , SO_4^{2-} , Mg^{2+} , Ca^{2+} , Na^+ , and K^+ . For ionic species quantified in water samples, excepting SO_4^{2-} , higher concentrations in samples collected in October were observed (Table 1). Figure S2 in the Supplementary Materials shows the linear regressions corresponding to the ionic balance for water and sediment samples including the estimated HCO_3^- contribution. For water samples (Figure S2a), compared to sediment samples (Figure S2b), an anion deficiency of 12% for samples collected in July and 18% for samples collected in October was observed. This could be associated with the presence of other organic compounds, such as amino acids and other carboxylic acids [38–41], that were not quantified in the present study.

Water hardness was calculated using the concentrations determined for Ca^{2+} and Mg^{2+} by ion chromatography (Table 1), and it was estimated as high as $352 \pm 18 \text{ mg L}^{-1} \text{ CaCO}_3$ in July and $412 \pm 58 \text{ mg L}^{-1} \text{ CaCO}_3$ in October. The values of electrical conductivity recorded in July and October were $474 \pm 121 \mu\text{S cm}^{-1}$ and $956 \pm 23 \mu\text{S cm}^{-1}$, respectively.

Table 1. Water-soluble ions concentrations in water (mg L^{-1}) samples ($n = 44$), pH, conductivity (S , $\mu\text{S cm}^{-1}$), acid-neutralizing capacity (ANC, meq L^{-1}), and hardness (in $\text{mg L}^{-1} \text{CaCO}_3$) and water-soluble ions concentrations in sediment ($\mu\text{g g}^{-1}$) samples ($n = 14$) from Podu Iloaiei Dam Lake, north-eastern Romania. Data are presented as mean $\pm$ stdev (median) for the entire pool of analyzed samples (no flagged data).

Species/ Parameter	Water		Sediment	
	July	October	July	October
Cl^-	48.0 ± 5.2 (46.8)	63.0 ± 17.7 (57.6)	139 ± 39 (134)	94.7 ± 64.8 (74.7)
SO_4^{2-}	234 ± 7 (235)	181 ± 24 (179)	1121 ± 546 (1155)	1297 ± 484 (1170)
Na^+	153 ± 4 (152)	177 ± 9 (175)	476 ± 169 (513)	595 ± 195 (578)
K^+	13.6 ± 8.3 (10.4)	19.8 ± 15.3 (12.6)	284 ± 98 (294)	564 ± 133 (625)
Mg^{2+}	56.7 ± 1.6 (56.6)	62.9 ± 4.1 (62.7)	550 ± 139 (538)	1639 ± 320 (1728)
Ca^{2+}	47.5 ± 6.7 (45.6)	61.1 ± 17.8 (58.7)	1338 ± 692 (1179)	5041 ± 1350 (5305)
N-NO_2^-	0.40 ± 0.27 (0.40)	0.98 ± 1.12 (0.52)	28.0 ± 40.1 (11.4)	<1.86
N-NO_3^-	0.56 ± 0.42 (0.47)	1.56 ± 2.18 (0.92)	18.8 ± 26.4 (6.2)	7.92 ± 6.83 (8.29)
N-NH_4^+	0.65 ± 0.46 (0.55)	2.74 ± 1.67 (2.28)	142 ± 55 (138)	106 ± 70 (87)
P-PO_4^{3-}	<1.06	3.40 ± 2.20 (3.38)	17.0 ± 10.4 (11.5)	45.9 ± 16.7 (44.8)
$\text{H}_3\text{C}_2\text{O}_2^-$	32.5 ± 30.5 (24.1)	43.0 ± 43.0 (26.3)	394 ± 462 (230)	223 ± 118 (202)
HCO_2^-	4.27 ± 0.74 (4.27)	5.72 ± 6.57 (3.75)	91.1 ± 66.3 (63.6)	98.2 ± 47.4 (86.2)
$\text{C}_2\text{O}_4^{2-}$	<7.00	<7.00	64.0 ± 24.2 (60.3)	83.1 ± 35.9 (71.2)
pH	9.09 ± 0.15 (9.11)	8.25 ± 0.07 (8.24)		
S	474 ± 121 (491)	956 ± 23 (948)		
CaCO_3	366 ± 19 (349)	412 ± 58 (404)		
ANC	7.80 ± 0.52 (7.71)	10.8 ± 0.8 (10.6)		

F^- , Br^- , Li^+ species were below the LoD.

The investigated inorganic ions containing nitrogen or phosphorus were NO_2^- (N-NO_2^-), NO_3^- (N-NO_3^-), NH_4^+ (N-NH_4^+), and PO_4^{3-} (P-PO_4^{3-}). The N-NH_4^+ concentrations at the surface water level were $0.65 \pm 0.46 \text{ mg L}^{-1}$ in July and $2.74 \pm 1.67 \text{ mg L}^{-1}$ in October (Table 1). Oxalate could only be quantified in the water extracts of sediment samples, presenting lower concentrations than acetate and formate, $64.0 \pm 24.2 \mu\text{g g}^{-1}$ compared to $394 \pm 462 \mu\text{g g}^{-1}$ and $91.1 \pm 66.3 \mu\text{g g}^{-1}$ in July, and $83.1 \pm 35.9 \mu\text{g g}^{-1}$ compared to $222 \pm 118 \mu\text{g g}^{-1}$ and $98.2 \pm 47.4 \mu\text{g g}^{-1}$ in October (Table 1). $\text{C}_2\text{O}_4^{2-}$ is known to be an important component of plants [42]. It largely undergoes the process of bacterial decomposition with the formation of CO_2 , but, in the case of hard water, $\text{C}_2\text{O}_4^{2-}$ precipitates in the form of CaC_2O_4 [43].

The water acid-neutralizing capacity (ANC) calculated with Equation (1) had the average values of $7.80 \pm 0.52 \text{ meq L}^{-1}$ in July and $10.8 \pm 0.8 \text{ meq L}^{-1}$ in October. These values indicate that the water is not susceptible to acidification. This aspect was confirmed by the pH measurements made in July and October, the mean values being 9.09 ± 0.15 and 8.25 ± 0.07 , respectively.

$$\text{ANC} = ([\text{Ca}^{2+}] + [\text{Mg}^{2+}] + [\text{Na}^+] + [\text{K}^+]) - ([\text{SO}_4^{2-}] + [\text{NO}_3^-] + [\text{Cl}^-]) \quad (1)$$

3.2. Water-Soluble Elements

Table 2 shows the average concentrations of determined elements in water samples and aqueous sediment extracts for the interest sampling sessions. Higher concentrations of the quantified elements were observed for the October sampling session compared with the July sampling session.

The mean Cr concentration values were $0.019 \pm 0.011 \text{ mg L}^{-1}$ and $0.064 \pm 0.048 \text{ mg L}^{-1}$, in July and October, respectively. The average values of Cr concentration (Table 2) classify the lake water in quality class II according to Order 161/2006 [13]. Variations in Cr concentrations in water can be associated with adsorption/desorption and precipitation/solubilization processes [44].

The average concentrations of Pb in water samples for both sampling sessions of $0.071 \pm 0.062 \text{ mg L}^{-1}$ and $0.078 \pm 0.116 \text{ mg L}^{-1}$ exceeded the limits of quality class IV (according to Order 161/2006), and a concentration of 0.025 mg L^{-1} was associated with

the waste water class. Measured concentrations of Ni and Mn in water samples collected in October were higher than the regulated values of 0.025 mg L^{-1} and 0.30 mg L^{-1} , respectively, corresponding to quality class IV.

Table 2. Averages of water-soluble elements' concentrations in water (mg L^{-1} , $n = 44$) and sediment ($\mu\text{g g}^{-1}$, $n = 14$) samples from Podu Iloaiei Dam Lake, north-eastern Romania. Data are presented as mean $\pm$ stdev (median).

Element	Water		Sediment	
	July	October	July	October
Al	1.00 ± 2.03 (0.48)	1.35 ± 1.70 (0.68)	96.5 ± 57.1 (79.6)	143 ± 80 (120)
Ti	<0.60	<0.60	8.67 ± 4.99 (7.60)	5.36 ± 4.93 (2.94)
Cr	0.019 ± 0.011 (0.019)	0.064 ± 0.048 (0.051)	1.21 ± 0.81 (0.79)	1.13 ± 0.80 (0.84)
Mn	0.097 ± 0.083 (0.072)	0.33 ± 0.21 (0.34)	20.0 ± 9.6 (18.7)	45.4 ± 26.9 (38.2)
Ni	0.12 ± 0.17 (0.09)	1.08 ± 3.04 (0.41)	14.4 ± 3.8 (14.2)	17.2 ± 5.3 (17.2)
Zn	0.79 ± 1.67 (0.12)	1.88 ± 2.52 (1.27)	15.3 ± 6.5 (17.7)	97 ± 161 (37)
Ge	0.14 ± 0.11 (0.13)	0.19 ± 0.13 (0.15)	19.6 ± 4.4 (20.3)	16.8 ± 4.1 (16.9)
Sr	0.54 ± 0.09 (0.52)	0.60 ± 0.42 (0.52)	10.6 ± 4.1 (9.4)	40.6 ± 11.5 (39.5)
Ag	0.075 ± 0.037 (0.073)	0.13 ± 0.10 (0.10)	0.61 ± 0.39 (0.45)	0.95 ± 0.75 (0.63)
Sb	0.006 ± 0.005 (0.005)	0.04 ± 0.06 (0.02)	0.26 ± 0.20 (0.18)	0.24 ± 0.13 (0.25)
Ba	0.059 ± 0.041 (0.054)	0.16 ± 0.14 (0.12)	22.1 ± 3.6 (21.7)	30.3 ± 8.3 (31.5)
Pb	0.071 ± 0.062 (0.062)	0.08 ± 0.12 (0.05)	1.93 ± 1.49 (1.52)	1.20 ± 1.99 (0.62)

Be, B, V, Fe, Co, Cu, Ga, Rb, Mo, Ru, Pd, Cd, Sn, Te, Ir, Tl, Bi, and U were below the LoQ.

4. Discussion

4.1. Water-Soluble Ions and Elements Related to Lake Water Typology

In both water and sediment samples the concentrations of the major ions collected in October were higher compared to July (Table 1). This was most likely the result of a significant contribution from the anthropogenic factors and less from the pedological factors or from the microbiological processes that naturally take place in the aquatic system. The Bahluet River supply water could be a source of waste for Podu Iloaiei Dam Lake because along its course fish farms, villages without sewerage, and agricultural lands are located. Differences between the two sampling seasons might also be due to the weather conditions during the collection time. In 2017, dilution of water-soluble ionic species and elements could occur in June and July due to more heavy raining events if compared to September and October. In water systems with a high-density fish population water quality can be altered by the chemicals added in order to maintain the parameters at an appropriate level. An increase in temperature, the consumption of oxygen by zooplankton, and the intensification of fodder residues' microbiological degradation processes may induce a critical decrease in dissolved oxygen. To prevent these, calcium hypochlorite ($\text{Ca}(\text{ClO})_2$) is added to stabilize the amount of dissolved oxygen in the investigated system.

Figure 2 shows the percentage distributions of ionic species quantified in water (Figure 2a) and sediment (Figure 2b) samples and were calculated using the mean concentrations in meq L^{-1} for water and $\mu\text{eq g}^{-1}$ (dry sediment) for sediment. From the percentage distributions presented in Figure 2, it was observed that for the water samples the major ions are present in the order $\text{Na}^+ > \text{HCO}_3^- > \text{Mg}^{2+} > \text{SO}_4^{2-} > \text{Ca}^{2+} > \text{Cl}^- > \text{K}^+$ and for the sediment samples $\text{HCO}_3^- > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{SO}_4^{2-} > \text{Na}^+ > \text{K}^+ > \text{Cl}^-$. The dominant water anion was HCO_3^- followed by SO_4^{2-} . The high contributions of Na^+ (24.1%) and SO_4^{2-} (14.5%) ions can be associated with the pedological factor, the investigated area having characteristic saline soils with high levels of sodium sulphate [11]. An additional source of SO_4^{2-} could be represented by air pollution generated by rail transport (at ~250 m) and or by intense traffic on the road nearby.

Nitrogen and phosphorus are considered macronutrients, often limiting the development of phytoplankton. In the absence of nutrient pollution sources (fertilizers, wastewater rich in PO_4^{3-} , etc.), natural waters have low amounts of these species because there is a natural cycle that does not allow their accumulation in the environment. Unpolluted

natural surface waters have inorganic nitrogen concentrations of less than 0.01 mg L^{-1} N-NO_2^- , 0.2 mg L^{-1} N-NO_3^- , and 0.02 mg L^{-1} N-NH_4^+ [45]. Low levels of the dissolved oxygen in the water increase the anoxic processes at the water–sediment interface. Higher concentrations of N-NH_4^+ (Table 1) can be determined by biodegradation processes of organic matter under anoxic conditions. NO_2^- does not accumulate in the water because it is formed mainly as an intermediate in the nitrification process and has a low stability. Variations in the concentrations of P-PO_4^{3-} , N-NO_2^- , and N-NO_3^- could be attributed to local processes of organic matter biodegradation. For N-NH_4^+ , the possibility of an anthropogenic source of contamination can be considered. A seasonal source for NH_4^+ could be the phytoplankton degradation in early autumn, local accumulations of organic matter being possible.

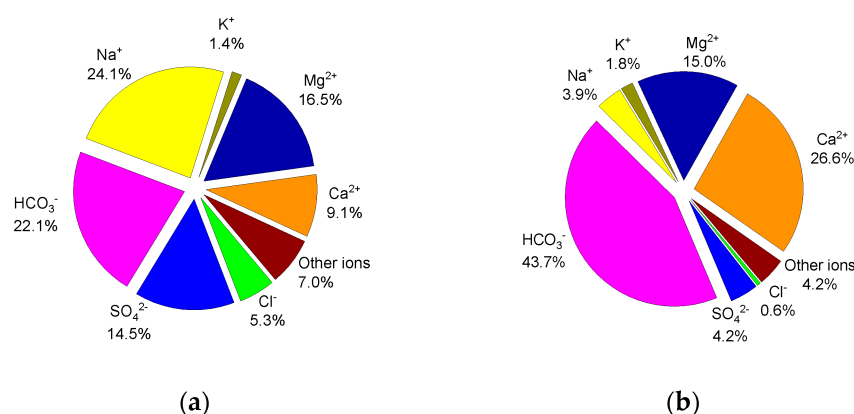


Figure 2. Relative concentration distribution of water-soluble ions quantified in water (a) and sediment (b) samples collected from Podu Iloaiei Dam Lake (other ions: $\text{H}_3\text{C}_2\text{O}_2^-$, HCO_2^- , $\text{C}_2\text{O}_4^{2-}$, PO_4^{3-} , NO_2^- , NO_3^- , NH_4^+).

In order to indicate the dominant typology of water, Piper diagrams were used. They allow the identification of water character by using the ratio of major ions. For water samples, the Piper diagram (Figure 3a) does not indicate the existence of a dominant water character, but the orientation towards $\text{Na}^+ + \text{K}^+$, $\text{HCO}_3^- + \text{CO}_3^{2-}$, and SO_4^{2-} can be observed. This could suggest the presence of Na^+ , K^+ , and SO_4^{2-} sources other than the solubilization process of sediment minerals, for example, the use of fertilizers in agriculture or the discharge of wastewater from households [6]. The difference between the diagrams can also be explained by the higher solubility of the Na^+ and K^+ salts compared to those of Mg^{2+} and Ca^{2+} . Additionally, among the major cations (Ca^{2+} , Mg^{2+} , K^+ , Na^+), Ca^{2+} has the lowest hydrated ion radius that enhance its adsorption on the sediment. The physicochemical properties of the soil must be studied in order to explain the ion exchange processes that take place.

For sediment (Figure 3b) samples, a dominant character of Ca^{2+} (Mg^{2+}) HCO_3^- was observed. Higher concentrations of $\text{Ca}(\text{HCO}_3)_2$ and CaCO_3 in samples collected in October compared to July could be determined by the increase in the solubility of these species when the temperature decreases, a phenomenon considered in other study [46].

Both for water (Figure 4a) and sediment (Figure 4b) samples, important variations were observed between the sampling periods for most of the elements' concentrations. These could indicate a waste accumulation in the water and sediment due to the Bahluet River contributions and fish food addition. The variations could indicate the presence of temporary pollution sources such as waste discharge and secondary pollution sources represented by the selective mobilization of metals from sediment enhanced by higher major ions concentrations in the samples collected in October compared to July.

As previously presented, the Podu Iloaiei Dam Lake water is characterized by a high content of major ions. Acosta and co-workers [47] highlighted the mobilization of Pb enhanced by an increase in CaCl_2 , MgCl_2 , NaCl , and Na_2SO_4 salinity. These could be

determined by the high concentrations of major ions, especially Ca^{2+} , Mg^{2+} , Na^+ , which can lead to the mobilization of heavy metals from the sediment by the ion exchange process [2].

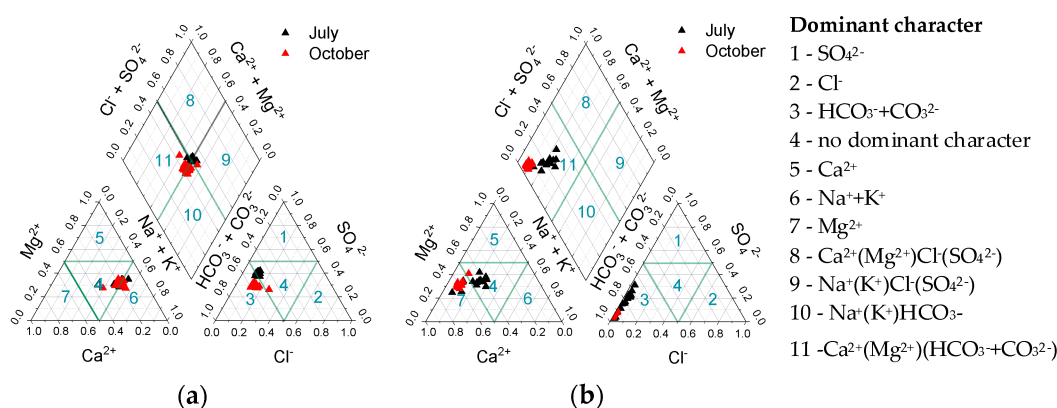


Figure 3. Piper diagrams corresponding to water (a) and sediment (b) samples collected from Podu Iloaiei Dam Lake.

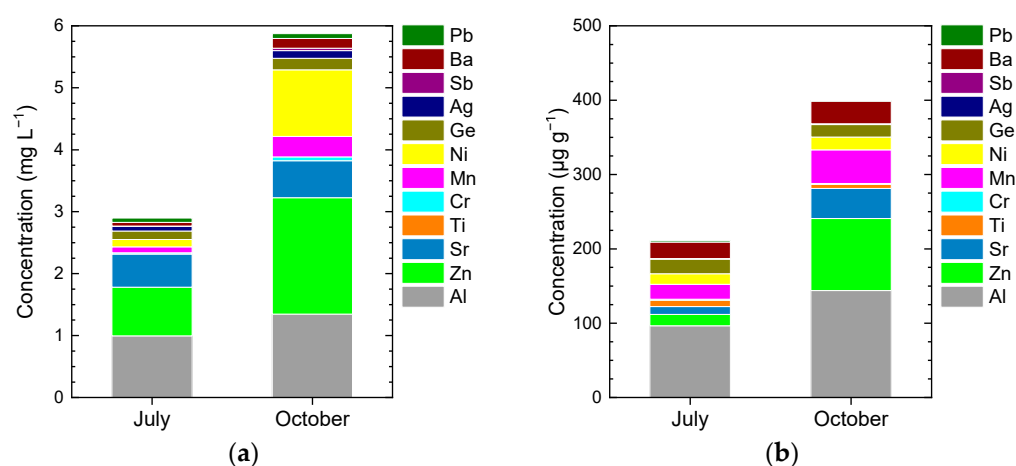


Figure 4. The cumulative concentrations of the water-soluble elements quantified in water (a) and sediment (b) samples collected from Podu Iloaiei Dam Lake in each sampling session.

4.2. Distribution of Chemical Parameters in the Podu Iloaiei Dam Lake

The dendrograms obtained by the Ward method for selected species quantified in water and sediment samples collected in both July and October sampling sessions are presented in Figure 5. Prior to this analysis, the data were normalized. The distribution of chemical species within the clusters suggests that Sr, Mg^{2+} , Cl^- , SO_4^{2-} , Na^+ , and Ca^{2+} can be associated with the pedological factor. The association is highlighted by the Pearson's correlation coefficient values calculated and presented in Tables S4 and S5 in the Supplementary Materials. Natural contributions for these species could be soil runoff and mobilization of soluble species in water from the sediment and soil.

For the water samples (Figure 5a), a cluster including Al, Zn, Pb, NH_4^+ , and K^+ was highlighted, indicating fish food administration as a possible source for these species. A common source for NH_4^+ and K^+ could be the use of fertilizers in agriculture and the bacterial degradation of plant residues rich in organic compounds with N and K^+ . The Sb, Ti, Ge, Ba, Mn, Cr, Zn, and Ag determined in sediment were grouped in one cluster, suggesting that the main contribution for these elements could be attributed to the pedological factor. A strong association between Pb and Al in sediment could indicate their anthropogenic origin. Additionally, a statistically significant correlation factor of 0.77 ($p < 0.001$) (Table S5 in the Supplementary Materials) between these elements was observed.

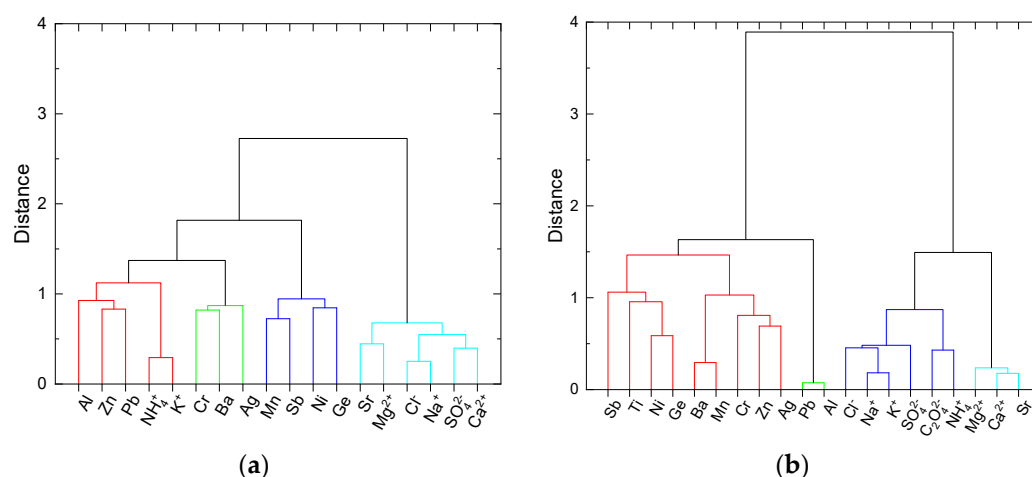


Figure 5. Hierarchical dendrograms showing clustering of water-soluble ions and elements in water (a) and sediment (b) samples collected in July and October sampling sessions.

Geospatial distributions in the water samples of the pH and conductivity parameters, beside those of water-soluble ions as Mg^{2+} , Ca^{2+} , NH_4^+ , Na^+ , SO_4^{2-} , Cl^- , and NO_3^- , are shown in Figure 6. Figure S3 of the Supplementary Materials presents the geospatial distributions of K^+ , NO_2^- , $\text{H}_3\text{C}_2\text{O}_2^-$, and HCO_2^- concentrations in both water and sediment samples. There was a clear discrimination between areas with two different particularities in terms of potential existent acidity and alkaline driven species. From Figure 6 it is clearly observed that water-soluble Mg^{2+} , Ca^{2+} , and NH_4^+ are major ionic species controlling alkalinity. While over the July session, the NH_4^+ species seemed to play an important role in the area where the water depth was lower, in the October session, it was obvious that the importance of this ion in controlling water pH might enhance in the feeding area. The values of the pH parameter measured for both July and October sessions allow us to suggest the potential transition of NH_4^+ to the toxic and volatile NH_3 , which might occur in the investigated water lake.

In water samples, several common point sources are easily identified in the geospatial distributions of Ca^{2+} , Cl^- , and NO_3^- (Figure 6). Areas with higher conductivity (Figure 6) correspond to areas with higher Mg^{2+} , NH_4^+ (Figure 6), and K^+ (Figure S3 in the Supplementary Materials) concentrations.

Figure 7 shows the distribution of Mg^{2+} , Ca^{2+} , NH_4^+ , Na^+ , SO_4^{2-} , Cl^- , NO_3^- , and $\text{C}_2\text{O}_4^{2-}$ in sediment samples. Similar geospatial distributions of Mg^{2+} , Ca^{2+} , Na^+ , SO_4^{2-} (Figure 6), and K^+ (Figure S3 in the Supplementary Materials) concentrations were observed. $\text{C}_2\text{O}_4^{2-}$ was quantified only in sediment samples with higher concentration values in the feeding area (Figure 6). Since the investigated water lake is assigned as hard water, $\text{C}_2\text{O}_4^{2-}$ is most probably present as a precipitate in the form of CaC_2O_4 .

The spatial distributions for the elements Sr, Cr, Pb, Mn, Zn, Ba, Ni, and Sb in the water and sediment samples collected from Podu Iloaiei Dam Lake are presented in Figures 8 and 9, while Figure S4 of the Supplementary Materials shows the distributions of Al, Ge, and Ag. The Sr concentration variations in the sediment (Figure 9) present a similar profile with Mg^{2+} , Ca^{2+} , Na^+ , and SO_4^{2-} (Figure 6). In the south-eastern part of the lake, at the lateral end of the dam, in both sampling sessions, a spot corresponding to high concentrations for Cr, Pb, Mn, Zn, Ba, Ni (Figures 8 and 9), and Al (Figure S4 in the Supplementary Materials) was observed, indicating the existence of a punctual and persistent source of pollution. Geospatial distributions describe different areas with high and low concentrations for Cr and Pb in water (Figure 6) and sediment (Figure 7) samples. These highlight different sources or mobilization processes for these elements. For water samples collected in October, an increase in Mg^{2+} (Figure 6), K^+ (Figure S3 in the Supplementary Materials), Mn, and Zn (Figure 8) concentrations was observed in the feeding area, possibly generated by the fish food addition.

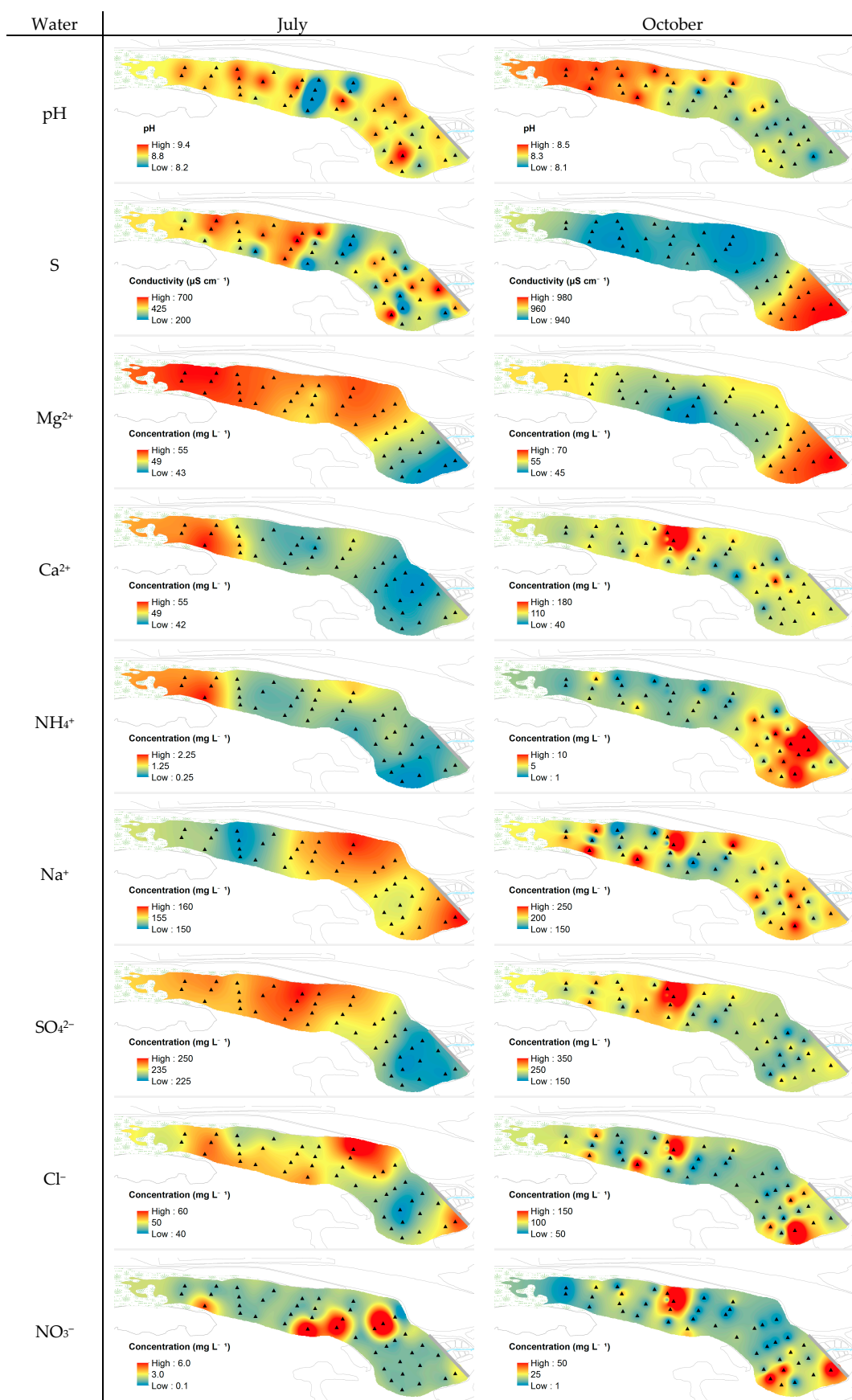


Figure 6. Spatial distribution of pH, conductivity (S), Mg²⁺, Ca²⁺, NH₄⁺, Na⁺, SO₄²⁻, Cl⁻, and NO₃⁻ in water of Podu Iloaiei Dam Lake for July and October sampling sessions.

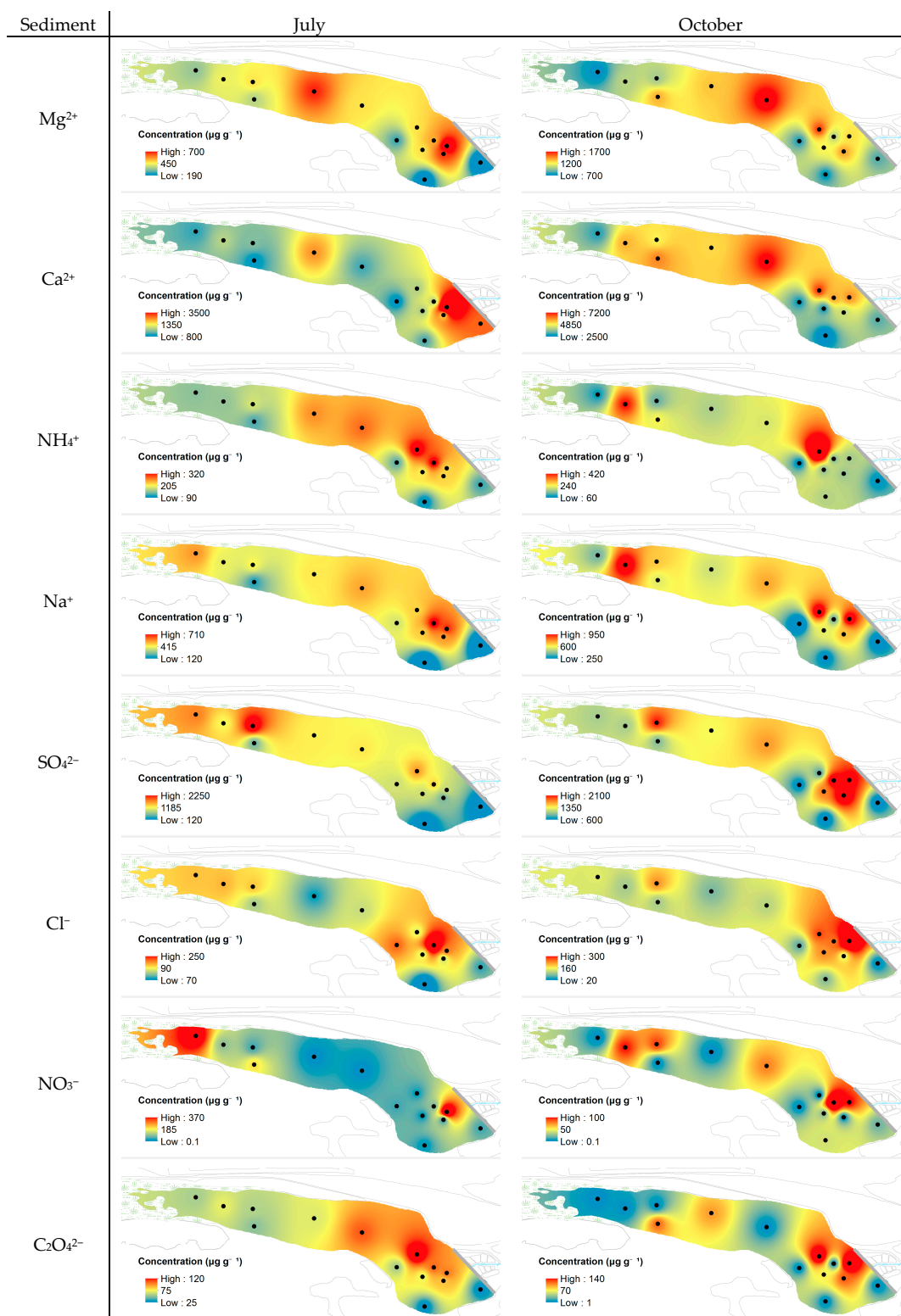


Figure 7. Spatial distribution of Mg^{2+} , Ca^{2+} , NH_4^+ , Na^+ , SO_4^{2-} , Cl^- , NO_3^- , and $C_2O_4^{2-}$ in sediment of Podu Iloaiei Dam Lake for July and October sampling sessions.

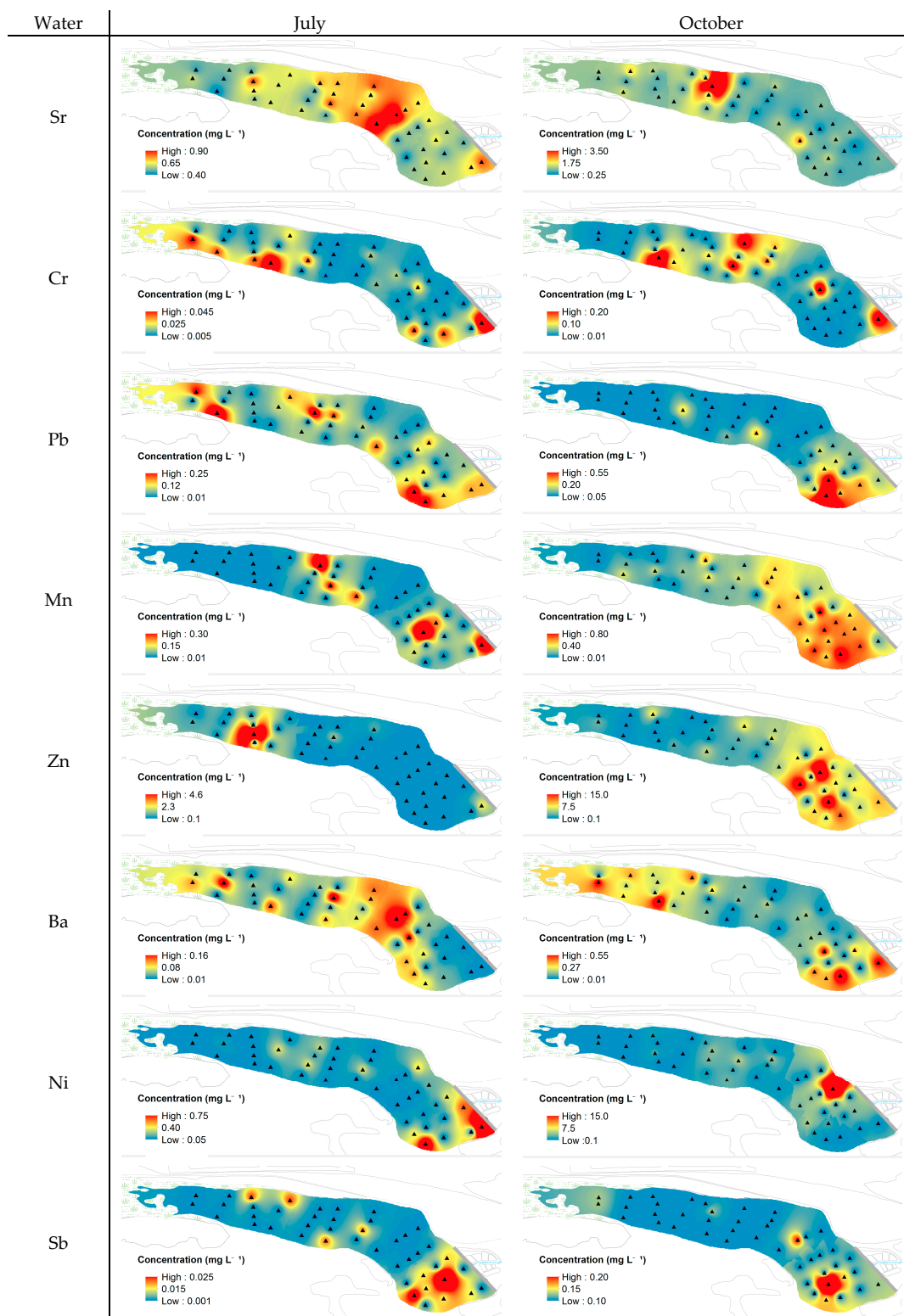


Figure 8. Spatial distribution of Sr, Cr, Pb, Mn, Zn, Ba, Ni, and Sb in water of Podu Iloaiei Dam Lake for July and October sampling sessions.

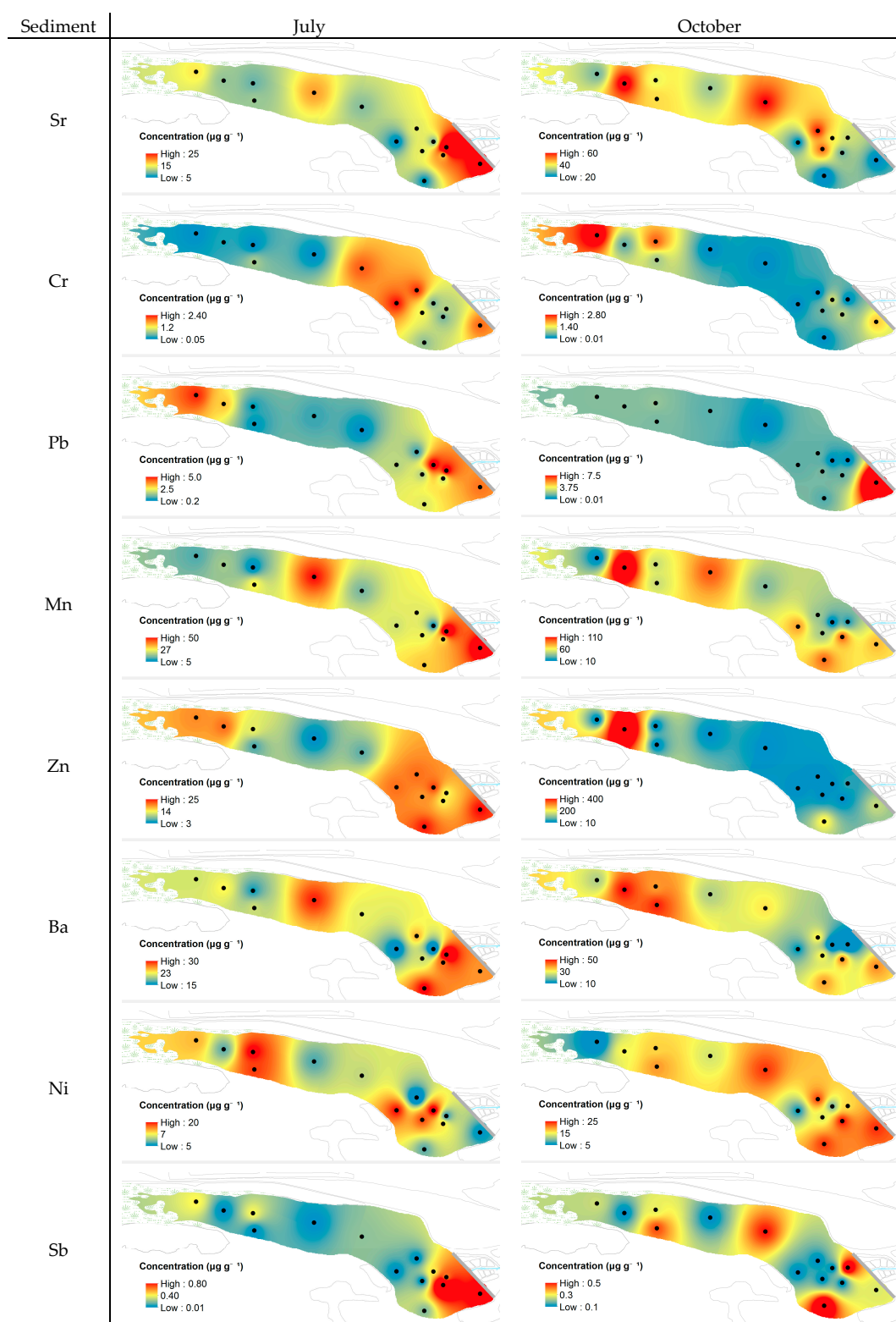


Figure 9. Spatial distribution of Sr, Cr, Pb, Mn, Zn, Ba, Ni, and Sb in sediment of Podu Iloaiei Dam Lake for July and October sampling sessions.

The Kolmogorov–Smirnov test applied to the database indicated significant different distributions of Cr, Mn, Ni, Zn, Sb, Ba, Cl^- , SO_4^{2-} , Na^+ , NH_4^+ , K^+ , Mg^{2+} , and Ca^{2+} concentrations. For Al, Ge, Sr, Ag, and Pb present in water samples collected in different sampling sessions from Podu Iloaiei Dam Lake the differences were not significant. Additionally,

significant different concentrations were observed for Al, Ti, Mn, Sr, Ag, Ba, Pb, Cl^- , K^+ , Mg^{2+} , and Ca^{2+} , while insignificant differences were noticed for Cr, Ni, Zn, Ge, Ag, Sb, SO_4^{2-} , $\text{C}_2\text{O}_4^{2-}$, Na^+ , and NH_4^+ in sediment samples collected in both seasons from the investigated water.

4.3. Suitability of the Podu Iloaiei Lake for Aquaculture Purposes and Potential Practical Implications

Water quality is one of the main concerns in aquaculture [9]. Changes in the chemical or physical parameters can cause negative effects on the growth of the aquatic organisms, their physiological state, or even mortality, with major losses in production.

The physicochemical parameters measured in small-scale fish production systems are pH, conductivity, and dissolved oxygen. Elements' presence or other ions in water sources are not generally measured. Besides the water source, the quality of the effluent water is highly important when considering environmental aspects of fish production. Aquaculture's increase over the last years could have an important impact on the environment and natural water resources. Some concerns include: water pollution resulting from pond effluents (i.e., salinization of water by effluents, seepage, and sediment), excessive use of ground water and other freshwater sources to increase the water level in ponds, the spread of aquatic animal diseases from cultured organisms to native populations, and negative effects on biodiversity caused by the escape of non-native species introduced for aquaculture [9].

The lake water (Podu Iloaiei Dam Lake) investigated in the present study had a hardness higher than $180 \text{ mg L}^{-1} \text{ CaCO}_3$, and therefore it was considered a very hard water. Waters with a hardness higher than $300 \text{ mg L}^{-1} \text{ CaCO}_3$ do not provide optimal conditions for high fish productivity [7]. It is recommended that the pH of the water be in the 7.0–8.5 range because fish blood has an average pH of 7.4 [1]. The pH values measured in the present work over both the July and October sampling sessions allowed us to suggest that precautions be taken by the Podu Iloaiei Dam Lake administrator in order to prevent the potential negative influence of increased alkalinity on fish productivity.

Moreover, attention should be given to the water status in full compliance with the requirements derived from the National Agency for Environmental Protection Report on the state of the environment in the Iasi County [25]. The report clearly shows that from six dam lakes located in the Prut basin, five lakes did not meet the moderate ecologic potential (Class III) [25]. However, while in the report from 2018, the Podu Iloaiei Dam Lake was classified as moderate with no traceable measurements for specific chemical parameters [25], in the report covering measurements from 1997 to 2004, the lake water was included either in class IV (pH, CBO_5 , CCO-Mn , NH_4^+ , Mg^{2+}) or in class III (NO_2^- , NO_3^- , PO_4^{3-}) [14] of quality. Considering the total nitrogen and phosphorus levels reported in 2014 [15] the water lake was assigned as hypertrophic.

In the present study, according to the classification of waters in the quality classes, used to establish the ecological status of water bodies [13], the Podu Iloaiei Dam Lake water falls in water quality class III based on the SO_4^{2-} , Na^+ , Mg^{2+} and nutrient contents. This suggests that Podu Iloaiei Dam Lake can be suitable for aquaculture, but it is not recommended to breed fish species sensitive to high hardness and high ionic strength because they can suffer imbalances at the osmoregulatory system level. The productivity could also be reduced due to the difficulty of nutrient adsorption in such conditions [7]. Higher concentrations of water-soluble ions in October could indicate an increase in dissolved solids, which has the effect of decreasing the gases' solubility in water, which can also negatively affect the osmotic balance of fish [48].

Considering the trophicity classes proposed by Dodds and co-researchers [49], with regard to nutrient concentration limits, the Podu Iloaiei Dam Lake water has an oligotrophic character in July, while, in October, the nutrient level corresponds to the eutrophic waters. Factors that could cause this variation are the discharge of waste waters, the administration of fertilizers in the agricultural area, the administration of fish food, and low rainfall that implied reduced discharge in order to keep the optimal level of water.

From the investigated elements, Pb seems to be highly influenced by the anthropogenic factor, considering that the average concentration of Pb in water samples exceeded the limits for the quality class IV associated with the waste water category.

Overall, the Podu Iloaiei Dam Lake seems to have chemical characteristics of a system controlled by both natural and anthropogenic origin sources. A complete database in terms of common chemical parameters; chemical pollutants; parameters representative for aquaculture activities, such as dissolved oxygen, biological oxygen demand, and chemical oxygen demand; and potential chemical processing of the specific water system would be of great benefit for the administration of such water resources in order to develop appropriate planning and lake exploitation. Moreover, such information might be used by experts in the field of developing lake management policies for a sustainable exploitation of various aquatic systems.

5. Conclusions

Water and sediment samples from Podu Iloaiei Dam Lake located on the Bahluiet River from the Bahlui hydrographic basin, north-eastern Romania, were investigated in order to determine their chemical composition in terms of the water-soluble constituents.

Anthropogenic and natural (pedologic) related sources seem to control the chemical composition of the water and sediment samples in the area. Experimental evidence obtained within the present work allowed us to infer that the Podu Iloaiei Dam Lake water was not susceptible to acidification. The trophicity of the investigated lake water seemed to present seasonal variability, changing from oligotrophic during warm periods to eutrophic over cold periods. Moreover, the Podu Iloaiei Dam Lake water traces the characteristics of a potential saline soil existent in the nearby region. The abundance of water-soluble chemical species suggests not only the solubilization process of sediment minerals but also the use of fertilizers in agriculture as important sources in the water body of interest. Uncontrolled or accidental waste discharge and secondary pollution sources might have contributions to the water characteristics.

The complex interplay between the water body's main characteristics, meteorological factors, and anthropogenic activities in the area control the abundances and the association of chemical species present in the water body. The results of the present study allow us to suggest that the Podu Iloaiei Dam Lake is suitable for aquaculture activities, but it is not recommended to breed fish species sensitive to high hardness and high ionic strength because they can suffer imbalances at the osmoregulatory system level.

The present study reports on the investigation of chemical parameters that are not routinely monitored at the European scale but which might have relevance for further studies concerning photochemical processing or when investigating health issues related to the consumption of aquaculture products exposed to potential toxics. However, due to various sources of water pollution, further studies might also evaluate and consider other important parameters such as dissolved oxygen, biological oxygen demand, and chemical oxygen demand as indicators for pollution. Moreover, further research could also involve measurements of physicochemical parameters in other water bodies (e.g., Bahluiet River) in the region of interest. The evaluation of different water chemical treatments' impact on fish farming productivity and water quality in the Bahlui hydrographic basin might also be of interest.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/w13172395/s1>, Table S1: Classification of waters in the quality classes in order to establish the ecological status of water bodies (extracted from Order no. 161/2006), Table S2: Limits of detection (LoD) and limits of quantification (LoQ) for ion chromatography determined water-soluble ions in the water and sediment samples, Table S3: Limits of detection (LoD) and limits of quantification (LoQ) for inductively coupled plasma mass spectrometry determined elements in the water and sediment samples, Table S4: Pearson's correlation coefficient of chemical species, pH, and conductivity (S) determined in water samples collected from Podu Iloaiei Dam Lake, Table S5: Pearson's correlation coefficient of chemical species quantified in sediment samples collected from Podu Iloaiei Dam Lake,

Figure S1: Linear regression between ($\Sigma\text{cations} - \Sigma\text{identified anions}$) and ($[\text{Mg}^{2+}] + [\text{Ca}^{2+}]$) for water samples (a) and sediment (b) samples in both sampling sessions, Figure S2: Linear regression for the ionic balance evaluation of water (a) and sediment (b) samples (including the HCO_3^{3-} estimation), Figure S3: Spatial distribution of K^+ , NO_2^{2-} , $\text{H}_3\text{C}_2\text{O}_2^{2-}$, and HCO_2^{2-} in water and sediment of Podu Iloaiei Dam Lake, Figure S4: Spatial distribution of water-soluble Al, Ge, Ag, and Sb in water and sediment of Podu Iloaiei Dam Lake.

Author Contributions: Conceptualization, C.A. (Cornelia Amarandei), S.-M.C.-M., R.-I.O., and C.A. (Cecilia Arsene); methodology, C.A. (Cornelia Amarandei), R.-I.O., and C.A. (Cecilia Arsene); methods validation, C.A. (Cornelia Amarandei), A.-G.N., and L.-V.S.; formal analysis, C.A. (Cornelia Amarandei), A.-G.N., L.-V.S., S.-M.C.-M., R.-I.O., and C.A. (Cecilia Arsene); investigation, C.A. (Cornelia Amarandei), A.-G.N., L.-V.S., S.-M.C.-M., R.-I.O., and C.A. (Cecilia Arsene); resources, S.-M.C.-M., R.-I.O., and C.A. (Cecilia Arsene); data curation, C.A. (Cornelia Amarandei), A.-G.N., L.-V.S., S.-M.C.-M., R.-I.O., and C.A. (Cecilia Arsene); writing—original draft preparation, C.A. (Cornelia Amarandei); writing—review and editing, A.-G.N., L.-V.S., S.-M.C.-M., R.-I.O., and C.A. (Cecilia Arsene); supervision, C.A. (Cecilia Arsene). All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: Data are available upon request to the contact author Cecilia Arsene (carsene@uaic.ro).

Acknowledgments: The authors express their gratitude to the Administration of the Podu Iloaiei Dam Lake for facilitating access in the area for sampling purposes. Acknowledgment is given by S.-M.C.-M., R.-I.O., and C.A. (Cecilia Arsene) to the infrastructure support from the Operational Program Competitiveness 2014–2020, Axis 1, under POC/448/1/1 research infrastructure projects for public R&D institutions/Sections F 2018, through the Research Center with Integrated Techniques for Atmospheric Aerosol Investigation in Romania (RECENT AIR) project, under grant agreement MySMIS no. 127324. Acknowledgments are given to the CNFIS-FDI-2021-0501 project as well.

Conflicts of Interest: The authors declare no conflict of interest.

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Size-resolved measurements of PM_{2.5} water-soluble elements in Iasi, north-eastern Romania: Seasonality, source apportionment and potential implications for human health

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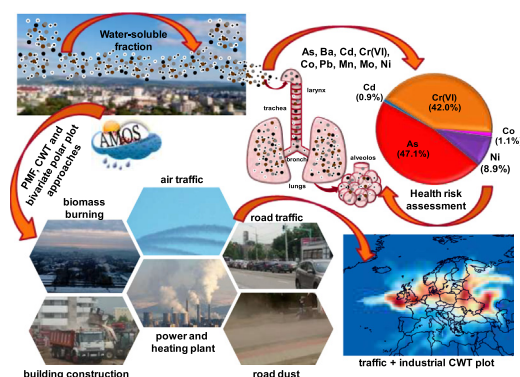
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HIGHLIGHTS

- Several PM_{2.5} water-soluble heavy metals have higher concentrations in cold season.
- High concentration levels of water-soluble elements from soil-dust resuspension or brake lining and tires
- Clear fine mode distribution (maxima at ~ 381 nm) for anthropogenic elements
- Five sources with seasonal dependent pattern identified by PMF analysis
- As and Cr(VI) with the largest cancer risks, exceed the critical value (1×10^{-6}).

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 28 May 2019

Received in revised form 26 July 2019

Accepted 7 August 2019

Available online 12 August 2019

Editor: Wei Huang

Keywords:

Fine particle

Water-soluble metals

Positive matrix factorization

Emission sources

Health risks

ABSTRACT

The present paper reports the first size-resolved element measurements in the PM_{2.5} fraction collected throughout 2016 in the Iasi urban area in north-eastern Romania. Concentrations of water-soluble elements (Ag, Al, As, B, Ba, Be, Bi, Cd, Co, Cu, Cr, Fe, Ga, Mg, Mn, Mo, Ni, Pb, Rb, Se, Sr, Te, Ti, U, V, Zn) were determined using inductively coupled plasma mass spectrometry. Several water-soluble heavy metals (Al, Fe, Zn, As, Cr, Pb) exhibit clear seasonal patterns with maxima over the cold season and minima over the warm season. Elements as Al, Fe, Mg, Zn, Ni, Mn, and Cu present the highest levels in the PM_{2.5} fraction, indicating significant contributions from soil-dust resuspension or brake lining and tires. Clear fine mode size-dependent distributions were observed for anthropogenic source-origin elements (Pb, Zn, Cd, V, etc.) due to an acidity-driven metals dissolution process. Positive matrix factorization, concentration weighted trajectory and bivariate polar plot analyses were applied to the entire PM_{2.5} database. Based on relative concentrations of various elements, five factors associated with specific sources were identified. The most important contributions to the total PM_{2.5} mass concentration (during the total period) come from secondary formation of the ammonium sulfate form (~44%) and from nitrate (~37%). Resuspended dust accounts for a contribution of about 16%, while biomass burning mixed with NaCl salt/sea-salt sources contribute as much as ~3%. Traffic and industrial sources seem to yield little contribution (<0.05%). An assessment investigation of non-carcinogenic and carcinogenic health risks revealed water-soluble arsenic and chromium (VI) as elements with the largest incremental carcinogenic risks. Both metals have traffic and

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industrial related sources and therefore it is believed that in the future, at the local/regional level, these sources should receive attention by implementing appropriate emission control measures.

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1. Introduction

Air pollution in urban environments is one of the greatest current environmental challenge (Zhang et al., 2015). Atmospheric aerosols, known also as ambient particulate matter (PM), are chemically non-specific pollutants originating from various types of emission sources. They influence global climate change, air quality and, consequently, human health (von Schneidmesser et al., 2015; Ueda et al., 2017). The negative impacts of airborne particles depend on their complexity and variability, including particle size, heterogeneity, chemical composition and strength of the emission sources (Kelly and Fussell, 2012; Mukherjee and Agrawal, 2017). Assessment of particle oxidative potential is presently a routine method for estimation of human exposure to various atmospheric pollutants (Crobeddu et al., 2017; Fang et al., 2017a, 2017b; Bates et al., 2018; W.J. Liu et al., 2018b; Pietrogrande et al., 2018). Studies on aerosol health effects usually involve a wide range of time intervals (Ueda et al., 2017; Lipfert, 2018).

Urban fine particles (i.e. PM_{2.5}, particulate matter <2.5 µm in diameter) present as solid or liquid forms of very complex chemical composition in the atmosphere, are emitted either directly from various natural and anthropogenic sources or as a result of gas-to-particle conversion processes (Zhang et al., 2015). Fine particle chemical components, including especially heavy metal soluble fractions along with those of secondary SO₄²⁻, might exert important toxic effects on human health (Fang et al., 2015, 2017a, 2017b). Increased morbidity and mortality are associated with ambient PM level (Burnett et al., 2000; Gwynn et al., 2000; Li et al., 2008; Guaita et al., 2011; Kim et al., 2015; Cohen et al., 2017). For 2016, about 4.2 million deaths globally were attributed to ambient air pollution (WHO, 2018). Moreover, recent estimates suggest that the contribution of outdoor air pollution to premature mortality in children up to 5 years and adults above 30 years could double by 2050 (Lelieveld et al., 2015). In Europe, air pollution has recently been predicted to lead to a reduction in the mean life expectancy by about 2.2 years (Lelieveld et al., 2019).

Several studies report on the composition of water-soluble elements in size-resolved particle samples in different European (Birmili et al., 2006; Perez et al., 2008; Manousakas et al., 2014) and non-European (Fang et al., 2015, 2017a, 2017b; Maudlin et al., 2015; Ma et al., 2019) countries. Particle origin, atmospheric transport, size, aerosol surface property, chemical processing, chemical form and pH variations influence the solubility of an element present in ambient PM (Desboeufs et al., 2001; Mukhtar and Limbeck, 2013; Schleicher et al., 2011; Fang et al., 2015, 2017a, 2017b). Water solubility of individual elements in atmospheric PM differs significantly with the size range, suggesting the existence of different chemical speciated forms (Birmili et al., 2006). Extraction in water, buffer, salt or chelating solutions and *in vitro* surrogates or synthetic body fluids are often used for determining bioaccessible or bioavailable element fractions present in ambient PM (Stopford et al., 2003; Smichowski et al., 2005; Mukhtar and Limbeck, 2013). Aqueous extraction procedure is thought to closely simulate particle dissolution at close to neutral pH, such as occur in the human lung.

Water-soluble fraction of particle-bound elements is most likely to become bioavailable and therefore harmful to humans (Birmili et al., 2006). The dose of bioavailable transition elements seems to be the primary reason for the acute inflammatory response to ambient PM (Costa and Dreher, 1997). Several PM_{2.5} water-soluble transition elements, such as Fe, Cu, and Mn, exert important roles in the formation of free radicals or reactive oxygen species (ROS) (Landreman et al., 2008; Shen and Anastasio, 2011; Charrier and Anastasio, 2012; Cheung et al., 2012; Saffari et al., 2014; Verma et al., 2014, 2015; Bates et al., 2015).

Many other PM_{2.5} related elements act as toxicity factors with significant adverse health effects (Knaapen et al., 2002; Akhtar et al., 2010; IARC Monographs, 2016). Metal elements of industrial and traffic origin are important constituents of atmospheric urban PM in terms of their potential toxic effect (IARC Monographs, 2016; Suvarapu and Baek, 2017). Atmospheric PM chemical forms containing As, Be, Cd, and Cr (VI) belong to Group 1 of cancer hazard agents, while those containing Pb are classified as probably carcinogenic (Group 2A). Nickel-containing chemicals are possibly carcinogenic (Group 2B), and Mn compounds belong to pollutants of potential interest (IARC Monographs, 2016).

Recent studies report source-specific health risks due to metal elements present in PM_{2.5} by integrating the presence and prevalence of those sources with health risk assessments of residents affected *via* breathing (J. Liu et al., 2018a; Huang et al., 2018; Lurie et al., 2019). Mathematical simulation based on receptor models is extensively used for sources' contribution quantification at local and regional levels (Viana et al., 2008; Belis et al., 2014; Brown et al., 2015).

The Positive Matrix Factorization model (EPA PMF 5.0) relying on pollutant measurements allows identification of optimal factor solutions by three error estimation (EE) methods, i.e. classical bootstrap (BS), displacement of factor elements (DISP), and bootstrap enhanced by displacement (BS-DISP) (Paatero and Tapper, 1994; Paatero, 1997; Norris et al., 2014; Brown et al., 2015). The EPA PMF 5.0 model is the most advanced factor-analysis tool widely used to accurately perform PM_{2.5} source apportionments at a global level (Karagulian et al., 2015), in Europe (Richard et al., 2011; Minguillón et al., 2012, 2014; Cesari et al., 2016, 2018; Grivas et al., 2018; Perrone et al., 2018), America (Polissar et al., 1998, 2001; Lee et al., 2006; Han et al., 2017; Masiol et al., 2017; Dadashazar et al., 2019; Miller et al., 2019), and Asia (Heo et al., 2009; Zhang et al., 2013; Liu et al., 2017; Mukherjee and Agrawal, 2018).

Concentration weighted trajectory (CWT) analysis (Stohl, 1998; Polissar et al., 2001) based on PMF assessment is successfully used for identifying potential regional/global emission areas of specific sources (Kong et al., 2013; Dimitriou et al., 2015; Salamalikis et al., 2015; Masiol et al., 2017; Liu et al., 2017; Petit et al., 2017a; Cesari et al., 2018; Dadashazar et al., 2019). Bivariate polar plots (BPPs) analysis (Carslaw et al., 2006; Carslaw and Ropkins, 2012) is another modeling tool based on wind speed and direction to estimate potential local contributions (Masiol et al., 2017; Mukherjee and Agrawal, 2018; Miller et al., 2019).

In Eastern Europe the sources of PM_{2.5} are not well known because this fraction is not widely measured. Chemical composition of major water-soluble ions in atmospheric particles from the Iasi urban area, Romania, has been reported previously in a few studies (Arsene et al., 2011; Galon-Negru et al., 2018). The present study reports for the first time, to our knowledge, detailed chemical analysis of water-soluble metal elements of natural and anthropogenic origin sources in the PM_{2.5} fraction. These samples were collected at the Air Quality Monitoring Station (AMOS) of the Integrated Centre of Environmental Science Studies in the North-Eastern Development Region belonging to the "Alexandru Ioan Cuza" University of Iasi, Romania. Chemical composition of the water-soluble elements in the PM_{2.5} fraction (major ions as reported in Galon-Negru et al. (2018) and trace metal elements determined in the present study) were used to: a) understand chemical characteristics of water-soluble PM_{2.5} elements, b) identify sources and contributions using the PMF receptor model, c) investigate the transport pathway and potential emission sources of PM_{2.5} using the CWT and BPP models, and d) perform non-carcinogenic and carcinogenic health risks assessments.

2. Material and methods

2.1. Measurement site and sample collection

Iasi is a city located in the north-eastern Romania with a population of 362,142 according to a recent estimate of the Romanian National Institute of Statistics (Ichim et al., 2016). Comprehensive demogeographical aspects of this region are elsewhere reported (Arsene et al., 2007, 2011; Galon-Negru et al., 2018).

Aerosol sampling was carried out at AMOS (47° 9' N latitude and 27° 35' E longitude), at 35 m altitude above the ground level. Size-resolved aerosol samples were collected during one year (2016) using a 13-stage cascade Dekati Low-Pressure Impactor (DLPI) (size cuts at 0.0276, 0.0556, 0.0945, 0.155, 0.260, 0.381, 0.612, 0.946, 1.60, 2.39, 3.99, 6.58, and 9.94 μm , at 50% calibrated aerodynamic cut-point diameters). The protocol and system characteristics are according to Galon-Negru et al. (2018) procedure. A total of 1092 aerosol samples were collected throughout 2016 (840 for $\text{PM}_{2.5}$ fraction). On average, $64.33 \pm 0.85 \text{ m}^3$ of air was sampled at a flow of 29.85 L min^{-1} . Total period (TP), cold season (CS, from October to March 2016) and warm season (WS, from April to September 2016) were considered for further data analysis.

2.2. Chemical analysis of water-soluble trace metals

Preparative steps and procedures for investigating chemical composition of $\text{PM}_{2.5}$ and PM_{10} (i.e. PM_{10} , particulate matter $<10 \mu\text{m}$ in diameter) fraction are presented elsewhere (Galon-Negru et al., 2018). The present work deals only with aspects related to $\text{PM}_{2.5}$ fraction. The aqueous extracts prepared for the analysis of water-soluble ionic components have been also used for the determination of water-soluble trace elements. Aliquots of 1.5 mL of filtered aqueous extracts (filtered through a $0.2 \mu\text{m}$ pore size cellulose acetate filters, ADVANTEC, Toyo Roshi Kaisha, Ltd., Japan) were acidified with 4.5 mL of 3% HNO_3 in aqueous solution. The 3% solution was prepared by diluting of a Suprapur 65% HNO_3 (Merck, Darmstadt, Germany). Addition of diluted HNO_3 solution was necessary in order to prevent losses of metal species during storage prior to inductively coupled plasma mass spectrometry (ICP-MS) analysis. Indium ICP standard (Merck, Darmstadt, Germany), at a $50 \mu\text{g L}^{-1}$ concentration level, was used as an internal standard (^{115}In) in order to correct instrument drift. All processed samples were stored in sterile Eppendorf tubes (Carl Roth GmbH, Karlsruhe, Germany) and kept refrigerated at 4°C for $<48 \text{ h}$ prior to chemical analysis. All the glasswares used for the analysis of traces of water-soluble metal elements were soaked first in 6 N HNO_3 followed by ultrapure water of $18.2 \text{ M}\Omega\cdot\text{cm}$ resistivity (produced by a Milli-Q Advantage A10 water purification system, Merck, Darmstadt, Germany). Each soaking cycle was of 24 h and ultrapure water was used repeatedly to rinse each vessel.

Determination of trace metal concentrations in all aerosol samples (1092) was performed by inductively coupled plasma mass spectrometry (ICP-MS) on an ICP-MS 7700 $\times$ system (Agilent Technologies, USA) equipped with an Agilent ASX-520 auto-sampler, a MicroMist concentric nebulizer, and a Quartz torch. The following isotopes ^9Be , ^{11}B , ^{24}Mg , ^{27}Al , ^{51}V , ^{52}Cr , ^{55}Mn , ^{56}Fe , ^{59}Co , ^{60}Ni , ^{63}Cu , ^{66}Zn , ^{69}Ga , ^{75}As , ^{78}Se , ^{85}Rb , ^{88}Sr , ^{95}Mo , ^{107}Ag , ^{114}Cd , ^{125}Te , ^{135}Ba , ^{205}Tl , ^{208}Pb , ^{209}Bi , and ^{238}U were monitored in order to analyze water-soluble trace elements from the $\text{PM}_{2.5}$ fraction. The analysis batch sequence included frequent checks on instrumental blank and calibration solution. Tuning, data acquisition and data analysis were performed through the ICP-MS MassHunter WorkStation software (Agilent Technologies, USA).

Calibration curves (with r^2 Spearman coefficients >0.99) were obtained by appropriate dilution with 3% HNO_3 of a commercially available ICP-MS multi-element standard solution (Merck, Darmstadt, Germany). Calibration samples were also spiked with ^{115}In as an internal standard. For each element the limit of detection (LOD) has been

estimated considering the standard deviation of 10 blank measurements. The detection limits in ng m^{-3} on a 36 h measurement period are presented in Table S1 from Section S1 of the Supplementary material (SM). Filters loaded with collected particles and blank filters (laboratory and field) were processed and analyzed using a similar analytical procedure. Concentrations of water-soluble metals in each analyzed sample were obtained by subtracting the average level of elements from blank filters. Cross-validation between water-soluble magnesium concentrations obtained from ICP-MS measurements and those determined by ion chromatography (IC) for its ionic form (reported previously in Galon-Negru et al., 2018) led to a ratio close to 1, with an r^2 of 0.97 (Fig. S1, Section S1 of the SM). The comparison between ICP-MS and IC measurements shows that both techniques measure similar concentrations for the water-soluble fraction of a specific element.

2.3. Positive matrix factorization (PMF) analysis

To identify each source's contribution, the Positive Matrix Factorization (PMF) model proposed by Paatero and Tapper (1994) was applied to $\text{PM}_{2.5}$ water-soluble chemical species database taken during TP, CS and WS periods (Section S2 of the SM). The results of PMF settings are summarized in Table 1. No censoring of data below detection limit was done and samples with missing data were not included in the PMF runs. The assessment of size-resolved samples included in the PMF category selection process was performed according to EPA PMF 5.0 version following the criteria proposed by Norris et al. (2014) (Section S3 in the SM).

Although the $\text{PM}_{2.5}$ fraction database includes 840 samples (410 samples for CS and 430 samples for WS), the data refining process led to only 326 samples for TP, 133 for CS, and 179 for WS. Species with a percentage of missing values $>75\%$ were excluded from the analysis to generate a more robust PMF solution. In the present work, estimated $Q_{\text{true}}/Q_{\text{expected}}$ and Signal/Noise values allowed classification of Cr, Zn, As, Sr, Ba, Pb, NO_3^- , SO_4^{2-} , NH_4^+ , K^+ , and Mg^{2+} as "strong" species, while $\text{PM}_{2.5}$, Mn, Fe, Cu, Cd, Cl^- , Na^+ , and Ca^{2+} were classified as "weak" species. Variable uncertainties were estimated as presented in Section S4 of the SM (Norris et al., 2014). The goodness-of-fit parameter (Q_{true}) was calculated including all points, while Q_{expected} was estimated by the difference between the number of non-weak data values in the data matrix and number of elements in factor contributions and factor profiles, taken together.

2.4. Meteorology and trajectory associated models

Ambient air temperature, total solar radiation, wind speed and direction, relative humidity (RH), and barometric pressure were measured using a Hawk GSM-240 weather station (WEATHERHAWK, Logan, Utah, USA). All calculations and graphics related to meteorology and trajectory associated models were carried out with ZeFir v.3.70 (Petit et al., 2017b), an Igor-based tool for the investigation of the geographical origins of atmospheric pollution.

Back trajectories were calculated from January 2016 to December 2016 following the $\text{PM}_{2.5}$ sampling time schedule. Air mass back trajectories reaching the site at 500, 1000, and 2000 m above ground level were obtained for a 72 h time period using a PC version of the HYSPLIT model 4 (Stein et al., 2015; Rolph et al., 2017) controlled by ZeFir tool (Petit et al., 2017b).

For the $\text{PM}_{2.5}$ fraction, concentration weighted trajectory (CWT) analysis details are presented in Section S5 of the SM. The modeling tool was used in order to locate the air area contributing to high concentrations of analyzed chemical species at the investigated site (Stohl, 1998). Bivariate polar plot (BPP) analysis was performed to generate meaningful information about potential local/regional source areas' contributions for pollutants. For BPP analysis the average pollutant concentrations were obtained by mapping wind speed (36 h averaged value) and direction (36 h averaged vector), with continuous surface

Table 1
Summary of PMF settings for PM_{2.5} datasets corresponding to total period (TP), cold season (CS) and warm season (WS).

Parameter	TP	CS	WS
Months	Jan 2016-Dec 2016	Jan, Feb, Mar, Oct, Nov, Dec	Apr, May, Jun, Jul, Aug, Sept
Data type; averaging time frame	every DLPI stage; 36-h	every DLPI stage; 36-h	every DLPI stage; 36-h
N species	19	19	19
N samples	326	155	179
N factors	4–6	4–6	4–6
Robust mode	Yes	Yes	Yes
Constraints	None	None	None
Seed value	30	30	30
N bootstraps in BS	100	100	100
r ² for BS	0.6	0.6	0.6
BS block size	Suggested	Suggested	Suggested
DISP dQ ^{max}	4, 8, 16, 32	4, 8, 16, 32	4, 8, 16, 32
DISP active species	Cr, Zn, As, Sr, Ba, Pb, NO ₃ ⁻ , SO ₄ ²⁻ , NH ₄ ⁺ , K ⁺ , Mg ²⁺	Cr, Zn, As, Sr, Ba, Pb, NO ₃ ⁻ , SO ₄ ²⁻ , NH ₄ ⁺ , K ⁺ , Mg ²⁺	Cr, Zn, As, Sr, Ba, Pb, NO ₃ ⁻ , SO ₄ ²⁻ , NH ₄ ⁺ , K ⁺ , Mg ²⁺
N bootstraps; r ² for BS in BS-DISP	100; 0.6	100; 0.6	100; 0.6
BS-DISP active species	Cr, Zn, As, Sr, Ba, Pb, NO ₃ ⁻ , SO ₄ ²⁻ , NH ₄ ⁺ , K ⁺ , Mg ²⁺	Cr, Zn, As, Sr, Ba, Pb, NO ₃ ⁻ , SO ₄ ²⁻ , NH ₄ ⁺ , K ⁺ , Mg ²⁺	Cr, Zn, As, Sr, Ba, Pb, NO ₃ ⁻ , SO ₄ ²⁻ , NH ₄ ⁺ , K ⁺ , Mg ²⁺
BS-DISP dQ ^{max}	0.5, 1, 2, 4	0.5, 1, 2, 4	0.5, 1, 2, 4

modes calculation, by using smoothing techniques (Carslaw et al., 2006; Carslaw and Ropkins, 2012). For both CWT and BPP analyses, PMF runs were performed by summation of individual species concentration reported per sampling event. CWT was applied for each period (TP, CS, WS). BPP analysis could be applied only for TP since only a relatively small number of events were available for CS and WS.

2.5. Health risk assessment

The non-carcinogenic and carcinogenic health risks caused by airborne As, Ba, Cd, Co, Cr, Pb, Mn, Mo, and Ni *via* direct inhalation of PM_{2.5} were calculated using the **RAIS Contaminated Media (Risk) Calculator**. RAIS is a tool developed based on the United States Environmental Protection Agency Human Health Risk Assessment Methods (US EPA, 2009, 2011). More details concerning non-carcinogenic and carcinogenic approaches are presented in Section S6 of the SM.

3. Results and discussions

3.1. Measured concentrations of water-soluble trace metals in the PM_{2.5} fraction

Table 2 provides the mean, standard deviation and median for PM_{2.5} and selected water-soluble elements' mass concentrations (Ag, Al, As, Ba, Bi, Cd, Co, Cr, Cu, Fe, Ga, Mg, Mn, Mo, Ni, Pb, Rb, Se, Sr, Te, Tl, V, Zn). Details concerning meteorological conditions over the investigated period are presented also in Table 2. The annual average PM_{2.5} mass concentration over TP was 16.92 ± 9.07 (14.51) µg m⁻³. PM_{2.5} showed higher concentrations during CS (20.03 ± 9.94 µg m⁻³) and lower during WS (14.02 ± 7.15 µg m⁻³). As observed from Table 2, the average mass concentrations of water-soluble trace metals span from 0.02 to 90.76 ng m⁻³, values which are consistent with those reported by Manousakas et al. (2014).

Regarding element concentrations, the highest levels were found for Al, followed by Fe, Mg, Mn, Zn, Ni, and Cu, indicating significant contribution from soil-dust resuspension or brake linings and tires (Hjortenkranz et al., 2007). Average concentrations lower than 10 ng m⁻³ have been observed for other elements (V, Cr, Co, Ga, As, Se, Rb, Sr, Mo, Ag, Cd, Te, Ba, Tl, Pb, and Bi). The values obtained for the water-soluble fraction of Zn are consistent with the value reported by Fang et al., (2015) for an urban site of significant transportation (Birmingham, Alabama), and much smaller than those reported by Manousakas et al. (2014) for the cities of Patras (163 ng m⁻³) and Megalopolis (51.7 ng m⁻³) in Greece.

Water-soluble Ni annual average concentration was 20.53 ± 19.33 ng m⁻³, while that of As was 6.59 ± 5.69 ng m⁻³ (Table 2). These values slightly exceed the total annual PM₁₀ element target limits set by the European Environment Agency, with 20 ng m⁻³ for Ni and 6 ng m⁻³ for As (EEA, 2017). The presence of Ni and As in anthropogenic sources including combustion processes in motor vehicles or coal combustion (EEA, 2017) must be considered at the investigated site. Coal

Table 2
The mean, standard deviation and median (parenthesis) for PM_{2.5} (in µg m⁻³) and selected water-soluble elements mass concentrations (in ng m⁻³), and meteorological conditions for TP, CS and WS.

Element/parameter	TP	CS	WS
PM _{2.5}	16.92 ± 9.07 (14.51)	20.03 ± 9.94 (16.94)	14.02 ± 7.15 (12.29)
RH (%)	52.15 ± 20.27 (50.36)	65.00 ± 17.74 (67.91)	40.51 ± 14.67 (38.20)
T (°C)	12.35 ± 8.68 (12.87)	5.07 ± 5.25 (5.62)	18.95 ± 5.16 (19.63)
Wind speed (m s ⁻¹)	4.02 ± 2.64 (3.23)	4.29 ± 2.83 (3.25)	3.77 ± 2.45 (3.23)
Ag	0.25 ± 0.27 (0.18)	0.25 ± 0.33 (0.15)	0.25 ± 0.21 (0.25)
Al	72.53 ± 47.68 (57.80)	84.66 ± 56.93 (67.01)	61.54 ± 34.58 (48.01)
As	6.59 ± 5.69 (3.91)	5.70 ± 5.89 (3.59)	7.46 ± 5.42 (5.67)
Ba	1.98 ± 0.97 (1.83)	2.44 ± 1.04 (2.43)	1.59 ± 0.70 (1.43)
Bi	0.09 ± 0.05 (0.08)	0.09 ± 0.04 (0.09)	0.09 ± 0.06 (0.08)
Cd	0.29 ± 0.19 (0.24)	0.33 ± 0.22 (0.25)	0.26 ± 0.15 (0.23)
Co	0.07 ± 0.15 (0.02)	0.09 ± 0.18 (0.02)	0.02 ± 0.03 (0.01)
Cr	2.14 ± 1.36 (1.72)	1.78 ± 1.50 (1.33)	2.49 ± 1.12 (2.29)
Cu	9.71 ± 5.95 (8.51)	7.70 ± 5.04 (6.26)	11.63 ± 6.17 (10.31)
Fe	69.85 ± 66.57 (55.20)	90.76 ± 76.44 (77.50)	52.92 ± 52.42 (45.57)
Ga	0.19 ± 0.20 (0.15)	0.25 ± 0.28 (0.15)	0.14 ± 0.05 (0.14)
Mg	34.06 ± 24.34 (26.57)	32.98 ± 18.86 (29.89)	35.10 ± 28.81 (25.11)
Mn	9.90 ± 8.03 (6.54)	9.06 ± 8.11 (6.05)	10.70 ± 7.97 (7.84)
Mo	0.20 ± 0.18 (0.15)	0.22 ± 0.21 (0.15)	0.18 ± 0.13 (0.15)
Ni	20.53 ± 19.33 (17.01)	24.32 ± 22.52 (21.50)	17.64 ± 16.18 (13.43)
Pb	2.00 ± 1.69 (1.52)	1.99 ± 1.39 (1.67)	2.02 ± 1.96 (1.52)
Rb	3.28 ± 1.35 (3.08)	2.71 ± 1.38 (2.38)	3.82 ± 1.07 (3.89)
Se	6.66 ± 3.45 (6.33)	5.97 ± 3.19 (5.66)	7.33 ± 3.60 (7.92)
Sr	1.40 ± 1.55 (0.90)	1.11 ± 1.11 (0.84)	1.66 ± 1.85 (1.11)
Te	0.26 ± 0.22 (0.21)	0.25 ± 0.25 (0.19)	0.30 ± 0.17 (0.24)
Tl	0.07 ± 0.04 (0.06)	0.08 ± 0.05 (0.07)	0.06 ± 0.03 (0.06)
V	0.44 ± 0.22 (0.38)	0.41 ± 0.24 (0.33)	0.48 ± 0.20 (0.50)
Zn	29.45 ± 18.50 (23.99)	33.94 ± 20.34 (29.20)	25.39 ± 15.82 (22.22)

combustion may account for higher Ni values in CS ($24.32 \pm 22.52 \text{ ng m}^{-3}$) compared to WS ($17.64 \pm 16.18 \text{ ng m}^{-3}$). Higher concentration of water-soluble As and Ni are probably due to low pH values of analyzed atmospheric particles (Galon-Negru et al., 2018). Lower pH values are responsible for the increased solubility of toxic metals (Desboeufs et al., 2005; EEA, 2017; Fang et al., 2017a). Metals tend to be more labile in anthropogenic particles than metals bound to crustal material, because they are coming from metal-dominated abrasion processes, hot-vapor generated metals or from condensation of particles on to the surface of other particles (Heal et al., 2005).

3.2. Seasonal size distributions of water-soluble trace metals

The seasonal variations for selected water-soluble trace metals determined in the $\text{PM}_{2.5}$ fraction collected in 2016 in the Iasi area are shown in Fig. 1.a-i. A seasonal pattern is observed for water-soluble metal elements such as Al, Fe, and Zn with minima over WS and maxima over CS (Fig. 1.a,b,c). This behavior is similar to that reported by Galon-Negru et al. (2018) for sulfate, nitrate, and oxalate anions. Most probably over CS (autumn/winter), Al, Fe and Zn form soluble salts with these anions, while over WS (spring/summer) these elements are most likely present in water-insoluble silicate chemical forms. The pattern shown for Mg (Fig. 1.d) and Sr (Fig. 1.e) reflects the likely predominant contribution of local/regional soil dust. Contribution from the long range transport of dust from the Black Sea and Mediterranean Sea shores and the Sahara Desert could be identified in several events which occurred in spring. In Romanian upper continental crust, relative

enrichment smaller than 1.5 are reported for Mg and Sr elements (Dinescu et al., 2004).

Seasonal variations of the water-soluble fractions of As and Cr (Fig. 1.f and Fig. 1.g, respectively) show similar profiles, with maxima in the autumn season, which most probably indicate an bursting increase in the coal combustion process (Pakkanen et al., 2001; EEA, 2017). Diesel vehicular emission and combustion of fossil fuels for heating purposes can be responsible for the Pb seasonal pattern with maxima over CS and minima over WS (Fig. 1.h). This observation is in good agreement with other reports (Manousakas et al., 2014; EEA, 2017). Vanadium exhibits an almost constant distribution (Fig. 1.i), mainly attributable to the emission associated with the burning of fossil fuels, especially diesel oil (Fujiwara et al., 2006; Shafer et al., 2012), or power and heat plant activities (WHO, 2000).

Fig. 2 shows the size distributions of seasonally averaged concentrations of Zn, Pb, Mg, Sr, and Ba elements in the $\text{PM}_{2.5}$ fraction, together with the mass concentrations determined during both CS and WS. For these metals, significant size-dependent patterns were observed due to the increased solubility of Zn and Pb in fine particles (maximum at 381 nm), and of Mg, Sr, and Ba in the coarse particles ($1.6\text{--}2.39 \mu\text{m}$). Other elements with size-dependent patterns included Cd and V (Fig. S2, Section 7 of the SM).

For the $\text{PM}_{2.5}$ fraction collected in the Iasi area, Galon-Negru et al. (2018) report pH values ≤ 2 for particles ranging between 155 and 612 nm. Moreover, the authors suggested that particles distributed in this size range were strongly acidic due to dissociation of strong acids such as H_2SO_4 and HNO_3 . Under such low pH conditions an acidity-

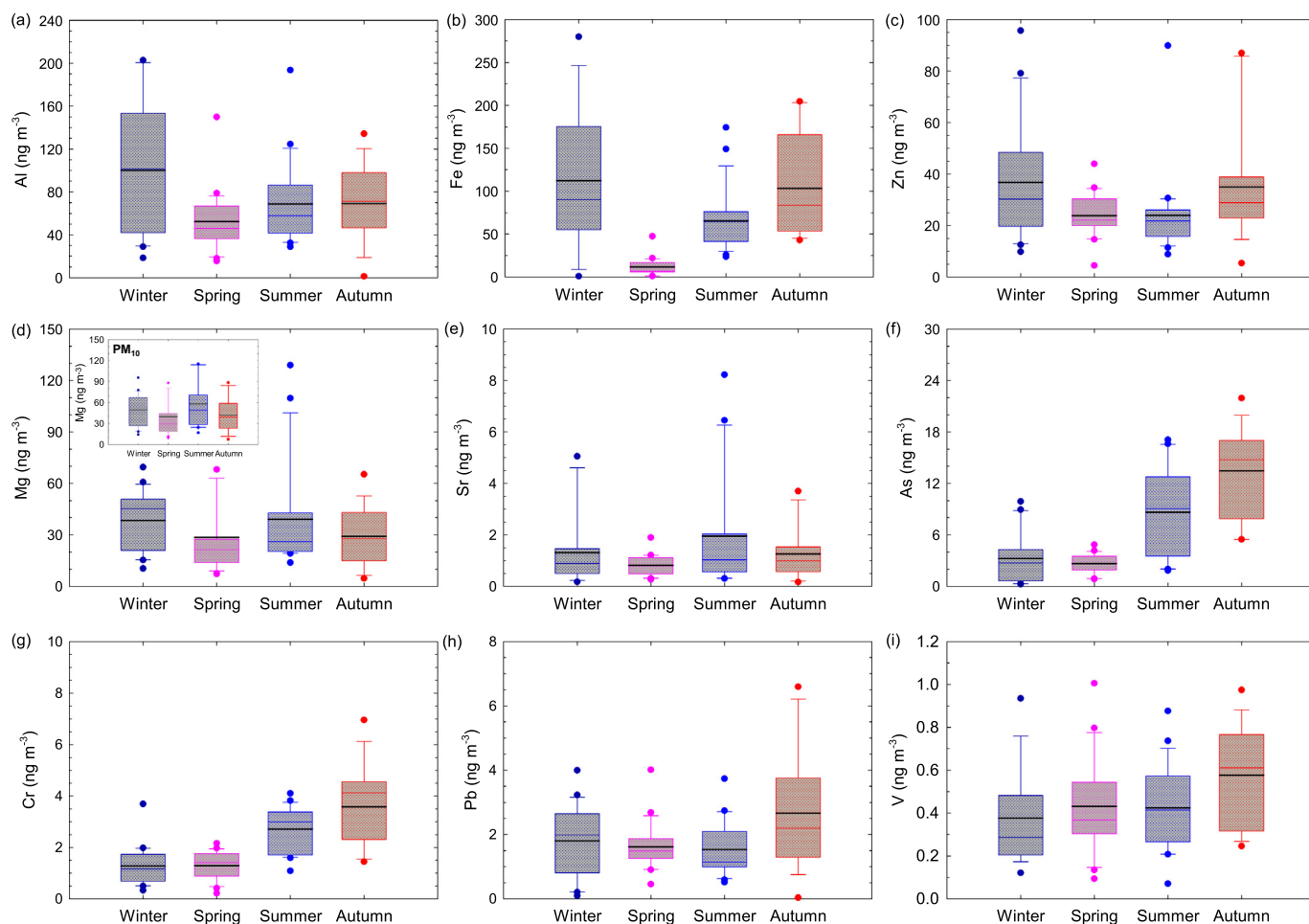


Fig. 1. Seasonality of selected water-soluble trace metals in the $\text{PM}_{2.5}$ fraction (a-i). The inset distribution presented within Mg seasonal variation reflects the contribution of the coarse fraction over WS (horizontal black line – mean; horizontal colored line – median; box – 25–75% percentiles; length of the whiskers plot – 10 and 90% of observed concentrations; circles – outliers).

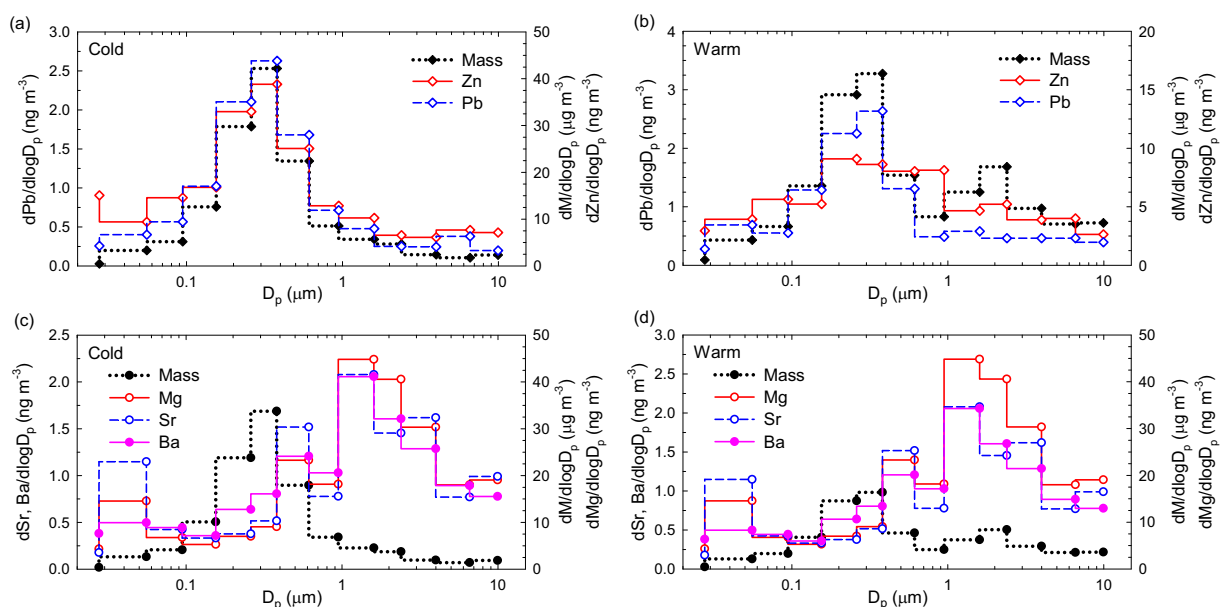


Fig. 2. Size distributions of seasonal averaged mass concentrations for Zn, Pb (a,b), and Mg, Sr, Ba (c,d) trace metals, together with mass concentration gravimetrically determined during both CS and WS, respectively.

driven metals dissolution process is most likely to account for Zn, Pb, Cd, and V solubilization. Since the pH values were higher than 3 and slightly below 8 for particles distributed above the 1 μm size range (Galon-Negru et al., 2018), it is assumed that a different process would account for the solubility of elements distributed in the coarse fraction (e.g., by forming new species with an organic acid such as oxalate (Fang et al., 2017a)). For Fe and Mn, the size distribution pattern did not present a clear trend. At the present time, neither acidity-driven dissolution nor new species formation can be inferred as being responsible for their solubility. The observed size distributions of selected elements are generally in line with the findings reported by other authors (Duan et al., 2012; Padoan et al., 2016; Malandrino et al., 2016).

Fig. 2.a,b show that Pb presents the largest mass distribution in the fine mode (maximum at ~ 381 nm) in both CS and WS. Zn presents a dominant fine mode in the CS (maximum at ~ 381 nm) and a broad distribution in the WS over 240–946 nm size range. Both elements might be of anthropogenic origin source, mainly from combustion of coal (Duan et al., 2012) and lubricating oil or vaporization on hot braking surfaces (Lough et al., 2005). Direct vehicular emissions (i.e., exhaust emissions and tire wear) have been found to be responsible for the

presence of Zn in atmospheric particles (Birmili et al., 2006). Mg and Sr have monomodal mass distributions with one maximum in the 1.6 to 2.39 μm size range. Natural source contributions from mineral dust might be responsible for the observed pattern. Although Ba presents similar distribution pattern as Mg and Sr (Fig. 2.c,d), anthropogenic sources (crumb tire, brakes, and even the vehicular chassis) are thought to be responsible for its observed distribution (Birmili et al., 2006).

Fig. 3 presents the seasonality in the percentage contributions of the identified and quantified water-soluble metals relative to the total elements' mass concentration in the $\text{PM}_{2.5}$ fraction. Contributions lower than 0.1% of the total detected components (Be, Co, Ga, Mo, Ag, Te, Tl, Bi and U) are reported as "other metals" in Fig. 3. Several elements (Al, Fe, Mg, Zn, Ni, Cu, and Mn) account for $\sim 87\%$ from the total water-soluble metal fraction of $\text{PM}_{2.5}$ ($\text{Al}_{(26.6 \pm 5.6)\%} > \text{Fe}_{(23.2 \pm 14.8)\%} > \text{Mg}_{(12.3 \pm 4.2)\%} > \text{Zn}_{(10.9 \pm 3.2)\%} > \text{Ni}_{(7.0 \pm 5.3)\%} > \text{Cu}_{(3.8 \pm 1.9)\%} > \text{Mn}_{(3.5 \pm 1.6)\%}$). For Mg the highest contribution was observed in April 2016 (20.5%). This could reflect that, during dry periods, Mg can mainly originate from dust resuspension (Galon-Negru et al., 2018). The significant fraction of water-soluble Fe might be a factor enhancing the role played by Fe

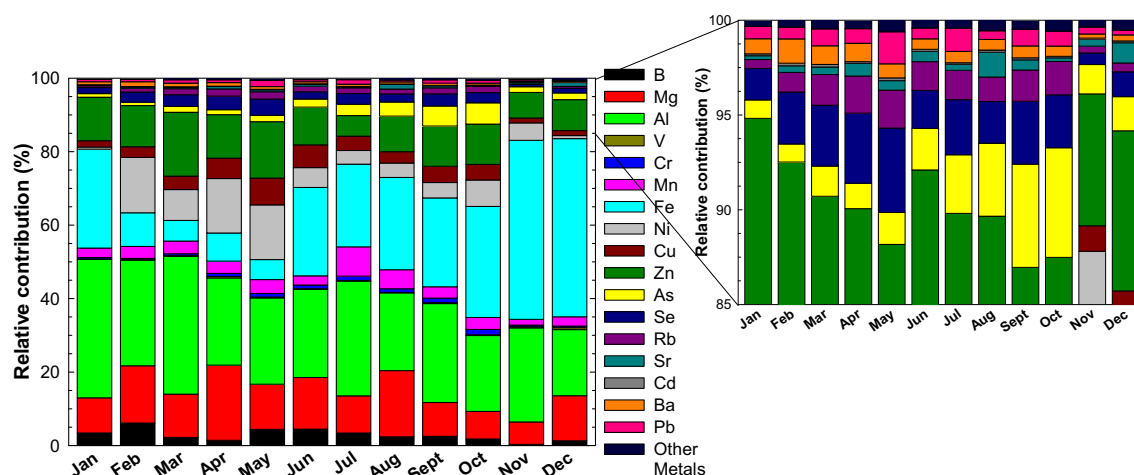


Fig. 3. The relative contributions, as monthly averages of identified and quantified water-soluble trace metals to the total water soluble-elements mass in the $\text{PM}_{2.5}$ fraction.

(III) species in the photochemistry of the atmospheric aerosol phase, both in droplets (dissolved Fe(III)) and in particles (Vione et al., 2006).

3.3. Sources apportionment

3.3.1. Selection and evaluation of PMF solution

In the present work, PM_{2.5} datasets corresponding to TP, CS and WS were investigated by the EPA PMF 5.0 model for the four-, five- and six-factor solutions. Table 3 summarizes PMF diagnostics for each investigated period. In the present study, solutions of the parameter related to the PMF rotations algorithm (F_{peak}) were not investigated since no edges were identified in the specific space plots. Moreover, constraints were not applied. Additional solution analysis data are presented in SM (see Table S2 and Table S3, Section S8 of the SM).

Convergence of all runs and stable Q values over 20 repeated runs (Q_{true} as the parameter used to examine the goodness-of-fit parameter by taking into account all points and Q_{robust} as the parameter used to examine the goodness-of-fit parameter calculated only with values of uncertainty-scaled residual >4) were observed for all investigated cases. Data presented in Table 3 show a smaller difference between the $Q_{\text{robust}}/Q_{\text{expected}}$ of the six-factor solution and that of the five-factor solution in comparison with that specific for the increment from the four-factor solution to the five-factor solution. These observations

would suggest that in the six-factor solution the number of potential apportioned sources is too high.

For the five-factor solution $Q_{\text{robust}}/Q_{\text{true}}$ values were higher than 0.96 in each period, indicating that extreme events do not significantly influence this model. On the other hand, some species had worse scaled residuals for the four- and six-factor solutions in comparison with the five-factor solution. In the five-factor solution, for each investigated seasonal period, apportioned factors were mapped with BS in higher than 91% of the runs. Three cases with BS in the 58% to 68% range were identified in the six-factor solution, suggesting that this factor solution was less stable. Moreover, for all investigated runs no swaps occurred in DISP mode (Table 3). Between 2% (CS) to 6% (WS) of BS-DISP runs have not been considered in the five-factor solution due to the factor swaps. The six-factor solution has higher numbers of BS-DISP runs which were not considered (13% for CS and 9% for WS). Detailed discussion on favorable solution diagnostics and associated specific sources for each investigated period is presented in Section S8 of the SM.

3.3.2. Identified sources of the PM_{2.5} fraction

The source profiles for the five-factor PMF solution of the PM_{2.5} fraction are shown in Fig. 4. For each investigated period (i.e., TP, CS, and WS) percentage contributions of apportioned sources in the five-factor solution are presented in Fig. 5. Source profiles for the four- or

Table 3
Summary of PMF diagnostics by runs for TP (a), CS (b), and WS (c) datasets.

Diagnostic	4 factors	5 factors	6 factors
(a) - TP			
Q_{expected}	2238.0	1901.0	1564.0
Q_{true}	10,057.1	7246.0	5444.9
Q_{robust}	9543.9	7060.1	5341.0
$Q_{\text{robust}}/Q_{\text{expected}}$	4.26	3.71	3.41
$Q_{\text{robust}}/Q_{\text{true}}$	0.95	0.97	0.98
Species with $Q_{\text{true}}/Q_{\text{expected}} > 3$	Cr, Cu, Zn, Ba, NH_4^+ , K^+ , Mg^{2+} , Ca^{2+}	PM _{2.5} , Zn, Ba, Cl^- , Na^+ , Ca^{2+}	PM _{2.5} , Zn, Ba, Na^+ , Ca^{2+}
DISP%dQ	0	0	0
DISP swaps	0	0	0
Factor with BS mapping < 100%	0	Traffic + industrial factor 99%; biomass burning factor 99%	Biomass burning 98%, chloride/unknown factor 58%
BS-DISP% of cases with swaps	0	3	11
(b) - CS			
Q_{expected}	1041	875	709
Q_{true}	3638.5	2665.6	1882.8
Q_{robust}	3576.6	2625.3	1865.1
$Q_{\text{robust}}/Q_{\text{expected}}$	3.44	3.00	2.63
$Q_{\text{robust}}/Q_{\text{true}}$	0.98	0.98	0.99
Species with $Q_{\text{true}}/Q_{\text{expected}} > 3$	Cr, Zn, Ca^{2+}	Zn, Ca^{2+}	Zn, Cl^- , Na^+ , Ca^{2+}
DISP%dQ	-0.0027	0	0
DISP swaps	0	0	0
Factor with BS mapping < 100%	Traffic + industrial + potassium factor 99%; Secondary formation factor 82%;	Biomass burning factor 97%, traffic + industrial factor 91%;	Nitrate factor 99%, chloride/unknown factor 68%, traffic + industrial factor 99%;
BS-DISP% of cases with swaps	3	2	13
(c) - WS			
Q_{expected}	1209	1019	829
Q_{true}	6369.2	4329.5	3139.4
Q_{robust}	5845.2	4161.7	3041.2
$Q_{\text{robust}}/Q_{\text{expected}}$	4.83	4.08	3.67
$Q_{\text{robust}}/Q_{\text{true}}$	0.92	0.96	0.97
Species with $Q_{\text{true}}/Q_{\text{expected}} > 3$	Cr, Zn, Ba, Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+}	Zn, Sr, Ba, Pb, Na^+ , NH_4^+ , Ca^{2+}	Sr, Ba, Pb, Cl^- , Na^+ , Ca^{2+}
DISP%dQ	0	0	0
DISP swaps	0	0	0
Factor with BS mapping < 100%	Nitrate factor 89%	Traffic + industrial factor 93%	Chloride/unknown factor 59%
BS-DISP% of cases with swaps	8	6	9

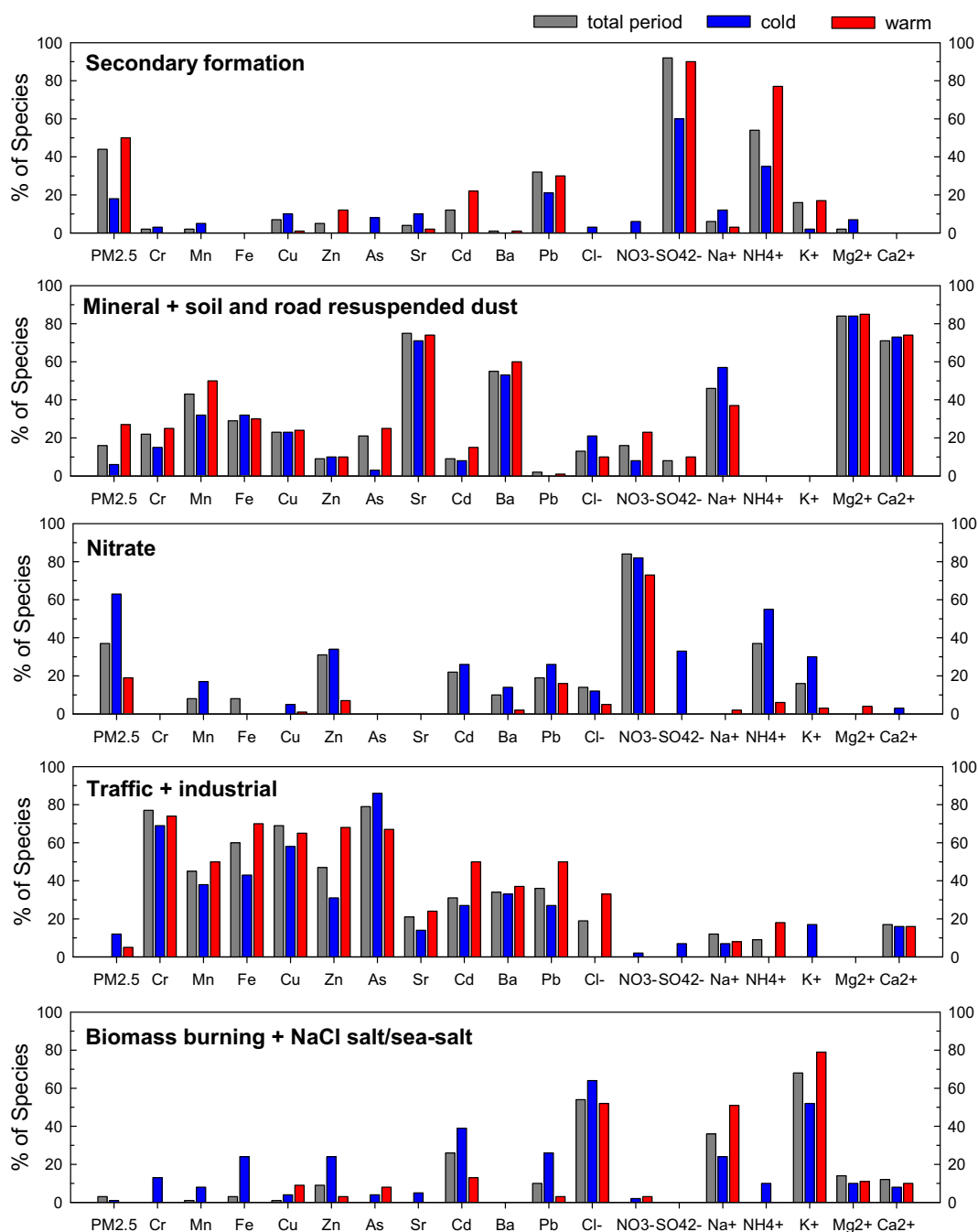


Fig. 4. Loadings of measured water-soluble chemical species into the five-factor PMF resolved solution for the TP, CS and WS periods.

six-factor solutions are given in SM (Fig. S3, and Fig. S4, Section S9 of the SM). Factor time series of sources' contribution to the PM_{2.5} fraction are presented in Fig. S5, Section S9 of the SM. For the total period, source profiles for the five-factor PMF solution of the PM_{2.5} fraction in different sizes are presented in Fig. S6, while percentage contribution of apportioned sources is presented in Fig. S7, Section S9 of the SM.

In the PMF five-factor solution of the PM_{2.5} fraction (Fig. 4, and Fig. 5), each factor has a distinctive group of species that can be related to a specific source. In the Iasi area, sources of atmospheric PM_{2.5} are comprised of secondary formation (factor 1, mainly ammonium sulfate), mineral + soil and road resuspended dust (factor 2), nitrate (factor 3, most probably in ammonium nitrate prevalent form), traffic + industrial (factor 4), and biomass burning + NaCl salt/sea-salt (factor 5).

The factor referred to as secondary formation accounts for 44% of the total period PM_{2.5} concentration. It shows significant contributions for SO₄²⁻ (92%) and NH₄⁺ (54%), with less significant contributions of Pb (32%), K⁺ (16%), Cd (12%), and Zn (5%). The relative contributions in WS (90% for SO₄²⁻, 77% for NH₄⁺, 30% for Pb, and 17% for K⁺) are higher than those during CS (60% for SO₄²⁻, 35% for NH₄⁺, 21% for Pb, and 2% for K⁺). These findings are in agreement with other reports (Fang et al., 2015; Masiol et al., 2017).

The factor labeled as "mineral + soil and road resuspended dust" in the TP investigated case contains high percentages of Mg²⁺ (84%), Sr (75%), Ca²⁺ (71%), Ba (55%), and moderate values of Na⁺ (46%), Mn (43%), Fe (29%), Cu (23%), and Cr (21%). Elements such as Ca, Mg, Na, Mn, and Sr are associated with crustal material (Fang et al., 2015; Alastuey et al., 2016), while Fe, Cu, Ba, and Cr are associated with road dust (Amato et al., 2009). Saharan dust, known to bring significant

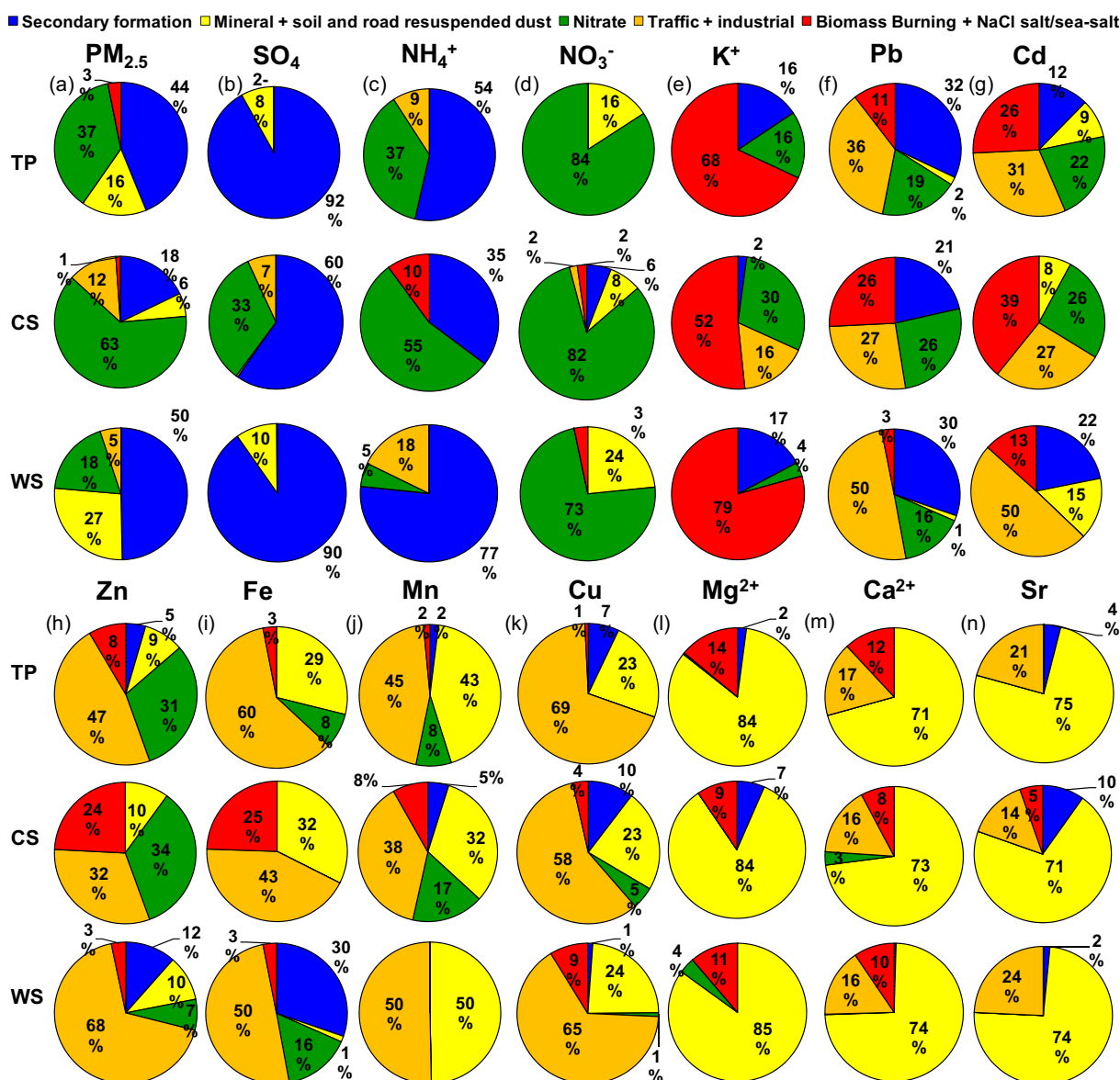


Fig. 5. Percentage contribution of PMF apportioned sources to selected analyzed $PM_{2.5}$ chemical components for TP, CS and WS databases.

contributions of minerals to the coarse fraction (Pederzoli et al., 2010), might account to some extent for the values reported in the present work for elements of mineral origin. Tire wear and brake pad wear could be responsible for Cr abundance (McKenzie et al., 2009) in the $PM_{2.5}$ fraction in the Iasi area. Surrounding soils account most probably for Fe and Mn abundances (Gunawardana et al., 2012). The mineral + soil and road resuspended dust factor shows the highest relative contributions over WS, in which dust resuspension is more likely to occur. Crustal material and/or road dust as sources for PM in urban areas is also reported elsewhere (Minguillón et al., 2012; Han et al., 2017).

Nitrate factor is mainly accounted by contributions of NO_3^- (84% – TP; 82% – CS; 73% – WS) and NH_4^+ (37% – TP; 55% – CS; 5% – WS). An additional contribution of SO_4^{2-} (33%) has been observed in the five-factor solution obtained for CS. Fig. 5 also shows other chemical species which contribute to this factor (K^+ , Pb, Cd, Zn, Fe, Mn, and traces of Cu, Mg^{2+} , and Ca^{2+}). In the present study, NO_3^- could be mainly assigned to NO_x ($NO_x = NO + NO_2$) emitted by gasoline- and diesel-powered vehicles, natural gas and coal combustion (Zhang et al., 2012). Ammonium nitrate fertilizers present in atmospheric dust particles may volatilize into gaseous NH_3 and HNO_3 and can therefore contribute to nitrate formation (Han et al., 2017). At the investigated site, based on an annual average,

nitrate factor seems to account for 37% of total $PM_{2.5}$, showing contribution three times higher during CS (63%) than that over WS (18%).

Traffic + industrial factor for TP has high contributions of As (79%), Cr (77%), Cu (69%), Fe (60%), Zn (47%), Mn (45%), and moderate contributions of Pb (36%), Ba (34%), and Cd (31%). This factor has a clear seasonal pattern, with contributions to $PM_{2.5}$ mass concentrations increasing from 5% in WS to 12% over CS. The existence of Cr, Cu, and Pb might indicate contributions from industrial sources as also suggested by Han et al. (2017). Mn, Fe, Cu, Zn, and Ba are elements related to traffic from non-exhaust emissions sources such as brake and tire wear, muffler ablation, and brake lining (Davis et al., 2001; Adachi and Tainosho, 2004; Lee, J.H. et al., 2006; Gietl et al., 2010; Pant and Harrison, 2013). Metals such as Zn, Cd, and As are most probably related to gasoline and diesel vehicles' engine emissions. Zn and Cd are tracers for the combustion of lubricating oil (Kleeman et al., 2008; Pulles et al., 2012), and As is known to be emitted from fuel combustion (Pulles et al., 2012). Coal combustion in power plants is assigned as a major source of Pb in airborne $PM_{2.5}$ (Zhang et al., 2013). However, it has been predicted that the percentage of PM non-exhaust of the total PM emissions will increase to about 90% by the end of this decade (Rexeis and Hausberger, 2009).

The fifth identified factor comprises mixed sources of biomass burning + NaCl salt/sea-salt. The biomass burning source was identified by high concentrations of water-soluble K^+ (68% – TP, 52% – CS, 79% – WS). In addition, in CS significant contributions of water-soluble Cd (39%), Pb (26%), Fe (25%), and Zn (24%) were observed for this factor. The main species in NaCl salt/sea-salt particles source are Na^+ (36% – TP; 24% – CS; 51% – WS) and Cl^- (54% – TP; 64% – CS; 52% – WS). K is reported as an important contributor in biomass burning aerosols (Lee et al., 2016), but Pb has also been found in emissions from wood (Richard et al., 2011) and coal (Zhang et al., 2013) combustion. Fe, Pb, Mn, Zn, and Cu have also been apportioned to biomass burning in other studies (Chang-Graham et al., 2011; Oakes et al., 2012; Fang et al., 2015).

The missing contributions of NO_3^- and SO_4^{2-} in the biomass burning mixed with NaCl salt/sea-salt factor to some extent exclude the existence of aged sea-salt particles in the Iasi area. However, high loading of Cl^- in this factor allows its association with fresh sea-salt particles (Qin et al., 2002). Although NaCl sea-salt is expected to reside in the coarse mode, atmospheric particles from the investigated area also have a significant contribution of Na^+ in the fine mode, with a maximum at 1.6 μm during WS and at 2.39 μm during CS (Galon-Negru et al., 2018). Galon-Negru et al. (2018) report on Cl^- bimodal distribution during CS (maxima at 381 nm and at 2.39 μm) and one modal distribution during WS spread over the 1.6 to 2.39 μm size range. The behavior in Na^+ and Cl^- distributions permits the inference of fresh sea-salt particles as a source of these two elements during WS (Galon-Negru et al., 2018), but also infers the existence of an additional source for Cl^- in the CS, such as biomass burning. Marine contributions in fine atmospheric particles were also reported in other studies (Arsene et al., 2011; Squizzato et al., 2016). Contributions of Na^+ and Cl^- from sources prevailing in winter, i.e. NaCl salt used in melting ice from the urban streets (de-icing NaCl), was previously reported (Arsene et al., 2011). Use of de-icing salt in winter and long-range transport in summer are suggested as possible emission sources for Na^+ in other studies (Minguillón et al., 2012).

Data presented in Fig. 5 show that the average sources' contribution to the $PM_{2.5}$ fraction over TP follows the order: secondary formation (44%), nitrate (37%), mineral + soil and road resuspended dust (16%), biomass burning + NaCl salt/sea-salt (3%), traffic + industrial emission (< 0.05%). During CS the highest contribution to the $PM_{2.5}$ fraction comes from NO_3^- (63%), followed by the secondary formation (18%), and traffic + industrial emissions (12%). In WS the secondary formation (50%) is the major source, followed by mineral + soil and road resuspended dust (27%), and nitrate (18%). The dominant presence of secondary formation and nitrate factors, either in CS or WS, indicate that the chemical reactions generating particulate secondary SO_4^{2-} and NO_3^- are temperature and humidity related. Lower temperatures and higher relative humidity facilitate NO_3^- formation (Galon-Negru et al., 2018). The mineral + soil and road resuspended dust factor is noteworthy in WS (27%) when precipitation events ceased to occur, while traffic + industrial factor prevail in CS (12%). Over the warm season, decreased human activities due to vacation might account for smaller contribution of the traffic + industrial factor (5%) to the $PM_{2.5}$ fraction. Similar temporal distribution of previously mentioned sources to $PM_{2.5}$ mass concentration was also reported in other recent studies (Fang et al., 2015; Han et al., 2017). The sources assigned to the investigated $PM_{2.5}$ fraction are generally in good agreement with those reported in recent studies for various European sites (Minguillón et al., 2012, 2014; Cesari et al., 2016; Squizzato et al., 2016).

3.3.3. Correlation of sources' contribution with meteorological parameters. CWT and BPP analyses

Fig. 6 shows results of CWT analysis for the CS and WS identified sources in the $PM_{2.5}$ fraction. Map values represent the contributions of average factors to the total $PM_{2.5}$ fraction. The distribution generated by BPP analysis is presented in Fig. 7. Average factor contributions to the

total $PM_{2.5}$ fraction from PMF have been taken into account. As Iasi is located at about 150 km NE linear distance from the Oriental Carpathians chain (highest altitude of 1907 m), air mass back trajectories arriving at the sampling site at an altitude of 2000 m have been considered in further CWT analysis (Fig. 6.a). For the air mass back trajectories arriving in Iasi at an altitude of 1000 m, the results of CWT analysis are presented in Fig. S8, Section 10 of the SM.

For secondary formation source (Fig. 6.b), CWT analysis reveals significant contributions of SE origin for CS (transport from the Balkan Peninsula) and of NE origin for WS (transport from wide-spread areas covering the Eastern European Plains). Similar origins of secondary aerosols have been reported by Perrone et al. (2018) for the Zagreb, Budapest and Sofia urban areas. For local/regional contributions of secondary formation (Fig. 7.a), high concentrations are observed even under low winds from all geographical directions. Higher temperature and solar radiation enhance photochemical reactions in WS, while increased coal combustion for heating purposes could account for the observed distribution during CS. Contributions of at least 0.8 ng m^{-3} are prevalent for all geographical directions and this is probably due to persistent air masses, which allow local/regional $(NH_4)_2SO_4$ formation. Higher values are observed when strong winds ($20\text{--}30 \text{ km h}^{-1}$) are coming from the NE-E quadrant, with the Iasi international airport located at about 3 km linear distance from the sampling point. Kerosene combustion is probably an important local source of gaseous SO_2 responsible on the formation of particulate SO_4^{2-} .

For the mineral + soil and road resuspended dust, the contribution of PMF factor (Fig. 6.c) is associated with long range transport of dust from the Black Sea and Mediterranean Sea shores and the Sahara Desert. Although CWT maps for both CS and WS show similar patterns, the highest probability was observed during dry periods of the year when resuspended dust prevails. A similar pattern for mineral dust has been reported for an urban site in Bulgaria (Perrone et al., 2018). Local/regional contributions to this factor (Fig. 7.b) are mainly associated with strong winds arriving from NE and E. In these quadrants resuspended dust from rural areas or neighboring streets might be a potential source.

The CWT map of the nitrate factor (Fig. 6.d) for CS shows a wide-spread area over Europe. Interestingly for WS, the Black Sea and Mediterranean Sea shores and the Sahara Desert are identified as probable sources, similar to the behavior observed in the CWT map for the mineral + soil and road resuspended dust (Fig. 6.c). This observed similarity suggests the importance, under favorable meteorological conditions, of resuspended dust in the formation of particulate NO_3^- upon reaction of HNO_3 with soil-containing $CaCO_3$ (Sharma et al., 2007) or $MgCO_3$ (Galon-Negru et al., 2018). The high probability that the particles come over the Atlantic Ocean is considered only suggestive of the transport path and not as a source area. Obtained CWT maps for secondary formation and nitrate highlight that the sources of their precursors differ, in agreement with the chemistry of particulate NO_3^- and SO_4^{2-} (Petit et al., 2017a). The polar plots for nitrate factor (Fig. 7.c) show increased contributions from NE and SE under moderate wind speeds (between 10 and 20 km h^{-1}) and from E at high wind conditions. This factor is probably linked to NO_x emissions from combustion of fuels used for both air and road traffic.

The CWT map of traffic + industrial factor (Fig. 6.e) for CS reveals an intense potential source-region located in the north-eastern Europe (Ukraine and Russia). A wide-spread region over northern Europe seems to be the major source over WS. Hot spot areas observed in both CS and WS might reflect significant contributions from important industrial emission areas over Europe. NE trans-sector contribution is more significant during CS, while contributions from both NE and NW trans-sectors are more important during WS. Several major industries exist in these European trans-sectors (Fig. S9, Section 10 of the SM). The polar plot analysis indicates that under strong E and/or W-NW winds, the traffic + industrial factor brings higher contributions (Fig. 7.d). Carol I boulevard, located at about 150 m W linear distance from the sampling point, can be assigned as the main local traffic

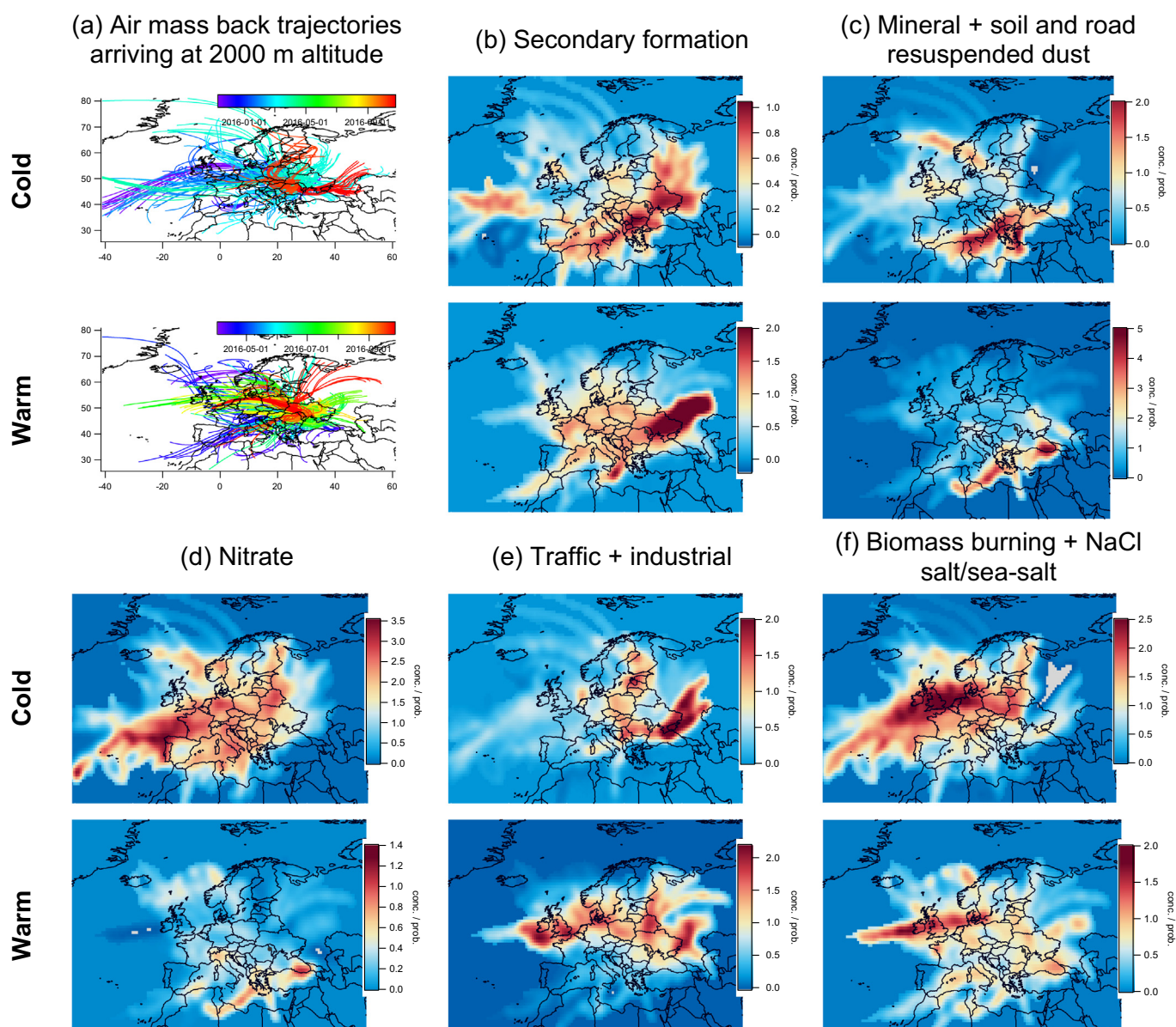


Fig. 6. The CWT maps for PMF apportioned sources for TP, CS and WS databases, using the air mass back trajectories arriving in Iasi at 2000 m altitude.

contributor. Winds blowing from the SE direction bring important contributions of industrial origin from a small brick plant (at about 8 km linear distance) and the Iasi power plant (at about 5 km linear distance). An antibiotic company (at about 7 km linear distance) might account for the contribution of local W direction.

The CWT biomass burning + NaCl salt/sea salt map highlights that northern Europe acts as the strongest potential source contributor during CS in the Iasi area (Fig. 6.f). During this season, wood and coal combustion processes most probably account for the source region transport. Wildfires or open field fires, likely associated with agricultural practices, might bring significant contributions during WS. Also, for this factor, high CWT scores over the Atlantic Ocean are considered only as an indication of the path and not as a source area. The polar plot for biomass burning + NaCl salt/sea salt sources (Fig. 7.e) does not reveal a prevailing direction. Higher concentrations are observed during both low and high wind speeds. Wood combustion for heating purposes is relevant especially during CS, while intense agricultural biomass burning for land clearing in the areas surrounding Iasi might be relevant in WS.

3.3.4. Health risk assessments of $PM_{2.5}$ water-soluble heavy metals

The non-carcinogenic and carcinogenic health risks of several heavy metals (As, Ba, Cd, Co, Cr(VI), Pb, Mn, Mo, and Ni) in the $PM_{2.5}$ fraction caused by long-term exposure via inhalation pathways were evaluated in the present work. It has been suggested that Cr exists in more than one oxidation state, even in air. This is especially true for Cr(VI) which acts as a human carcinogen (US EPA, 1998; IARC Monographs, 2016). Since discrimination between Cr(III) and Cr(VI) could not be performed through ICP-MS measurements, Cr(VI) concentration was assumed to be 1/7 of the determined value in the present work (US EPA, 2013; J. Liu et al., 2018a).

For the non-carcinogenic risk analysis of selected heavy metals in the $PM_{2.5}$ fraction, results of the inhalation hazard quotient (HQ) and sum of HQs or HI (hazard index) are shown in Table 4. For the total period, similar details for the non-carcinogenic risks classified in different sizes are presented in Table S4 (Section 11 of the SM).

The HI risk for all metals is 0.203 for TP and CS, and 0.210 for WS. For the TP case, As, Ni and Mn present the greatest contributions to HI (HQ values of 0.097 (47.7%), 0.050 (24.8%) and 0.044 (21.5%), respectively).

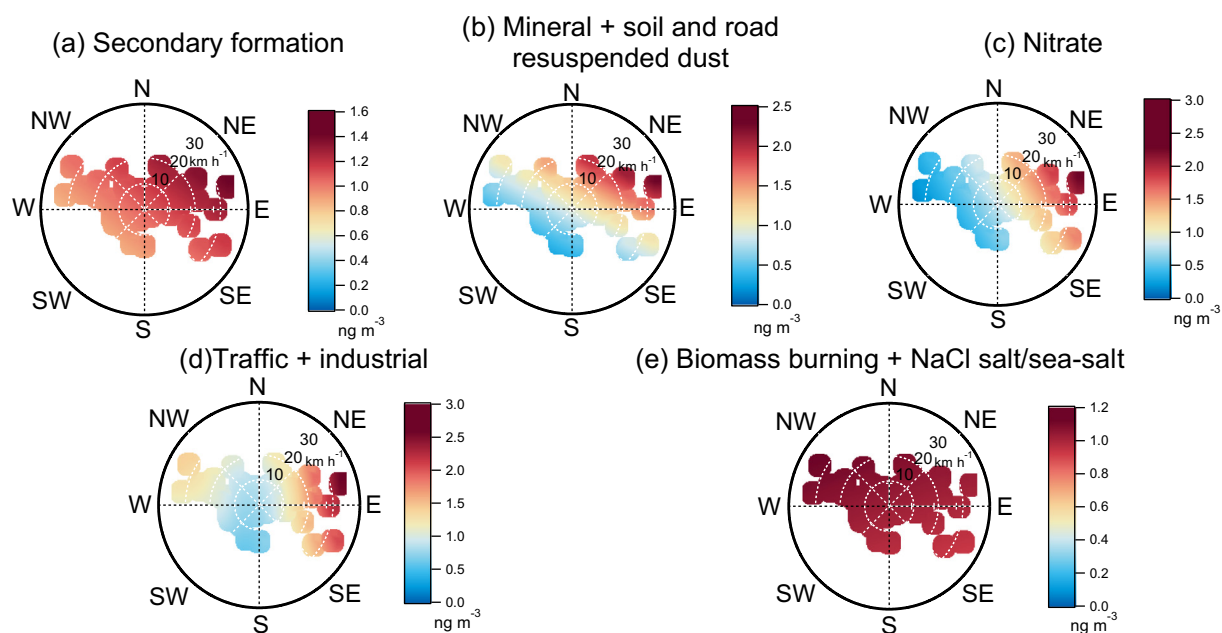


Fig. 7. Bivariate polar plots for the total period PMF apportioned sources to the PM_{2.5} fraction.

In this case, the HQ of PM_{2.5} water-soluble metals varies in the following order: As > Ni > Mn > Cd > Co > Ba > Cr(VI) > Mo > Pb. These results are consistent with the statements in Section 3.1 that the water-soluble As and Ni in the PM_{2.5} fraction slightly exceed the total element target values recommended by EEA (2017). However, it appears that, the non-cancerous risk from inhalation of PM_{2.5} water-soluble elements does not yet deserve attention, since neither HQ nor HI values exceed the critical value of 1 (US EPA, 1989).

The carcinogenic risk (CR) of As, Cr(VI), Cd, Co, Ni, and Pb, caused by inhalation exposure to the analyzed PM_{2.5} fraction, was evaluated in this study based on the inhalation unit risk (IUR) (Table 4). In the PM_{2.5} fraction, during the total period, the risks (R, %) of each carcinogenic metal and their corresponding relative contribution to the total inhalation risk are ranked in the following order: As (3.36×10^{-6} , 47.1%) > Cr(VI) (2.99×10^{-6} , 41.9%) > Ni (6.33×10^{-7} , 8.9%) > Co (8.00×10^{-8} , 1.1%) > Cd (6.4×10^{-8} , 0.9%) > Pb (2.84×10^{-9} , 0.04%). For arsenic, an incremental cancer risk of 7.04×10^{-6} is reported for PM_{2.5} collected in a central district of Beijing, China (J. Liu et al., 2018a).

For the investigated PM_{2.5} fraction, toxic elements of traffic + industrial origin sources (As, Cr) have values which are higher than the acceptable risk level of 1×10^{-6} (US EPA, 1989). The total cancer risk (CR) is as high as 7.12×10^{-6} for TP, 6.36×10^{-6} for CS and 8.02×10^{-6} for WS (Table 4). However, data for carcinogenic risks classified in different sizes (Table S4, Section 11 of the SM) show that, individually, none of the toxic elements present in a size fraction possess cancer risks higher than the acceptable level. Traffic- and coal combustion-related air pollution, due to high attributable contents of toxic metals, As, Cd, and Pb, is inferred as a important cancer risk in other studies (Dhaini et al., 2017; J. Liu et al., 2018a). Arsenic and chromium elements, at mg kg⁻¹ concentration level, are reported for several Romanian coals (Bugaru and Rujoi, 2014). Emission of arsenic in the few tenths to few hundred µg kg⁻¹ from diesel and petrol used in European vehicles, with no difference between samples from different countries, is also reported (Pulles et al., 2012). The results obtained in the present work show that water-soluble toxic As and Cr(VI) elements from the PM_{2.5} fraction in the Iasi area seem to possess the largest contributions to the inhalation risk, and therefore to carcinogenicity. It is also noteworthy that, in terms of ambient air pollution, the attributable death rate for 2016 (per 100,000 populations) from trachea, bronchus and lung cancers, ranks Romania in the 15th place, with 5 declared cases for

both sexes (World Health Organization, Global Health Observatory data repository for 2016, Deaths by country, <http://apps.who.int/gho/data/node.main.BODAMBIENTAIRDTHS?lang=en>). As coal combustion is still intensively used in Romania for heating purposes it is believed that this source should receive attention in the future by implementing appropriate emission control measures at the local /regional level.

4. Conclusions

For the first time to our knowledge, size-resolved element measurements are presented for the water-soluble fraction of fine particulate matter (PM_{2.5}) collected in 2016 in the Iasi area. Particle mass size distributions were resolved with a cascade Dekati Low-Pressure Impactor with 13 size cuts in the 0.0276 to 9.94 µm size range. Concentrations of water-soluble elements (Ag, Al, As, B, Ba, Be, Bi, Cd, Co, Cu, Cr, Fe, Ga, Mg, Mn, Mo, Ni, Pb, Rb, Se, Sr, Te, Ti, U, V, and Zn) were measured using inductively coupled plasma mass spectrometry.

Elements such as Al, Fe, Mg, Mn, Zn, Ni, and Cu, show concentrations which span over a wide range, from the detection limits to about 91 ng m⁻³. For all other elements, concentrations lower than 10 ng m⁻³ have been observed. Several elements (i.e., Al, Fe, Zn, As, Cr, and Pb) exhibit clear seasonal patterns with maxima over the cold season and minima over the warm season. Pb distribution suggests an increase in the use of fossil fuels combustion over diesel vehicular emissions.

Clear fine mode size-dependent distributions (maxima at ~ 381 nm) are specific for elements of anthropogenic origin sources (Pb, Zn, Cd, and V) most probably due to a likely acidity-driven metals dissolution process. Some elements of mineral origin sources (Mg, Sr) show bimodal distribution with abundant supermicronic mode.

For the analyzed PM_{2.5} fraction, five factors extracted by the Positive Matrix Factorization (PMF) model were associated with specific sources. The most important contributions to the total PM_{2.5} mass concentration (during the total period) come from the secondary formation of ammonium sulfate form (~44%) and from nitrate (~37%). Resuspended dust (minerals, soils and roads) accounts for a contribution of about 16%, while biomass burning mixed with NaCl salt/sea-salt sources bring contributions as high as ~3%. Traffic and industrial sources seem to bring less significant contributions (<0.05%).

Table 4

Non-carcinogenic and carcinogenic risks for selected heavy trace metals in the PM_{2.5} fraction for TP (a), CS (b), and WS (c) databases.

	IUR _i (μg/m ³) ⁻¹	RfC _i (mg/m ³)	CA _i (μg/m ³)	HQ _i	R _i	HQ _i (%)	R _i (%)
(a) - TP							
As	4.3E-03	1.5E-05	4.39E-03	9.76E-02	3.36E-06	48.0	47.1
Ba	–	5.0E-04	1.32E-03	8.80E-04	–	0.4	–
Cd	1.8E-03	1.0E-05	2.00E-04	6.67E-03	6.40E-08	3.3	0.9
Cr	8.4E-02	1.0E-04	2.00E-04	6.67E-04	2.99E-06	0.3	41.9
(VI)							
Co	9.0E-03	6.0E-06	5.00E-05	2.78E-03	8.00E-08	1.4	1.1
Pb	1.2E-05	–	1.33E-03	–	2.84E-09	–	0.04
Mn	–	5.0E-05	6.60E-03	4.40E-02	–	21.6	–
Mo	–	4.0E-04	1.40E-04	1.17E-04	–	0.1	–
Ni	2.6E-04	9.0E-05	1.37E-02	5.07E-02	6.33E-07	24.9	8.9
			HI =	CR =			
			0.203	7.12E-06			
(b) - CS							
As	4.30E-03	1.50E-05	3.80E-03	8.44E-02	2.90E-06	42.8	45.7
Ba	–	5.00E-04	1.62E-03	1.08E-03	–	0.6	–
Cd	1.80E-03	1.00E-05	2.20E-04	7.33E-03	7.04E-08	3.7	1.1
Cr	8.40E-02	1.00E-04	1.70E-04	5.67E-04	2.54E-06	0.3	39.9
(VI)							
Co	9.00E-03	6.00E-06	6.00E-05	3.33E-03	9.60E-08	1.7	1.5
Pb	1.20E-05	–	1.32E-03	–	2.82E-09	–	0.04
Mn	–	5.00E-05	6.04E-03	4.03E-02	–	20.4	–
Mo	–	4.00E-04	1.50E-04	1.25E-04	–	0.06	–
Ni	2.60E-04	9.00E-05	1.62E-02	6.00E-02	7.49E-07	30.5	11.8
			HI =	CR =			
			0.203	6.32E-06			
(c) - WS							
As	4.30E-03	1.50E-05	4.97E-03	1.10E-01	3.80E-06	52.6	47.4
Ba	–	5.00E-04	1.06E-03	7.07E-04	–	0.3	–
Cd	1.80E-03	1.00E-05	1.70E-04	5.67E-03	5.44E-08	2.7	0.7
Cr	8.40E-02	1.00E-04	2.40E-04	8.00E-04	3.58E-06	0.4	44.7
(VI)							
Co	9.00E-03	6.00E-06	2.00E-05	1.11E-03	3.20E-08	0.5	0.4
Pb	1.20E-05	–	1.34E-03	–	2.86E-09	–	0.0
Mn	–	5.00E-05	7.13E-03	4.75E-02	–	22.6	–
Mo	–	4.00E-04	1.20E-04	1.00E-04	–	0.1	–
Ni	2.60E-04	9.00E-05	1.18E-02	4.36E-02	5.44E-07	20.8	6.8
			HI =	CR =			
			0.210	8.02E-06			

Note: IUR_i – Inhalation Unit Risk of the carcinogenic element i; RfC – RfC_i = reference concentration for the element i – inhalation toxicity value; CA_i – concentration of the non-carcinogenic element i (daily average elemental concentrations calculated based on 36-h determined concentrations in this study); HQ_i – Hazard Quotient of element i (unitless); HI – Hazard Index (non-carcinogenic risk); R_i – carcinogenic risk of the element i (unitless); CR – total carcinogenic risk.

For the secondary formation, concentration weighted trajectory (CWT) analysis revealed significant contributions from the Balkan Peninsula or from the Eastern European Plains. Black Sea and Mediterranean Sea shores and the Sahara Desert are identified as important contributors of mineral elements. During the warm season, the CWT distribution of nitrate factor shows the importance of shores and desert areas to PM_{2.5} nitrate abundance, most probably due to HNO₃ reaction with MgCO₃ or CaCO₃ under favorable meteorological conditions. Several major industries in the northern, north-western and north-eastern European areas bring significant contributions to the PM_{2.5} fraction.

At regional/local level, as shown by bivariate polar plot (BPP) analysis, secondary formation of ammonium sulfate, biomass burning and NaCl salt/sea-salt sources are widely spread throughout all geographical directions. All other local sources prevail mainly from NE to SE quadrants which include large agricultural areas, the Iasi international airport and brick and heat/power plants.

Furthermore, the assessment of non-carcinogenic and carcinogenic risks to human health for several metals present in the investigated PM_{2.5} fraction was carried out for the first time. Among all investigated toxic metals, arsenic and chromium (VI) had presumably the largest

incremental carcinogenic health risks ($\sim 3.36 \times 10^{-6}$). As both metals have traffic and industrial related sources it is believed that these sources should receive attention in the future by implementing appropriate emission control measures at the local /regional level.

Acknowledgements

The authors acknowledge the financial support provided by UEFISCDI within the PN-III-P4-ID-PCE-2016-0299 (AI-FORECAST) project. European Union's Horizon 2020 – Research and Innovation Framework Programme, through the EUROCHAMP-2020 Infrastructure Activity Grant (grant agreement No 730997) and the COLOSSAL grant (CA16109), is gratefully acknowledged. The authors thank Dr. Nelu Grinberg and Ms. Cynthia Grinberg for very fruitful discussion.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2019.133839>.

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Chemical characteristics of size-resolved atmospheric aerosols in Iasi, north-eastern Romania: nitrogen-containing inorganic compounds control aerosol chemistry in the area

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Received: 2 November 2017 – Discussion started: 17 November 2017

Revised: 27 February 2018 – Accepted: 14 March 2018 – Published: 26 April 2018

Abstract. This study assesses the effects of particle size and season on the content of the major inorganic and organic aerosol ionic components in the Iasi urban area, north-eastern Romania. Continuous measurements were carried out over 2016 using a cascade Dekati low-pressure impactor (DLPI) performing aerosol size classification in 13 specific fractions over the 0.0276–9.94 μm size range. Fine-particulate Cl^- , NO_3^- , NH_4^+ , and K^+ exhibited clear minima during the warm season and clear maxima over the cold season, mainly due to trends in emission sources, changes in the mixing layer depth and specific meteorological conditions. Fine-particulate SO_4^{2-} did not show much variation with respect to seasons. Particulate NH_4^+ and NO_3^- ions were identified as critical parameters controlling aerosol chemistry in the area, and their measured concentrations in fine-mode ($\text{PM}_{2.5}$) aerosols were found to be in reasonable good agreement with modelled values for winter but not for summer. The likely reason is that NH_4NO_3 aerosols are lost due to volatility over the warm season. We found that NH_4^+ in $\text{PM}_{2.5}$ is primarily associated with SO_4^{2-} and NO_3^- but not with Cl^- . Actually, indirect ISORROPIA-II estimations showed that the atmosphere in the Iasi area might be ammonia rich during both the cold and warm seasons, enabling enough NH_3 to be present to neutralize H_2SO_4 , HNO_3 , and HCl acidic components and to generate fine-particulate ammonium salts, in the form of $(\text{NH}_4)_2\text{SO}_4$, NH_4NO_3 , and NH_4Cl . ISORROPIA-II runs allowed us to estimate that over the warm season $\sim 35\%$ of the total analysed samples had very strongly acidic pH (0–3), a fraction that rose to $\sim 43\%$ over the cold season. More-

over, while in the cold season the acidity is mainly accounted for by inorganic acids, in the warm ones there is an important contribution by other compounds, possibly organic. Indeed, changes in aerosol acidity would most likely impact the gas–particle partitioning of semi-volatile organic acids. Overall, we estimate that within the aerosol mass concentration the ionic mass brings a contribution as high as 40.6 %, with the rest still being unaccounted for.

1 Introduction

Despite dramatic progress made to improve air quality, global air pollution continues to harm people's health and the environment. The problem of aerosols or particulate matter (PM) is still a great concern (Olariu et al., 2015) in Europe and many other areas in the world (e.g. China, India, USA). Atmospheric aerosols, described as complex mixtures of liquid and/or solid particles suspended in a gas (Olariu et al., 2015), mainly originate from anthropogenic and natural sources (Querol et al., 2004). Fine $\text{PM}_{2.5}$ particles (airborne particles with an equivalent aerodynamic diameter $< 2.5\ \mu\text{m}$) are air pollutants with significant effects on human health (Pope et al., 2004; Dominici et al., 2006; WHO, 2006a; Directive 2008/50/EC, 2008; Sicard et al., 2011; Ostro et al., 2014) as well as air quality (Directive 2008/50/EC, 2008; Frenay et al., 2014), visibility (Directive 2008/50/EC, 2008; Tsai and Cheng, 1999), ecosystems, weather, and climate (Ramanathan et al., 2001; Directive 2008/50/EC, 2008;

IPCC, 2013). Aerosols are also known to play a significant role within the chemistry of the atmosphere (Prinn, 2003), acting as surfaces for heterogeneous chemical reactions (Ravishankara, 1997).

Safety threshold values for both $\text{PM}_{2.5}$ (10 or $17 \mu\text{g m}^{-3}$ air, as annual mean) and PM_{10} (airborne particles with an equivalent aerodynamic diameter $< 10 \mu\text{m}$; 20 or $28 \mu\text{g m}^{-3}$ air, as annual mean) are addressed by the WHO (2006b) or by the 2008/50/EC Directive (2008) on ambient air quality and cleaner air for Europe. With regard to the $\text{PM}_{2.5}$ fraction, the EEA Report (2015) indicates that in 2013 the European Union daily limit values for PM_{10} and $\text{PM}_{2.5}$ were exceeded in, respectively, 22 and 7 out of the 28 European Union member states. However, a decreasing trend was observed when compared with the WHO report data (2006b). Moreover, on a global scale the $\text{PM}_{2.5}$ exposure leads to about 3.3 million premature deaths per year (predominantly in Asia), a figure that could double by 2050 (Lelieveld et al., 2015). Indeed, PM air pollution imparts a tremendous burden to the global public health because it ranks as the 13th leading cause of mortality (Brook, 2008).

Up to now the chemical composition of atmospheric aerosols has been reported for various urban European sites (Bardouki et al., 2003; Hitzenberger et al., 2006; Tursic et al., 2006; Gerasopoulos et al., 2007; Schwarz et al., 2012; Laongsri and Harrison, 2013; Wonaschutz et al., 2015; Sandrini et al., 2016), but such information is very scarce in eastern Europe (Arsene et al., 2011). Sulfate (SO_4^{2-}), nitrate (NO_3^-), and ammonium (NH_4^+) ions, which are major inorganic particle constituents (Wang et al., 2005; Bressi et al., 2013; Hasheminassab et al., 2014; Voutsas et al., 2014), are mainly secondary species formed in the atmosphere by chemical reactions of their precursor gases and by physical processes (nucleation, condensation, etc.) (Aksoyoglu et al., 2017). Ammonium aerosols, with an atmospheric lifetime of 1–15 days, have a clear tendency to deposit at large distances from their emission sources (Aneja et al., 2000) and seem to play a very important role in atmospheric chemistry. In urban air, the abundance of NO_3^- on fine particles seems to mainly depend on the reaction between HNO_3 and NH_3 (Stockwell et al., 2000). On a global scale, HNO_3 heterogeneous reactions on mineral dust and sea salt particles might be the predominant source of particulate NO_3^- (Athanasopoulou et al., 2008; Karydis et al., 2011). The human health effects of atmospheric ammonia, primarily exerted through particulate NH_4NO_3 , are gradually acquiring importance compared to NO_x emissions (Sutton et al., 2011).

Relative humidity (RH; Jang et al., 2002) and gas–particle partitioning processes of semi-volatile species (NH_3 , HNO_3 , HCl , and some organic acids) affect the hydronium ion (H_3O^+) concentrations (Keene et al., 2004; Guo et al., 2016) as well as aerosol formation and chemical composition. Aerosol acidity is often estimated with ion balance methods (Trebs et al., 2005; Metzger et al., 2006; Arsene et al., 2011), phase partitioning (Meskhidze et al., 2003; Keene

et al., 2004), and thermodynamic equilibrium models, e.g. E-AIM (Clegg et al., 1998; Wexler and Clegg, 2002) or ISORROPIA-II (Nenes et al., 1999; Fountoukis and Nenes, 2007; Hennigan et al., 2015; Guo et al., 2015, 2016; Fang et al., 2017). Acidity might influence transition metals' solubility and enhance aerosol toxicity and the delivery of nutrients by atmospheric deposition in marine areas (Meskhidze et al., 2003; Fang et al., 2017).

Unfortunately, the aerosols' role in the global atmospheric system is not yet sufficiently understood. The main related challenges are the occurrence of multiple sources (e.g. soil erosion, sea spray, biogenic emissions, volcano eruptions, soot from combustion, condensation of precursor gases) and the complexity of interactions with other atmospheric constituents (Zhang et al., 2015). Today, sources, distribution, and behaviour of natural and anthropogenic aerosols are still a matter of debate, exacerbated by the scarcity of aerosol-related work for eastern European Union countries (EEA Report, 2015) but also by the existing discrepancies between models and field measurements. The main uncertainties are related to secondary inorganic aerosols that control the availability of atmospheric sulfuric acid (H_2SO_4), nitric acid (HNO_3), and ammonia (NH_3) (Ianniello et al., 2011). The existing knowledge gaps bring high uncertainty in the estimated radiative forcing, although they do not impair the conclusion that warming of the climate system is unequivocal (IPCC, 2013).

Despite a growing international recognition of the importance of air pollution and air quality problems, there is a definite need to assess air pollution patterns in Romania. The existing data for north-eastern Romania concern the chemical characteristics of ambient air pollutants such as the water-soluble ionic constituents of aerosols (Arsene et al., 2011) and rainwater (Arsene et al., 2007). Recent work performed by Arsene's group in the field of atmospheric chemistry has clearly shown that, in the Iasi urban environment (north-eastern Romania), $\sim 59\%$ of the total aerosol mass concentration is still unaccounted for. The present work reports, for the first time, detailed information on the chemical composition and seasonal variation in size-segregated, water-soluble ions in aerosol samples collected throughout 2016 in the Iasi urban area, also taking into account the potential ongoing chemistry and the contributions of critical driving forces such as meteorological factors (RH, temperature), mixing layer depth, and emission source intensity. As a first attempt to assess particle acidity in the area, the present work highlights the existence of significant aerosol fractions characterized by pH values in the very strong acidity range (0–3 pH units), with potentially important implications for acid rain. Moreover, the potential importance of gaseous precursors (e.g. NH_3 , HNO_3 , HCl) in secondary inorganic PM is also discussed.

2 Experiment

2.1 Measurement site

Measurements were performed in Iasi, north-eastern Romania, at the Air Quality Monitoring Station (AMOS, 47°9' N latitude and 27°35' E longitude) of the Integrated Centre of Environmental Science Studies in the North-Eastern Development Region, "Alexandru Ioan Cuza" University of Iasi, CERNESIM-UAIC, Romania. AMOS is located north-east from the city centre, on the rooftop of the highest university building (~35 m above the ground level), in a totally open area that characterizes the site as an urban receptor point most probably influenced by well-mixed air masses. A comprehensive demo-geographical characterization of Iasi is described in detail by Arsene et al. (2007, 2011). However, according to a more recent estimate of the Romanian National Institute of Statistics, in 2016 the population in Iasi reached about 362 142 inhabitants (Ichim et al., 2016).

2.2 Field measurements

Size-resolved atmospheric aerosols were collected on ungreased aluminium filters (25 mm diameter) using a cascade Dekati low-pressure impactor (DLPI) operating at a flow rate of 29.85 L min⁻¹. Similar devices have been successfully used in other studies (Kocak et al., 2007; Wonaschutz et al., 2015). The DLPI unit performs aerosol size classification in 13 specific fractions (with size cuts at 0.0276, 0.0556, 0.0945, 0.155, 0.260, 0.381, 0.612, 0.946, 1.60, 2.39, 3.99, 6.58, and 9.94 µm at 50 % calibrated aerodynamic cut-point diameters and at 21.7 °C, inlet pressure 1013.3 mbar, outlet pressure 100 mbar, and 29.85 L min⁻¹ flow rate). Sampling performance of the DLPI unit was verified through comparison with simultaneous measurements performed with a stacked filter unit (SFU) system previously used by Arsene et al. (2011). Before each reuse the sampler's components were cleaned with ultra-pure water and methanol. Dispensable polyethylene gloves were always used to avoid hand contact with sampler's components, which were assembled and disassembled in a Labgard Class II Biological Safety Cabinet, NuAire. The DLPI sampler was transported to and from the field in tightened polyethylene bags.

Sampling was performed in 2016 twice a week, on the weekend and working days, for a total of 84 sampling events (41 during the cold season from October to March, and 43 during the warm season from April to September), generating 1092 size-resolved aerosol samples. Sampling took place on a 36 h basis, with each sampling event starting at 18:00 local time. An average volume of 64.33 ± 0.85 m³ per sampling was collected. At least two field blanks (consisting of a loaded sampler taken to and from the field but never removed from its tightened bag) were generated and simultaneously analysed together with the laboratory blanks, in or-

der to assess possible contamination during sampler loading, transport, or analysis.

Meteorological parameters including atmospheric temperature, RH, wind speed, wind direction, and global radiation were provided by a Hawk GSM-240 weather station, running at the AMOS site. Information about the mixing layer depth (atmospheric boundary layer) and its ability to dilute atmospheric pollutants at the investigated site was obtained from the NOAA Air Resources Laboratory (ARL) website (Stein et al., 2015; Rolph et al., 2017).

2.3 Sample analyses

Aerosol masses for both the PM_{2.5} and PM₁₀ fractions were gravimetrically determined with a Sartorius microbalance (MSU2.7S-000-DF, ±0.2 µg sensitivity) by weighing aluminium filters before and after sampling. Before weighing, filters stored in petri dishes were kept for at least 3 days in a conditioned room at 40 ± 2 % RH and at 20 ± 2 °C. In between different procedures, they were appropriately stored in zipped plastic bags.

Chemical analyses for water-soluble anions (i.e. acetate, (C₂H₃O₂⁻), formate, (HCO₂⁻), fluoride, (F⁻), chloride, (Cl⁻), nitrite, (NO₂⁻), nitrate, (NO₃⁻), phosphate, (PO₄³⁻), sulfate, (SO₄²⁻), and oxalate, (C₂O₄²⁻)) and water-soluble cations (i.e. sodium, (Na⁺), potassium, (K⁺), ammonium, (NH₄⁺), magnesium, (Mg²⁺), and calcium (Ca²⁺)) were performed using ion chromatography (IC) on a ICS-5000⁺ DP Dionex system (Thermo Scientific, USA). Analyses were performed within a week from sampling, in aqueous extracts of the collected samples. For chemical analysis, steps in the analytical procedures were strictly quality controlled to avoid contamination.

After sampling and all other required preparative steps, one half of each collected filter was ultrasonically extracted for 45 min in 5 mL deionized water (resistivity of 18.2 MΩ.cm) produced by a Milli-Q Advantage A10 system (Millipore). Filtered extracts (0.2 µm pore size cellulose acetate filters, Advantec) were analysed on an IonPac CS12A (4 × 250 mm) analytical column for cations and an IonPac AS22 (4 × 250 mm) column for anions, running simultaneously on the IC system. The chromatographic instrumental set-up was completed by CSRS 300 × 4 mm and AERS 500 × 4 mm electrochemical suppressors and conductivity detectors. Ion analyses were performed under isocratic elution mode, using CO₃²⁻/HCO₃⁻ (4.5/1.4 mM, 1.2 mL min⁻¹) as the mobile phase for anions and methanesulfonic acid (20 mM, 1.0 mL min⁻¹) for cations.

Traceable standard solutions (Dionex Seven Anions II and Dionex Six Cations II) were used to generate calibration curves for each species of interest, all with correlation coefficients *R*² well above 0.995. The detection limits of the major species (defined as 3 times the standard deviation of blank measurements relative to the method sensitivity) on a 36 h measurement period were

$0.0003 \mu\text{g m}^{-3}$ for NH_4^+ ($3.2 \mu\text{g L}^{-1}$), $0.001 \mu\text{g m}^{-3}$ for Na^+ ($13.4 \mu\text{g L}^{-1}$), $0.0015 \mu\text{g m}^{-3}$ for K^+ ($19.8 \mu\text{g L}^{-1}$), $0.0002 \mu\text{g m}^{-3}$ for Mg^{2+} ($3.2 \mu\text{g L}^{-1}$), $0.0016 \mu\text{g m}^{-3}$ for Ca^{2+} ($20.6 \mu\text{g L}^{-1}$), $0.0010 \mu\text{g m}^{-3}$ for SO_4^{2-} ($13.2 \mu\text{g L}^{-1}$), $0.0012 \mu\text{g m}^{-3}$ for NO_3^- ($15.1 \mu\text{g L}^{-1}$), and $0.0019 \mu\text{g m}^{-3}$ for Cl^- ($24.9 \mu\text{g L}^{-1}$). Ion concentrations in analysed blank filters (laboratory and field) were subtracted from their corresponding concentrations in the aerosol samples.

The sum of the detected ions, or of the gravimetrically determined mass concentration, over all DLPI stages is hereafter termed “PM₁₀ fraction”, while the sum over impactor stages from 1 to 10 is termed “PM_{2.5} fraction”. Modal diameters of the size-segregated aerosol particles or of the analysed ionic components (individual or as a sum) were determined by fitting lognormal distributions.

2.4 Estimation of the aerosol acidity

The thermodynamic model proposed by Fountoukis and Nenes (2007), i.e. ISORROPIA-II (<http://isorro피아.eas.gatech.edu/>), was used to get an estimate of the in situ potential acidity of our PM_{2.5} fractions. The ISORROPIA-II thermodynamic equilibrium model calculates the gas–liquid–solid equilibrium partitioning of K^+ , Ca^{2+} , Mg^{2+} , NH_4^+ , Na^+ , SO_4^{2-} , NO_3^- , Cl^- , and aerosol water content, and it can predict particle pH. Up to now the model has been used in various field campaigns’ data analysis (Nowak et al., 2006; Fountoukis et al., 2009).

To obtain the best predictions of aerosol pH, ISORROPIA-II was run in the “forward mode” for the metastable aerosol state, as preliminary runs of the experimental data in the “reverse mode” did not supply suitable information. In the metastable mode the aerosol is assumed to be present only in the aqueous phase, either supersaturated or not (Fountoukis and Nenes, 2007). As model input data we used just aerosol-phase ion concentrations measured with IC, along with RH and temperature data from the Hawk GSM-240 weather station. Actually, in the absence of accompanying gas-phase data required to constrain the thermodynamic models, the accuracy of aerosol pH predictions can be enhanced by using the aerosol concentrations in forward mode calculations (Guo et al., 2015; Hennigan et al., 2015), which seem to be less sensitive to measurement errors than the reverse mode. Where required, NH_3 data predicted by ISORROPIA-II were used for the interpretation of the results.

2.5 Air mass back trajectories and air mass origin

Air mass back trajectories were calculated using the HYSPLIT 4 model of the NOAA Air Resources Laboratory (Stein et al., 2015; Rolph et al., 2017). Arriving at the investigated site at 18:00 local time (15:00 UTC), 48 h back trajectories were computed at 500, 1000, and 2000 m altitude above the ground level. Four major sectors of air mass origin were distinguished, and their contributions are shown in Fig. 1. The

most and least frequent sectors were the north-eastern (N–E, 36.6 %) and the south-south-eastern (S–SE, 11.4 %) ones, respectively. The W–SW sector mainly prevails during winter, while the NE sector is most common during summer. The NW sector had a slightly enhanced frequency in winter and summer that, according to James (2007), could reflect a possible European monsoon circulation. Events from the S–SE sector, prevailing mainly in spring, carried out marine chemical features highly influenced by the Black Sea. Air masses undertaking faster vertical transport most probably due to the locally or continentally driven buoyancy (Holton, 1979; Seinfeld and Pandis, 1998), travelling above large (long-range transport) or short (local) continental areas, were also identified. For instance, in April 2016 five sampled events out of a total of eight were highly influenced by fast vertical air mass transport. In these events, air masses from both 500 and 1000 m altitude went down to below 500 m (brushing the ground surface), with a strong impact on the chemical composition of the collected particles (vide infra).

3 Results and discussion

3.1 Variability in PM₁₀ and PM_{2.5} mass concentrations

Table 1 shows summary statistics (median, geometric mean, arithmetic mean, standard deviation, minimum, and maximum) for PM₁₀ and PM_{2.5} mass concentrations at the AMOS site for both working days and weekends. Statistical tests were applied to determine whether there are significant differences among working days and weekends. The Shapiro–Wilk normality test applied to both PM_{2.5} and PM₁₀ indicated that the entire database was normally distributed (detailed statistics are given in Table S1 in the Supplement). Moreover, the difference in the mean values of the two groups was not high enough to exclude random sampling variability, thereby suggesting that the differences are not statistically significant. Therefore, local anthropogenic activities seem to bring similar contribution to the aerosol burden in the area on both working days and weekends. However, the PM₁₀ annual mean mass concentration ($18.95 \mu\text{g m}^{-3}$) did not exceed the WHO $20 \mu\text{g m}^{-3}$ air annual mean value, while the PM_{2.5} annual mean mass concentration ($16.92 \mu\text{g m}^{-3}$) exceeded the $10 \mu\text{g m}^{-3}$ air annual mean value set by WHO (2006b).

Table 2 presents the annual and/or seasonal arithmetic means of PM₁₀ and PM_{2.5} mass concentrations in Iasi, compared to other European sites (mean $\pm$ SD). The annual averages obtained in the present work show differences in comparison with those reported by Arsene et al. (2011) for the same site. Arsene et al. (2011) have used a SFU system consisting of a $8.0 \mu\text{m}$ pore size, 47 mm diameter Isopore polycarbonate filter mounted in front of a $0.4 \mu\text{m}$ pore size, 47 mm diameter Isopore filter. However, the values determined in the present work for the fractions PM_{0.027–1.6}

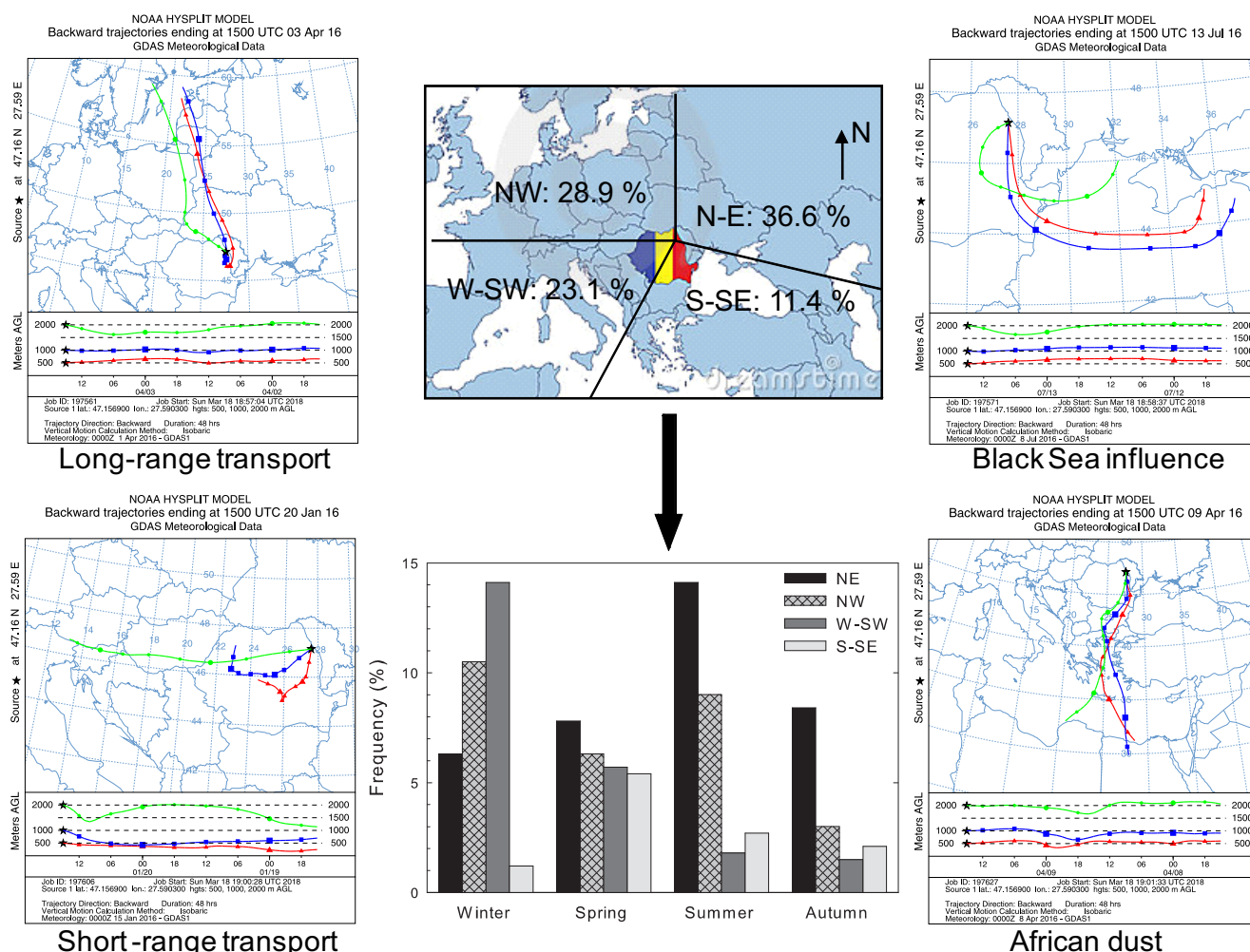


Figure 1. Sector contributions identified from classification of 2-day back trajectories of air masses ending at Iasi and representative backward trajectories of long- and short-range transport, Black Sea influence, and African dust (shown trajectories correspond to sampling events).

Table 1. Basic statistics for the PM_{10} and $\text{PM}_{2.5}$ fractions' mass concentrations determined over the investigated period ($n = 84$ sampling events) in Iasi, north-eastern Romania.

Statistical parameter	PM_{10} ($\mu\text{g m}^{-3}$)			$\text{PM}_{2.5}$ ($\mu\text{g m}^{-3}$)		
	Working day	Weekend	Annual	Working day	Weekend	Annual
Mean	19.25	18.60	18.95	17.31	16.47	16.92
Median	16.05	17.26	16.35	14.01	15.43	14.51
Geomean	16.90	16.91	16.90	14.86	14.83	14.84
SD	10.05	8.62	9.35	9.92	8.11	9.07
Min	5.56	7.11	5.56	5.08	6.30	5.08
Max	42.65	44.84	44.84	41.57	43.91	43.91

($15.6 \pm 8.7 \mu\text{g m}^{-3}$) and $\text{PM}_{0.381-1.6}$ ($9.1 \pm 5.6 \mu\text{g m}^{-3}$) are much closer to those reported by Arsene et al. (2011) for $\text{PM}_{1.5}$ ($10.5 \pm 11.2 \mu\text{g m}^{-3}$). The potential influence on the PM levels of particle size cut-off, differences in sampling site altitude, occurrence of precipitation events, long-range trans-

port phenomena, and air mass buoyancy is presented in detail in Sect. S1 in the Supplement.

Figure 2 shows monthly arithmetic mean mass concentrations ($\pm$ standard deviations) of PM_{10} and $\text{PM}_{2.5}$ in Iasi. The distribution of the $\text{PM}_{2.5} / \text{PM}_{10}$ ratio is presented in the same figure. The relative contribution of $\text{PM}_{2.5}$ toward PM_{10}

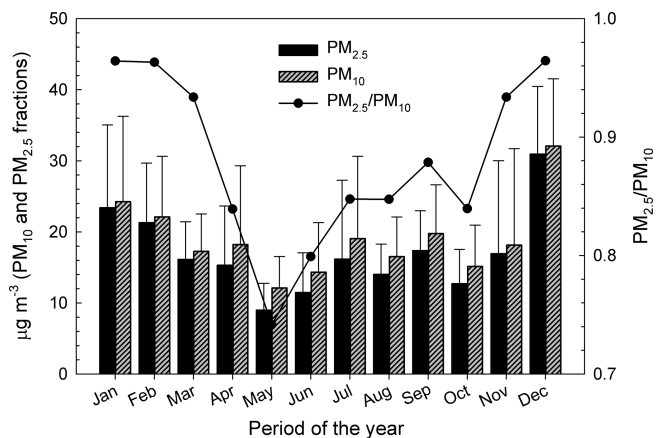
Table 2. Annual and/or seasonal arithmetic means of the PM₁₀ and PM_{2.5} fraction mass concentrations in Iasi, north-eastern Romania, and other various European sites (mean $\pm$ SD).

Site	Category	Sampling aa.g.l. ¹ (m)	Sampling period	PM _{2.5}	PM ₁₀	Reference
				($\mu\text{g m}^{-3}$)	($\mu\text{g m}^{-3}$)	
Iasi (Romania)	Urban	35	2016	16.9 $\pm$ 9.1 14.0 $\pm$ 7.1 (warm) 21.3 $\pm$ 13.0 (cold) 15.6 $\pm$ 8.7 ² 9.1 $\pm$ 5.5 ³	18.9 $\pm$ 9.3 16.8 $\pm$ 8.3 (warm) 22.6 $\pm$ 13.1 (cold) – –	This work
Iasi (Romania)	Urban	25	2007–2008	10.5 $\pm$ 11.2	38.3 $\pm$ 25.4	Arsene et al. (2011) ⁴
Paris (France)	Urban background	20	2009–2010	14.8 $\pm$ 9.6	–	Bressi et al. (2013)
Northern Europe (SE12)	EMEP and four regional background sites	–	2012–2013	–	3–8	Alastuey et al. (2016) ⁵
North-western Europe (IE321)					10–15 (S); $\sim$ 35 (W)	
Central western Europe (FR09)					10–15 (S); $\sim$ 25 (W)	
Central Europe (DE44)					20–25 (S); 25–30 (W)	
Eastern Europe (SK06, HU02)					10–15 (S); 15–25 (W)	
Eastern Europe (MD13)					$\sim$ 25 (S); 25–30 (W)	
South-western Europe (ES22)					20–25 (S); 5–10 (W)	
Central southern Europe (IT01)					25–35 (S); 20–25 (W)	
South-eastern Europe (GR02)					$\sim$ 25 (S); 35–40 (W)	
Thessaloniki (Greece)	Urban	7	2011–2012	37.7 $\pm$ 15.7	–	Tolis et al. (2015)
Thessaloniki (Greece)	Urban	3	2011–2012	21.5 $\pm$ 8.3 (warm) 33.9 $\pm$ 19.3 (cold)	–	Voutsas et al. (2014) ⁶
Finokalia (Greece)	Remote coastal	$\sim$ 5	2004–2006	18.2	30.8	Gerasopoulos et al. (2007)
Bologna (Italy)	Urban background	Courtyard	2005–2006	31.6 $\pm$ 21.0	44.5 $\pm$ 24.2	Tositti et al. (2014)
Venice (Italy)	Semi-rural coastal	–	2007–2008	–	22.5 $\pm$ 12.9	Masiol et al. (2012)
Prague (Czech)	Urban	12–25	2004–2005	–	33 $\pm$ 13	Schwarz et al. (2008)

¹ Sampling altitude above ground level. ² PM_{0.027–1.6} and ³ PM_{0.381–1.6} annual values given for discussion and comparison purposes with Arsene et al. (2011) study. ⁴ The total (coarse + fine) and the fine fractions reported (coarse fraction – particles of AED > 1.5 μm and fine fractions – particles of AED < 1.5 μm). ⁵ S: summer (8 June–12 July 2012); W: winter (11 January–8 February 2013). ⁶ Averaged value of warm and cold season data (error propagation method for uncertainty estimation); SE12: Aspöreten (Sweden); IE321: Mace Head (Ireland); FR09: Revin (France); DE44: Melpitz (Germany); SK06: Starina (Slovak Republic); HU02: K-Puszt (Hungary); MD13: Leova II (Moldavian Republic); ES22: Montsec (Spain); IT01: Montelibretti (Italy); GR02: Finokalia (Greece).

showed low variability amongst the months of the year, with ratios ranging from $\sim$ 0.75 to $\sim$ 1.0. For urban background and/or traffic sites, WHO (2006a) suggests PM_{2.5} / PM₁₀ ratios in the 0.42–0.82 range. Seasonal patterns, with maxima during the cold season and minima during the warm season, are observed for all of the PM_{2.5}, PM₁₀, and PM_{2.5} / PM₁₀ profiles and might be the combined result of seasonal emissions variations, local- and long-range air transport and dispersion, chemical processes, and deposition (Wang et al., 2016). The maxima of PM_{2.5} / PM₁₀ during the cold season are most probably caused by combustion processes as the burning of coal or petroleum for heating purposes enhances secondary aerosol generation (Li et al., 2012). The lower PM_{2.5} / PM₁₀ values during the warm season might be due to dust events and to more intense anthropogenic activities near the sampling site (e.g. excavation, construction, and building renewal) that would cause higher loading of coarse particles in the atmosphere. As suggested by Zhang et al. (2001), various land use categories (e.g. grass, crops, mixed farming, shrubs) corroborated with other particle-related characteristics (i.e. particle density, relevant meteorological variables) may enhance the dry deposition of sub-micron particles during the warm season and hence their fine / coarse ratio.

Another clear seasonal pattern was observed for the mass concentration size distribution (Fig. 3). Over the cold season, it had a clear monomodal feature with a maximum at 381 nm. In contrast, the warm season was characterized by the same

**Figure 2.** Patterns of the monthly arithmetic mean concentrations and standard deviations in the PM₁₀, PM_{2.5}, and PM_{2.5} / PM₁₀ variables at Iasi, north-eastern Romania.

dominant fine mode, but also by the occurrence of a super-micron mode between 1.60 and 2.39 μm . Again, changes in source contributions and meteorological conditions could account for the observed differences (details in Sect. S2).

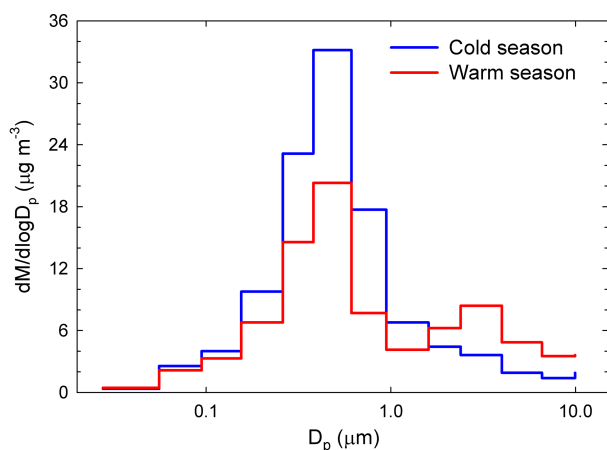


Figure 3. Size distribution histograms of aerosol particle mass concentration gravimetrically determined over both the cold and warm seasons.

3.2 Ionic balance, seasonality of water-soluble ions, and stoichiometry of $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3

3.2.1 Ionic balance and potential aerosol acidity

The completeness of the ionic balance was checked for the identified and quantified species (F^- , Cl^- , NO_2^- , NO_3^- , PO_4^{3-} , SO_4^{2-} , HCO_3^- , $\text{C}_2\text{H}_3\text{O}_2^-$, $\text{C}_2\text{O}_4^{2-}$, Na^+ , K^+ , NH_4^+ , Mg^{2+} , and Ca^{2+}) in both PM_{10} and $\text{PM}_{2.5}$. The slopes in the raw IC data related to $\sum_{\text{cations}}$ vs. $\sum_{\text{anions}}$ were < 1 in both $\text{PM}_{2.5}$ and PM_{10} (detailed statistics in Table S2), pointing to an important cation deficit that was higher in the cold compared to the warm season. However, for each sampling event, either cation or anion deficit was observed in various impactor stages. It should also be noted that, at the investigated site, a RH of $\sim 82\%$ was even observed during the cold season.

Predicting pH is suggested as the best method to analyse particle acidity (Guo et al., 2015). The ion balance method is usually based upon the principle of electroneutrality, and any deficit in measured cationic compared to anionic charge is assigned to the presence of unmeasured protons (H^+). The reverse occurs for unmeasured hydroxyl (OH^-) (Hennigan et al., 2015) or bicarbonate / carbonate ($\text{HCO}_3^- / \text{CO}_3^{2-}$) (Fountoukis and Nenes, 2007). In the present work, $\text{HCO}_3^- / \text{CO}_3^{2-}$ was assigned as the missing anion (details in Sect. S3 for $\text{HCO}_3^- / \text{CO}_3^{2-}$ estimation) while NH_4^+ was assigned as the main missing cation (details in Sect. S4 for the missing NH_4^+ assumptions). Detailed statistics of the $\sum_{\text{cations}}$ vs. $\sum_{\text{anions}}$ dependences, with $\text{HCO}_3^- / \text{CO}_3^{2-}$ and missing NH_4^+ included in the ionic balance, are presented in Table S3.

In an attempt to investigate whether or not the H^+ species would bring an important contribution within the ionic balance, the ISORROPIA-II thermodynamic equilibrium model proposed by Fountoukis and Nenes (2007) has been used

in the present work (more details about ISORROPIA-II can be found in Sect. S5). We investigated the relationship between ISORROPIA-II-predicted aerosol pH and the ionic balance for the present database, and the results are presented in Fig. 4a. The data remarkably follow a traditional titration curve, and they also clearly show that many of the analysed particles were approximately neutral (dashed lines at 0). A very important fraction of the investigated samples were in the acidic range ($\text{pH} < 3$ if samples were in cation deficit mode), while the remaining fraction were alkaline (pH slightly above 7 with anion deficit mode). However, as suggested by Hennigan et al. (2015), small uncertainties in the ionic balance (mainly due to measurement uncertainties and more likely in approximately neutral conditions) may lead to shifts that span over about 10 pH units. Moreover, the sensitivity to changes in the aerosol NH_4^+ concentration has been checked in predicted aerosol pH under forward-mode calculation. As shown in Fig. 4b, it seems that the predicted pH might decrease by 2 % when the ionic balance takes into account NH_4^+ (total) concentration (defined as the sum between that derived from raw IC data and the part estimated by using the rationale of Arsene et al., 2011). Details on the pH sensitivity tests for NH_4^+ concentrations are given in Sect. S6.

In Iasi, north-eastern Romania, an important fraction of the total analysed samples were alkaline while the remaining samples were acidic. A more detailed view of the samples' pH distribution can be obtained from the data presented in Fig. 4c, d. It seems that over the warm season about 55–56 % of the analysed samples were alkaline ($\text{pH} > 7$) and about 44–45 % were acidic ($\text{pH} < 7$), with the last fraction mainly distributed in the very strong acidity fraction ($\sim 35\%$ of the samples with pH in the 0–3 range, and about 2 % with an aerosol pH less than 0). Over the cold season only 47 % of the total analysed samples were alkaline ($\text{pH} > 7$) and 53 % were acidic ($\text{pH} < 7$). The acidity was also mainly distributed in the very strong acidity fraction ($\sim 43\%$ of the acidic samples with pH in the 0–3 range). Sulfuric, nitric, hydrochloric, and formic acids are the most likely contributors to aerosol pH in the 0–3 range. Note that strongly acidic aerosols affect air quality, health of aquatic and terrestrial ecosystems (especially through acid deposition), and atmospheric visibility and climate (Dockery et al., 1996; Gwynn et al., 2000; Hennigan et al., 2015). Possible impacts of strongly acidic aerosols are presented in more detail in Sect. S7. Moreover, aerosol acidity can impact the gas–particle partitioning of semi-volatile organic acids. While under strongly acidic conditions (pH 1–3) the pH contribution of organic acids is expected to be negligible as these conditions prevent their dissociation, the scenario may change completely at pH values of 3–7 (vide infra). Under these circumstances, formic acid with $\text{pK}_a = 3.75$ (Bacarella et al., 1955) might give a significant pH contribution to $\sim 7\%$ of the warm season samples and $\sim 10\%$ of the cold season ones.

Figure 5a, b present the size distribution of averaged aerosol mass and NO_3^- , SO_4^{2-} , and NH_4^+ concentrations

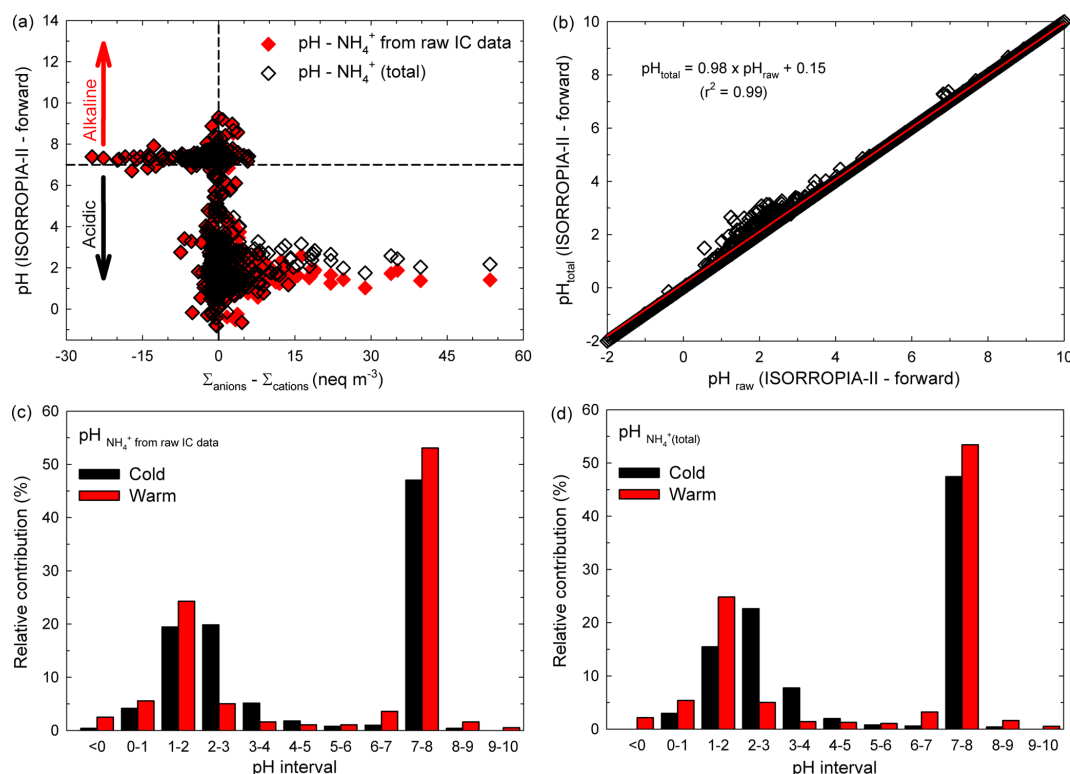


Figure 4. Distribution of the aerosol pH predicted by ISORROPIA-II (forward mode) vs. the ion balance (a), sensitivity of aerosol pH predicted with the model to small changes in the input aerosol NH_4^+ concentration (b), and bar chart distribution in aerosol pH over the warm and cold seasons for both NH_4^+ derived from raw IC data (c) and NH_4^+ (total) (d).

while Fig. 5c, d present ISORROPIA-II estimates for pH and H^+ mass concentration distributions, for both the cold (Fig. 5a, c) and the warm (Fig. 5b, d) seasons. Clear monomodal distribution seems to be specific for the cold season, while for the warm season the second mode (1.60–2.39 μm) mass concentration distribution seems to be predominated by NO_3^- . For the 155–612 nm size range, from details presented in Fig. 5c, d, it is quite clear that $\text{pH} \leq 2$. In the present work, the aerosol H^+ levels inferred indirectly from the ion balance as proposed by Hennigan et al. (2015) showed statistically significant correlation with the H^+ loadings predicted by ISORROPIA-II in the forward mode (Pearson coefficient of 0.72, $p < 0.001$). However, despite the good correlation, there were important discrepancies between the two estimated H^+ levels (intended as absolute values), with those from ISORROPIA-II being considerably lower than those from the ionic balance. The main issue with the model is that it may account only for partial dissociation, while the ionic balance may be affected by the uncertainty due to the propagation of measurement error. The latter may be particularly important in the presence of a slight anion deficit balance, which is interpreted as an H^+ -loaded system. Despite the uncertainties in the actual pH values, it is very likely that the 155–612 nm aerosol particles are strongly acidic and that H^+ is mainly contributed by completely dissociated strong

acids such as H_2SO_4 and HNO_3 . Contributions from free acidity (dissociated H^+) or total acidity (free H^+ and undissociated H^+ bound to weak acids) are expected to be more important in all other remaining fractions, and especially in the 27.6–94.5 nm particle size range (vide infra). Of course, a higher confidence in the estimate of particle pH would allow better prediction of the chemical behaviour of organics that, if dissociated at relatively low acidities, would significantly contribute to the ion balance.

In the literature it is suggested that the molar ratio approach may be a proxy for aerosol pH estimation (Hennigan et al., 2015). However, such a procedure is highly susceptible to bias in the results, either due to exclusion of minor ionic species or because it does not consider the effects of aerosol water or species activities on particle acidity. In this work, even when the aerosol was inferred to be highly acidic (samples with a molar ratio of $\text{NH}_4^+ / (\text{Cl}^- + \text{NO}_3^- + 2 \times \text{SO}_4^{2-}) < 0.75$), there was no statistically significant correlation between the cation / anion molar ratio and $[\text{H}^+]$ from either ion balance or model predictions. Therefore, the molar ratio does not appear to be a suitable tool to infer the acidity of atmospheric particles at the study site, but it could be a good parameter to distinguish between alkaline and acidic particles.

Data on gaseous NH_3 were not available, but the potential relationship was also investigated between $\text{NH}_3 / \text{NH}_4^+$ phase

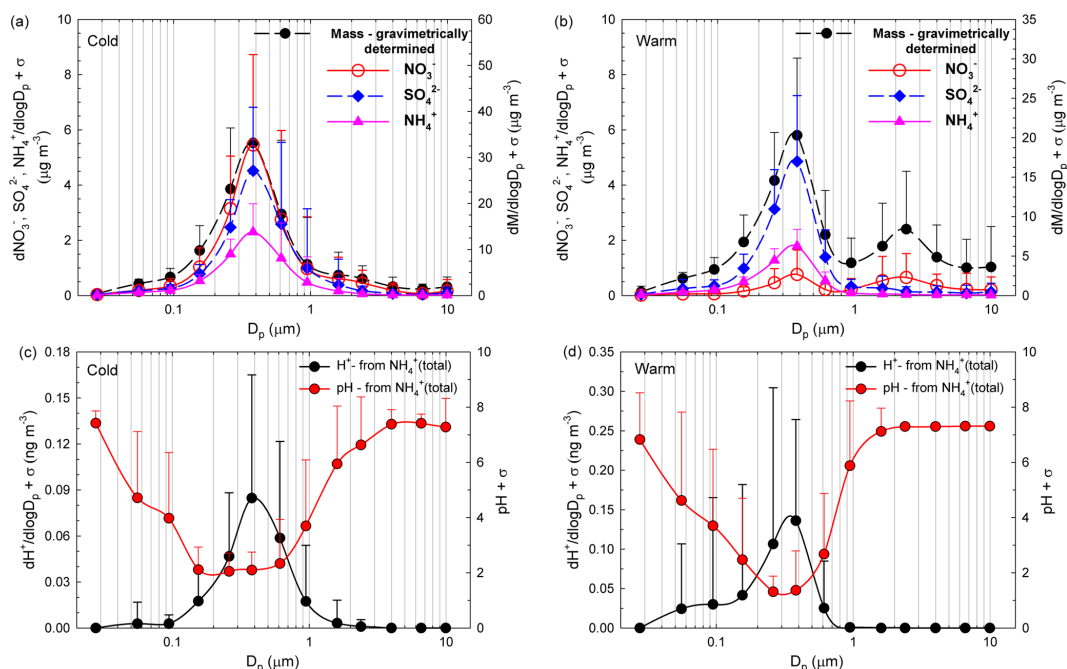


Figure 5. Size distribution of averaged aerosol mass and NO_3^- , SO_4^{2-} , and NH_4^+ concentrations over the cold (a) and warm (b) seasons accompanied by the size distribution of ISORROPIA-II-estimated pH and H^+ mass concentration over both the cold (c) and the warm (d) seasons.

partitioning (with NH_3 values predicted by ISORROPIA-II) and particle pH. The hypothesis of phase partitioning equilibrium is justified by the fact that the sampling time interval (36 h) was much longer than the equilibration time for submicron particles (seconds to minutes; Meng et al., 1995). As previously mentioned, in the present work the number of samples with a $\text{pH} < 0$ was significantly lower compared to those with a $\text{pH} > 0$. Moreover, ISORROPIA-II predicted that in the 94.5–612 nm size range there would be a significant NH_3 fraction in the gas phase.

The detailed $\text{NH}_3/\text{NH}_4^+$ partitioning as a function of RH is presented below, and considerations on the potential effects on the partitioning brought about by changes in the SO_4^{2-} and NO_3^- concentrations, and by temperature affecting both SO_4^{2-} and NO_3^- production, is given in Sect. S8. The potential role played by temperature on $\text{NH}_3/\text{NH}_4^+$ partition seems to be minimal, but one should also consider that highly acidic aerosols will affect a variety of processes and definitely the partitioning of HNO_3 to the gas phase, producing low nitrate aerosol levels. ISORROPIA-II runs predicted gas-phase NH_3 concentrations in Iasi as high as 0.52 ± 0.28 (0.46) (mean $\pm$ SD (median)) $\mu\text{g m}^{-3}$ at $\text{RH} < 40\%$, 0.61 ± 0.26 (0.49) $\mu\text{g m}^{-3}$ at $\text{RH} = 40\text{--}60\%$, and 0.96 ± 0.54 (0.92) $\mu\text{g m}^{-3}$ at $\text{RH} > 60\%$. These warm season values are smaller than those reported in a modelling study by Backes et al. (2016), who predicted NH_3 abundances as high as 1.6 to 2.4 $\mu\text{g m}^{-3}$ (data extracted from NH_3 concentration for the reference case, i.e. Fig. 3 in

Backes et al., 2016, for north-eastern Romania). In contrast, the 0.96 ± 0.54 (0.92) $\mu\text{g m}^{-3}$ value at $\text{RH} > 60\%$, which would be mainly found during the cold season, seems to be in reasonable agreement with the $\leq 0.8 \mu\text{g m}^{-3}$ value modelled by Backes et al. (2016) over winter. Moreover, from ISORROPIA-II runs performed at $\text{RH} < 40\%$, it was estimated that $(77.6 \pm 28.4)\%$ or $(79.3 \pm 26.2)\%$ (mean $\pm$ SD) of the NH_3 predicted by ISORROPIA-II could be present in the gaseous phase (with reference to both NH_4^+ derived from raw IC data and to the NH_4^+ (total) fraction). Similar but slightly decreasing values were predicted for gas-phase NH_3 as RH increased, namely $(76.5 \pm 30.9)\%$ or $(78.6 \pm 28.2)\%$ (raw IC and NH_4^+ (total), respectively) at $\text{RH} = 40\text{--}60\%$ and $(68.3 \pm 36.7)\%$ or $(74.5 \pm 29.7)\%$ at $\text{RH} > 60\%$.

In other studies, thermodynamic equilibrium calculations predicted that all of the NH_3 was mainly susceptible to partitioning to the particle phase at the equilibrium, and also that > 44 or 51% of the investigated samples presented an aerosol $\text{pH} < 0$ (Hennigan et al., 2015). However, it seems that at the investigated Romanian site the atmosphere could be rich enough in NH_3 so as to allow its occurrence in the gas phase while also promoting particle-phase partitioning. The seasonal trends in the NH_3 concentrations derived from ISORROPIA runs for Iasi are reported in Fig. S1 (Sect. S9). The same section reports considerations on possible interrelated emission factors governing the distribution in the NH_3 concentration levels in Iasi.

The ISORROPIA-II data referring to the 155–612 nm size range (regardless of RH) suggested that the aerosol ammonium fraction ($\text{NH}_4^+ / (\text{NH}_3 + \text{NH}_4^+)$) was over 0.20 irrespective of the calculation procedure (raw IC or NH_4^+ (total)). Clear ($\text{NH}_4^+ / (\text{NH}_3 + \text{NH}_4^+)$) maxima were observed at 381 nm (raw IC data: 0.71 at RH < 40 %, 0.63 at RH = 40–60 %, and 0.76 at RH > 60 %; NH_4^+ (total), defined as the sum between that derived from raw IC data and the part estimated by using the rationale of Arsene et al. (2011): 0.66 at RH < 40 %, 0.56 at RH = 40–60 %, 0.65 at RH > 60 %). As seen in Fig. 5c, d, the aerosol pH is very low in the 155–612 nm size range, while it often approaches 8 in the 27.6–94.5 and 612–9940 nm size ranges. Although not presented, in the 155–612 nm size range the aerosol ammonium fraction ($\text{NH}_4^+ / (\text{NH}_3 + \text{NH}_4^+)$) approaches 1, while in other two size ranges it is very low or close to 0, thereby suggesting the occurrence of gaseous NH_3 .

3.2.2 Seasonality of the major water-soluble ions

Table 3 shows monthly statistics for meteorological variables and mass concentrations of PM_{10} , $\text{PM}_{2.5}$, and major water-soluble ions in $\text{PM}_{2.5}$. Compared to the $\text{PM}_{2.5}$ fraction, in the PM_{10} fraction we observed increases in the mass concentrations of the following ions (notation for the % increase: min–max (mean)): 13–80 % (35 %) for Cl^- ; 1–107 % (32 %) for NO_3^- ; 1–170 % (17 %) for SO_4^{2-} ; 38–185 % (63 %) for HCO_3^- ; 14–171 % (41 %) for acetate; 4–136 % (22 %) for formate; 0–294 % (27 %) for oxalate; 16–48 % (32 %) for Na^+ ; 6–58 % (20 %) for K^+ ; 1–105 % (12 %) for NH_4^+ (total); 28–83 % (46 %) for Mg^{2+} , and 33–123 % (61 %) for Ca^{2+} . However, the PM_{10} and $\text{PM}_{2.5}$ mass concentration fractions show statistically significant correlation with a ratio of 1.1 (Pearson coefficient of 0.99, $p < 0.001$). Higher mass concentrations of specific water-soluble ions (Cl^- , NO_3^- , K^+ , NH_4^+ , and, to some extent, SO_4^{2-}) were observed during the cold compared to the warm season, probably because of the combination of increased strength of pollution sources and meteorological effects (inducing lower mixing heights or even temperature inversion), or due to different chemical or photochemical processing. Although lowering mixing heights over the cold season might increase pollutant concentration in the atmosphere, for some species additional phenomena should be taken into account in order to explain their distribution. For particulate SO_4^{2-} , high concentrations can be observed during winter and autumn but also in summer, and in the latter case they can be due to higher temperature and solar radiation that enhance photochemical reactions and the atmospheric oxidation potential because of the elevated occurrence of oxidant species such as ozone, hydroxyl, and nitrate radicals. These conditions favour the oxidation of SO_2 to particulate SO_4^{2-} . Also particulate $\text{C}_2\text{O}_4^{2-}$ was maximum in summer, possibly due to enhanced photochemical processing. Moreover, the maxima observed for SO_4^{2-} during the cold season might be due to the intensifica-

tion of coal burning for heating purposes. Higher abundances of particulate NO_3^- , SO_4^{2-} , NH_4^+ , and K^+ in winter compared to summer are reported for other European (Schwarz et al., 2012; Voutsas et al., 2014) and non-European sites as well (Sharma et al., 2007). Sharma et al. (2007) also suggest a potential role of CaCO_3 in controlling particulate NO_3^- abundance in Kanpur, India.

Seasonal variations for selected water-soluble ionic components in $\text{PM}_{2.5}$ are shown in Fig. 6a–h, while Fig. 6i shows the variation in the mixing layer depth at the investigated site. Fine-particulate Cl^- , NO_3^- , K^+ , NH_4^+ (total), and to some extent even SO_4^{2-} seem to exhibit distinct seasonal variations with maxima during the cold season and minima over the warm season, which might be related to changes in the mixing layer depth. The summer minima observed for both NO_3^- and NH_4^+ are not surprising because NH_4NO_3 is volatile and tends to dissociate to gas-phase NH_3 and HNO_3 at high temperatures. Coarse particulate $\text{C}_2\text{O}_4^{2-}$, Ca^{2+} , and Na^+ did not show much variation with respect to seasons. However, SO_4^{2-} and $\text{C}_2\text{O}_4^{2-}$ showed similar patterns (implying most probably common sources), and the Ca^{2+} trend suggests prevalent contribution from soil dust. Higher ion concentrations in winter than in summer are reported by Sharma et al. (2007) for Kanpur (India), while Ianniello et al. (2011) report opposite trends for Beijing (China).

Particulate Cl^- mass concentrations show a clear seasonal pattern, with higher values during the cold season than during the warm season (Fig. 6a). The chloride mass concentration in both $\text{PM}_{2.5}$ and PM_{10} had a statistically significant correlation with RH, temperature (only for PM_{10} fraction), particle loading, and mixing layer depth (detailed statistics in Table S4). The chloride maxima during the cold season might be the result of increased coal burning for heating purposes or of the use of NaCl in winter on icy and snowy roads. These observations are in agreement with other studies at eastern European sites (Arsene et al., 2011; Alastuey et al., 2016). However, the Cl^- mass concentration follows a pattern similar to that of K^+ (tracer of biomass burning), thereby suggesting that over the cold season wood burning might become an important heating source (Christian et al., 2010; Akagi et al., 2011).

Nitrate also shows cold season maxima and warm season minima (see Table 3 and Fig. 6b). The inset distribution presented within NO_3^- seasonal variation (Fig. 6b) suggests that, in summer, the coarse PM fraction can bring significant contributions to the aerosol atmospheric burden of nitrate. In our work, fine-particulate NO_3^- mass concentrations varied from 0.31 to $3.62 \mu\text{g m}^{-3}$ (Table 3) and these data are in very good agreement with those predicted for Europe in a modelling study performed by Backes et al. (2016). The data obtained in the present work over the cold season ($3.62 \pm 1.10 \mu\text{g m}^{-3}$ in January, February, and December as the coldest months of the year, and $2.65 \pm 0.38 \mu\text{g m}^{-3}$ over January, February, March, October, November, and Decem-

Table 3. Monthly averages of meteorological variables, PM₁₀ and PM_{2.5} fractions, and water-soluble ion mass concentrations ($\mu\text{g m}^{-3}$) in PM_{2.5} aerosol particles from Iasi, north-eastern Romania. Data are presented as mean $\pm$ SD (median). WS: wind speed; AT: atmospheric temperature.

Month	January	February	March	April	May	June	July	August	September	October	November	December
WS (m s^{-1})	6.41 $\pm$ 4.89 (5.60)	7.34 $\pm$ 4.74 (6.80)	6.49 $\pm$ 4.79 (5.70)	6.41 $\pm$ 5.05 (5.60)	5.45 $\pm$ 4.44 (4.90)	6.07 $\pm$ 4.36 (5.70)	6.28 $\pm$ 5.00 (5.40)	5.37 $\pm$ 4.72 (4.70)	4.67 $\pm$ 3.73 (4.40)	7.17 $\pm$ 4.57 (6.80)	5.72 $\pm$ 4.92 (4.90)	3.77 $\pm$ 3.76 (3.20)
AT ($^{\circ}\text{C}$)	-1.06 $\pm$ 4.71 (-1.42)	5.86 $\pm$ 1.98 (6.61)	6.50 $\pm$ 3.49 (5.35)	13.65 $\pm$ 4.15 (14.48)	15.65 $\pm$ 3.25 (15.70)	21.05 $\pm$ 4.75 (20.46)	23.27 $\pm$ 3.05 (24.58)	21.86 $\pm$ 2.13 (21.21)	18.20 $\pm$ 5.57 (20.30)	10.03 $\pm$ 5.11 (7.86)	7.41 $\pm$ 5.86 (6.23)	2.77 $\pm$ 2.41 (2.56)
RH (%)	71.27 $\pm$ 15.86 (69.57)	68.20 $\pm$ 6.97 (68.27)	46.30 $\pm$ 27.50 (37.88)	44.43 $\pm$ 13.19 (47.27)	50.32 $\pm$ 15.88 (47.47)	46.63 $\pm$ 16.69 (43.99)	32.95 $\pm$ 7.58 (33.97)	37.12 $\pm$ 13.14 (35.50)	31.56 $\pm$ 14.10 (28.71)	54.30 $\pm$ 10.58 (49.64)	69.92 $\pm$ 22.10 (72.41)	81.85 $\pm$ 13.22 (82.85)
RHD (%)	78.66 $\pm$ 3.61 (78.83)	73.54 $\pm$ 1.38 (73.01)	73.14 $\pm$ 2.34 (73.86)	68.59 $\pm$ 2.49 (68.02)	67.37 $\pm$ 1.92 (67.30)	64.38 $\pm$ 2.54 (64.62)	63.16 $\pm$ 1.62 (62.46)	63.88 $\pm$ 1.13 (64.21)	65.98 $\pm$ 3.16 (64.71)	70.87 $\pm$ 3.17 (72.17)	72.61 $\pm$ 3.81 (73.27)	75.71 $\pm$ 1.73 (75.85)
n^*	5	5	8	8	9	8	5	9	7	7	7	6
PM _{2.5}	23.39 $\pm$ 11.65 (26.19)	21.30 $\pm$ 8.37 (20.65)	16.10 $\pm$ 5.31 (14.98)	15.29 $\pm$ 8.34 (11.67)	8.98 $\pm$ 3.78 (6.88)	11.45 $\pm$ 5.61 (9.19)	16.15 $\pm$ 11.12 (14.19)	14.00 $\pm$ 4.27 (13.70)	17.36 $\pm$ 5.60 (17.77)	12.71 $\pm$ 4.81 (13.29)	16.93 $\pm$ 13.09 (12.04)	30.94 $\pm$ 9.51 (24.55)
PM ₁₀	24.25 $\pm$ 11.99 (27.86)	22.11 $\pm$ 8.50 (21.43)	17.25 $\pm$ 5.28 (16.08)	18.22 $\pm$ 11.08 (13.18)	12.11 $\pm$ 4.43 (14.25)	14.33 $\pm$ 6.98 (10.24)	19.05 $\pm$ 11.57 (16.00)	16.59 $\pm$ 5.52 (16.17)	19.76 $\pm$ 6.87 (20.20)	15.13 $\pm$ 5.81 (16.49)	18.13 $\pm$ 13.58 (13.49)	32.08 $\pm$ 9.44 (26.12)
Cl ⁻	0.32 $\pm$ 0.15 (0.34)	0.35 $\pm$ 0.10 (0.37)	0.14 $\pm$ 0.10 (0.10)	0.21 $\pm$ 0.16 (0.15)	0.14 $\pm$ 0.08 (0.13)	0.14 $\pm$ 0.08 (0.14)	0.20 $\pm$ 0.11 (0.18)	0.26 $\pm$ 0.15 (0.31)	0.19 $\pm$ 0.06 (0.18)	0.38 $\pm$ 0.24 (0.32)	0.24 $\pm$ 0.24 (0.19)	0.55 $\pm$ 0.19 (0.64)
NO ₃ ⁻	3.54 $\pm$ 1.93 (4.14)	3.21 $\pm$ 1.36 (3.14)	2.42 $\pm$ 1.09 (2.43)	1.36 $\pm$ 0.86 (1.22)	0.47 $\pm$ 0.28 (0.41)	0.31 $\pm$ 0.17 (0.26)	0.31 $\pm$ 0.11 (0.30)	0.41 $\pm$ 0.17 (0.33)	0.69 $\pm$ 0.41 (0.57)	1.25 $\pm$ 0.82 (1.13)	1.88 $\pm$ 1.27 (2.12)	3.62 $\pm$ 1.10 (4.07)
SO ₄ ²⁻	2.76 $\pm$ 1.66 (2.49)	2.58 $\pm$ 0.91 (2.50)	2.03 $\pm$ 0.71 (2.15)	1.96 $\pm$ 0.75 (1.82)	1.70 $\pm$ 0.81 (1.53)	2.39 $\pm$ 1.31 (2.32)	2.04 $\pm$ 0.98 (1.58)	2.22 $\pm$ 0.76 (2.04)	2.15 $\pm$ 0.84 (2.18)	1.96 $\pm$ 1.00 (2.05)	1.17 $\pm$ 0.27 (1.16)	2.16 $\pm$ 0.69 (2.33)
CH ₃ COO ⁻	0.51 $\pm$ 0.31 (0.45)	0.79 $\pm$ 0.50 (0.63)	0.30 $\pm$ 0.18 (0.29)	0.84 $\pm$ 0.36 (0.82)	0.64 $\pm$ 0.44 (0.49)	0.58 $\pm$ 0.34 (0.57)	0.82 $\pm$ 0.53 (0.48)	0.69 $\pm$ 0.71 (0.57)	0.70 $\pm$ 0.26 (0.60)	0.80 $\pm$ 0.28 (0.89)	0.46 $\pm$ 0.33 (0.43)	0.59 $\pm$ 0.12 (0.54)
HCOO ⁻	0.07 $\pm$ 0.05 (0.06)	0.06 $\pm$ 0.03 (0.06)	0.09 $\pm$ 0.09 (0.05)	0.15 $\pm$ 0.20 (0.07)	0.04 $\pm$ 0.02 (0.05)	0.05 $\pm$ 0.03 (0.04)	0.12 $\pm$ 0.11 (0.07)	0.08 $\pm$ 0.02 (0.08)	0.09 $\pm$ 0.02 (0.10)	0.09 $\pm$ 0.04 (0.08)	0.03 $\pm$ 0.02 (0.04)	0.07 $\pm$ 0.02 (0.07)
C ₂ O ₄ ²⁻	0.08 $\pm$ 0.06 (0.08)	0.08 $\pm$ 0.04 (0.08)	0.08 $\pm$ 0.04 (0.07)	0.08 $\pm$ 0.05 (0.08)	0.06 $\pm$ 0.04 (0.06)	0.09 $\pm$ 0.06 (0.08)	0.12 $\pm$ 0.09 (0.10)	0.14 $\pm$ 0.05 (0.15)	0.10 $\pm$ 0.08 (0.11)	0.06 $\pm$ 0.06 (0.04)	0.02 $\pm$ 0.02 (0.02)	0.10 $\pm$ 0.04 (0.09)
HCO ₃ ⁻	0.39 $\pm$ 0.12 (0.43)	0.48 $\pm$ 0.24 (0.39)	0.39 $\pm$ 0.20 (0.36)	0.65 $\pm$ 0.67 (0.39)	0.32 $\pm$ 0.17 (0.38)	0.64 $\pm$ 0.56 (0.45)	0.51 $\pm$ 0.24 (0.56)	2.23 $\pm$ 1.95 (1.73)	0.63 $\pm$ 0.18 (0.60)	0.25 $\pm$ 0.17 (0.24)	0.25 $\pm$ 0.34 (0.10)	0.35 $\pm$ 0.25 (0.42)
Na ⁺	0.14 $\pm$ 0.05 (0.13)	0.17 $\pm$ 0.08 (0.16)	0.12 $\pm$ 0.08 (0.10)	0.41 $\pm$ 0.31 (0.41)	0.19 $\pm$ 0.14 (0.10)	0.13 $\pm$ 0.05 (0.12)	0.13 $\pm$ 0.08 (0.12)	0.18 $\pm$ 0.09 (0.17)	0.14 $\pm$ 0.09 (0.11)	0.25 $\pm$ 0.16 (0.26)	0.12 $\pm$ 0.15 (0.08)	0.17 $\pm$ 0.09 (0.16)
NH ₄ ⁺ total	2.07 $\pm$ 1.08 (2.39)	1.94 $\pm$ 0.70 (1.97)	1.48 $\pm$ 0.58 (1.57)	0.93 $\pm$ 0.25 (0.96)	0.80 $\pm$ 0.29 (0.67)	0.90 $\pm$ 0.36 (0.86)	0.94 $\pm$ 0.40 (0.78)	0.84 $\pm$ 0.16 (0.82)	0.97 $\pm$ 0.23 (0.92)	1.10 $\pm$ 0.48 (1.22)	1.17 $\pm$ 0.57 (1.25)	2.09 $\pm$ 0.49 (2.37)
K ⁺	0.54 $\pm$ 0.25 (0.67)	0.48 $\pm$ 0.20 (0.44)	0.27 $\pm$ 0.12 (0.25)	0.30 $\pm$ 0.13 (0.27)	0.26 $\pm$ 0.16 (0.15)	0.28 $\pm$ 0.16 (0.24)	0.37 $\pm$ 0.21 (0.31)	0.31 $\pm$ 0.11 (0.32)	0.45 $\pm$ 0.14 (0.48)	0.41 $\pm$ 0.13 (0.41)	0.43 $\pm$ 0.32 (0.36)	0.71 $\pm$ 0.18 (0.65)
Mg ²⁺	0.03 $\pm$ 0.01 (0.03)	0.03 $\pm$ 0.02 (0.03)	0.02 $\pm$ 0.02 (0.01)	0.04 $\pm$ 0.04 (0.02)	0.01 $\pm$ 0.00 (0.01)	0.02 $\pm$ 0.02 (0.02)	0.02 $\pm$ 0.00 (0.01)	0.05 $\pm$ 0.04 (0.03)	0.02 $\pm$ 0.01 (0.02)	0.03 $\pm$ 0.02 (0.03)	0.01 $\pm$ 0.01 (0.01)	0.03 $\pm$ 0.01 (0.03)
Ca ²⁺	0.21 $\pm$ 0.07 (0.22)	0.27 $\pm$ 0.08 (0.26)	0.22 $\pm$ 0.07 (0.19)	0.28 $\pm$ 0.24 (0.21)	0.15 $\pm$ 0.05 (0.17)	0.30 $\pm$ 0.25 (0.22)	0.25 $\pm$ 0.12 (0.23)	0.92 $\pm$ 0.84 (0.65)	0.30 $\pm$ 0.08 (0.31)	0.15 $\pm$ 0.08 (0.15)	0.16 $\pm$ 0.17 (0.10)	0.20 $\pm$ 0.12 (0.20)
pH _{total}	4.20 $\pm$ 2.32 (2.88)	4.17 $\pm$ 2.53 (3.27)	3.94 $\pm$ 2.81 (2.51)	3.88 $\pm$ 2.97 (1.80)	3.95 $\pm$ 3.10 (2.82)	4.14 $\pm$ 2.92 (2.27)	4.58 $\pm$ 2.87 (4.26)	5.06 $\pm$ 2.73 (7.14)	4.24 $\pm$ 3.19 (3.55)	4.25 $\pm$ 2.75 (3.60)	3.86 $\pm$ 2.55 (2.54)	4.12 $\pm$ 2.16 (2.87)

Note: * n represents the number of aerosol sample events collected each month.

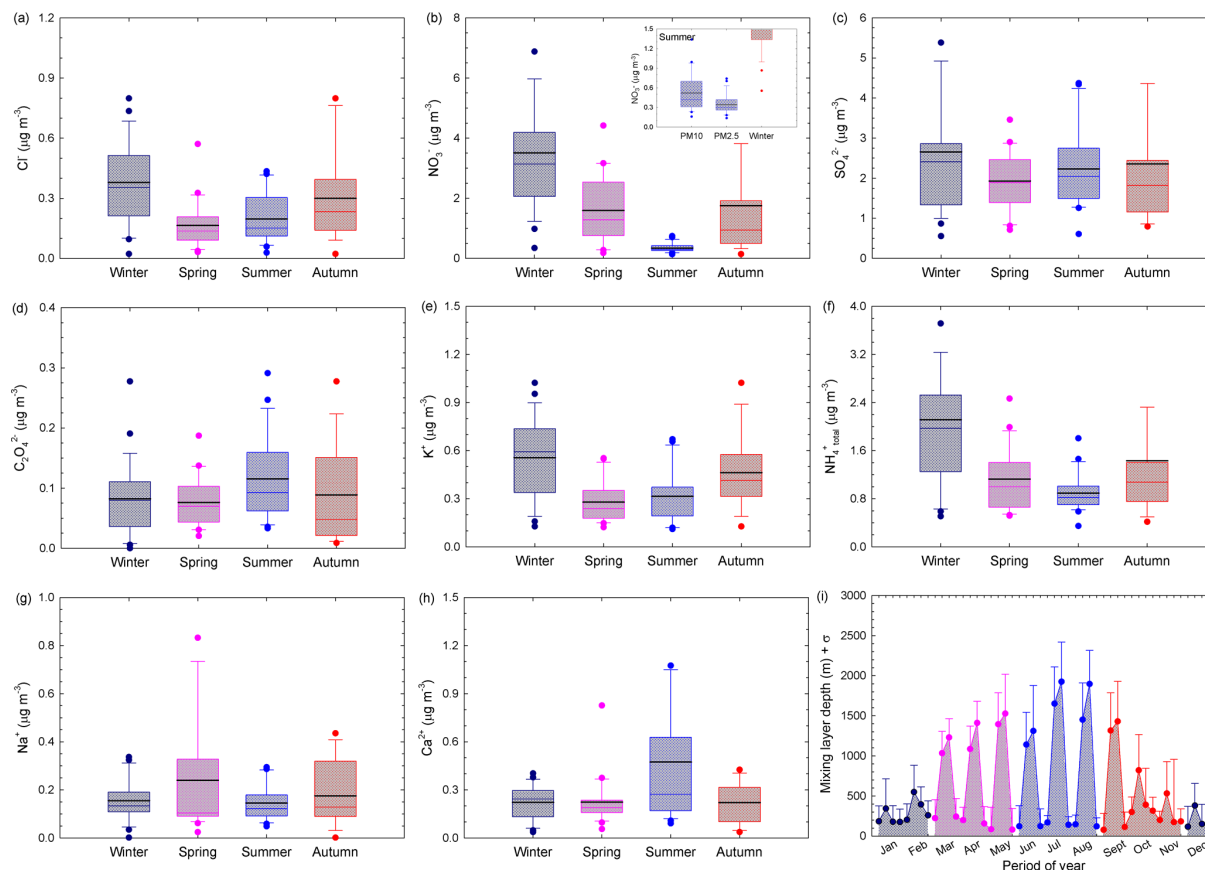


Figure 6. Seasonal variations for selected water-soluble ionic components in the PM_{2.5} fraction (a–h) and variation in the mixing layer depth at the investigated site (i). The inset distribution presented within NO₃⁻ seasonal variation reflects the contribution of the coarse fraction over the warm season. The horizontal black line represents the mean, the horizontal coloured line the median, the box the 25–75 % percentiles, the length of the whiskers plot 10 and 90 % of observed concentrations, and circles the outliers.

ber) seem to be in reasonably good agreement with those predicted for Europe by Backes et al. (2016). In contrast, the $0.59 \pm 0.30 \mu\text{g m}^{-3}$ NO₃⁻ concentration in PM_{2.5} measured over the warm season (including the April month characterized by predominant air mass buoyancy, and decreasing down to $0.44 \pm 0.12 \mu\text{g m}^{-3}$ if the April month is excluded) is lower than that predicted by Backes et al. (2016) (abundances as high as $0.8 \mu\text{g m}^{-3}$ over summer). Similar to the NH₄⁺ case, this might reflect the susceptibility of NO₃⁻ to be transferred to the gas phase over the warm season.

The NO₃⁻ mass concentrations in both PM_{2.5} and PM₁₀ had a statistically significant correlation with RH, temperature, mixing layer depth, and particle loading (Table 3, detailed statistics in Table S4). However, it has to be observed that highly acidic aerosols expected over all seasons have the potential to affect the partitioning of HNO₃ to the gas phase, producing low nitrate aerosol levels. Guo et al. (2015) also report low nitrate aerosol levels during summer. Moreover, NO₃⁻ heterogeneous formation (i.e. condensation or absorption of NO₂ in moist aerosols or N₂O₅ oxidation and HNO₃ condensation) generally relates to RH and the partic-

ulate loading (Wang et al., 2006; Ianniello et al., 2011). At the investigated site, this process might be of similar importance as the gas–particle conversion, which implies oxidation of precursor gases, such as NO_x, to nitrate via HNO₃ formation and involving photochemical processes. The high concentration of NO₃⁻ during the cold season might also be caused by higher NH₃ atmospheric levels from yet unaccounted sources, which could neutralize gas-phase H₂SO₄ and HNO₃ to produce ammonium salts (vide infra). Reactive nitrogen species are emitted to the atmosphere mainly in the forms of NO_x (from transport or power generation) and NH₃ (agriculture). In Iasi, the animal husbandry sector (open and closed barns, manure storage or spreading) is most likely an important NH₃ source. Moreover, the high RH observed in the cold season could offer suitable conditions for significant fractions of HNO₃ and NH₃ to be dissolved in humid particles, therefore enhancing particulate-phase NO₃⁻ and NH₄⁺ (Pathak et al., 2009, 2011; Ianniello et al., 2010; Sun et al., 2010). From measurements performed in October 2004 in Beijing, China, Kai et al. (2007) also concluded

that high RH, stable atmosphere, and high NH_3 levels can enhance transformation of NO_x into NO_3^- .

Particulate SO_4^{2-} maxima are observable during both cold and warm seasons. However, the particulate SO_4^{2-} mass concentrations showed statistically significant correlation with the measured meteorological parameters only at a 68 % confidence level (detailed statistics in Table S4). The data presented in Fig. 6c show that the seasonal trend of the monthly SO_4^{2-} mean mass concentrations is not as clear as that of NO_3^- and NH_4^+ , which might suggest the occurrence of regional SO_4^{2-} sources as well (Wang et al., 2016). Moreover, high RH (in Iasi, especially during cold months) may aid the conversion of SO_2 to SO_4^{2-} (Kadowaki, 1986), with a significant enhancement of SO_4^{2-} production rate in the aqueous phase (Sharma et al., 2007). However, the oxidation of SO_2 to sulfate may be induced not only by H_2O_2 in the aqueous phase, but also by gas-phase radical hydroxyl (Vione et al., 2003). This issue can explain the PM sulfate maxima during the warm season because of higher sunlight irradiance and temperature (Stelson and Seinfeld, 1982; Stockwell and Calvert, 1983; Kadowaki, 1986; Wang et al., 2005).

The data reported in Table 3 and Fig. 6f show that particulate NH_4^+ (total) has a clear seasonal pattern with maxima during the cold and minima over the warm season, in agreement with reports at other European (Schwarz et al., 2012; Bressi et al., 2013; Tositti et al., 2014; Voutsas et al., 2014) or non-European sites (Sharma et al., 2007; Wang et al., 2016). This behaviour is opposite to that reported by Ianniello et al. (2011). The cold season maxima and warm season minima we observed can be due to the effect of variations in the mixing layer depth, combined with gas-phase transfer of NH_4NO_3 to NH_3 and HNO_3 as temperature increases. In our dataset, NH_4^+ (total) varied from 0.8 to $2.09 \mu\text{g m}^{-3}$, a much lower range than that reported by Meng et al. (2011) for a more polluted site (Beijing, China, with concentrations varying between 4.73 and $9.04 \mu\text{g m}^{-3}$ among various seasons). However, the data we measured in the cold season ($2.03 \pm 0.30 \mu\text{g m}^{-3}$ over January, February, and December; $1.65 \pm 0.23 \mu\text{g m}^{-3}$ over January, February, March, October, November, and December) seem to be in reasonable agreement with those predicted for Europe by Backes et al. (2016). In contrast, the $0.90 \pm 0.09 \mu\text{g m}^{-3}$ NH_4^+ (total) measured concentration over the warm season is much lower than that predicted by Backes et al. (2016), and the discrepancy might actually reflect the limitation of the experimental measurement techniques concerning NH_4NO_3 volatility. Moreover, the NH_4^+ (total) mass concentration correlated significantly with RH and particle loading in both the $\text{PM}_{2.5}$ and PM_{10} fractions, and it anti-correlated significantly with temperature and mixing layer depth (detailed statistics in Table S4). The $\text{PM}_{2.5}$ fraction also showed statistically significant correlation with the mixing depth (Pearson coefficient higher than 0.67, $p = 0.016$). The seasonal variation in particulate NH_4^+ (total) especially

follows that of particulate NO_3^- and Cl^- , which would indicate that most probably NH_4^+ (total) largely originates from neutralization among NH_3 , HNO_3 , and HCl (Wang et al., 2006), or that the cited particulate species derive from similar gas-to-particle processes (Huang et al., 2010). Although in the present work gaseous NH_3 was not measured, ISORROPIA-II runs predicted that the atmosphere was often in a gaseous ammonia-rich state, independent of the RH values ($[\text{NH}_3] / ([\text{HNO}_3] + [\text{HCl}]) \gg 1$).

At the investigated site, $\text{C}_2\text{O}_4^{2-}$ and SO_4^{2-} show similar behaviour and the $\text{C}_2\text{O}_4^{2-}$ maxima during summer may suggest photochemical and/or biogenic contributions to its abundance (Laongsri and Harrison, 2013). The Na^+ ion, tracer of sea salt or NaCl aerosols, shows higher concentrations during spring when one has a predominant long-range transport of air masses from the S-SE sector, with contributions from natural sources and especially sea spray aerosols from the Black Sea. Particulate K^+ mass concentrations also show a clear seasonal pattern, with higher values during the cold season compared to the warm season (Fig. 6e). This phenomenon could be due to increased wood burning combined with a limited mixing layer depth. However, particulate K^+ mass concentrations also had some maxima when one expects intense agricultural biomass burning for field clearing (i.e. April, July, and September). The K^+ mass concentrations follow a pattern similar to Cl^- (Pearson coefficient of 0.79, $p = 0.002$) but a different one compared to SO_4^{2-} . Therefore, we suggest that intense wood burning may be a common source for K^+ and Cl^- species in the study area (Christian et al., 2010; Akagi et al., 2011).

High mass concentrations of Ca^{2+} and Mg^{2+} (with Mg^{2+} shown in Table 3 but not in Fig. 6), as soil or dust tracers, were observed especially during spring and summer. Over these seasons, lower precipitation frequency and high wind speed contribute to the observed behaviour. During the cold season, low wind speeds might prevent mineral dust resuspension and produce low values for these ions. However, Mg^{2+} and Ca^{2+} as mineral ions did not correlate with either $\text{PM}_{2.5}$ or PM_{10} , which suggests that inorganic particles would be mainly produced by NH_3 -triggered secondary processes.

3.2.3 Stoichiometry of $(\text{NH}_4)_2\text{SO}_4$, NH_4NO_3 , and NH_4Cl

Table 4 presents the correlation matrix (Pearson coefficients) for the major ionic species (Cl^- , NO_3^- , SO_4^{2-} , CH_3COO^- , HCOO^- , $\text{C}_2\text{O}_4^{2-}$, HCO_3^- , Na^+ , NH_4^+ (total), K^+ , Mg^{2+} , Ca^{2+}) in $\text{PM}_{2.5}$, for both the cold (Table 4a) and the warm seasons (Table 4b). Despite similar correlations in PM_{10} as well, $\text{PM}_{2.5}$ was selected for the correlation matrix analysis because of higher representativeness. For the cold season there are significant correlations (at the 99.9 % confidence level) among many chemical pairs, suggesting an important occurrence of $(\text{NH}_4)_2\text{SO}_4$, NH_4NO_3 , and $(\text{NH}_4)_2\text{C}_2\text{O}_4$. In

Table 4. Correlation matrix (Pearson coefficients) for major ionic species (Cl^- , NO_3^- , SO_4^{2-} , CH_3COO^- , HCOO^- , $\text{C}_2\text{O}_4^{2-}$, HCO_3^- , Na^+ , NH_4^+ (total), K^+ , Mg^{2+} , Ca^{2+}) in fine aerosol particles from Iasi, north-eastern Romania, for both cold (a) and warm (b) seasons. Bold font reflects statistical significant correlation at the 99.9 % confidence level.

(a)												
PM _{2.5} (cold)	Cl^-	NO_3^-	SO_4^{2-}	CH_3COO^-	HCOO^-	$\text{C}_2\text{O}_4^{2-}$	HCO_3^-	Na^+	NH_4^+ (total)	K^+	Mg^{2+}	Ca^{2+}
Cl^-	1.00	0.75	0.59	0.56	0.57	0.71	0.22	0.49	0.73	0.80	0.35	0.04
NO_3^-		1.00	0.91	0.37	0.74	0.87	0.13	0.04	0.98	0.85	0.00	0.06
SO_4^{2-}			1.00	0.43	0.72	0.87	0.05	0.02	0.96	0.72	0.07	0.11
CH_3COO^-				1.00	0.56	0.63	0.13	0.17	0.45	0.47	0.01	0.03
HCOO^-					1.00	0.85	0.04	0.01	0.76	0.65	0.12	0.09
$\text{C}_2\text{O}_4^{2-}$						1.00	0.23	0.08	0.89	0.76	0.16	0.17
HCO_3^-							1.00	0.56	0.17	0.05	0.76	0.98
Na^+								1.00	0.03	0.06	0.83	0.50
NH_4^+ (total)									1.00	0.82	0.08	0.12
K^+										1.00	0.08	0.09
Mg^{2+}											1.00	0.66
Ca^{2+}												1.00
(b)												
PM _{2.5} (warm)	Cl^-	NO_3^-	SO_4^{2-}	CH_3COO^-	HCOO^-	$\text{C}_2\text{O}_4^{2-}$	HCO_3^-	Na^+	NH_4^+ (total)	K^+	Mg^{2+}	Ca^{2+}
Cl^-	1.00	0.57	0.10	0.81	0.37	0.08	0.81	0.87	0.02	0.76	0.83	0.63
NO_3^-		1.00	0.34	0.02	0.14	0.17	0.63	0.71	0.23	0.08	0.86	0.39
SO_4^{2-}			1.00	0.01	0.66	0.76	0.17	0.05	0.97	0.43	0.03	0.01
CH_3COO^-				1.00	0.32	0.11	0.30	0.07	0.11	0.55	0.05	0.08
HCOO^-					1.00	0.58	0.32	0.01	0.66	0.59	0.02	0.01
$\text{C}_2\text{O}_4^{2-}$						1.00	0.58	0.04	0.71	0.46	0.01	0.15
HCO_3^-							1.00	0.45	0.06	0.13	0.12	0.99
Na^+								1.00	0.11	0.19	0.76	0.38
NH_4^+ (total)									1.00	0.49	0.12	0.12
K^+										1.00	0.02	0.03
Mg^{2+}											1.00	0.81
Ca^{2+}												1.00

the warm season, $(\text{NH}_4)_2\text{SO}_4$, $\text{Mg}(\text{NO}_3)_2$, and NaCl seem to be the most important. However, $\text{Ca}(\text{HCO}_3)_2$ might play a role during both cold and warm seasons. Over the cold season, K^+ shows statistically significant correlation with many inorganic (NO_3^- , Cl^- , and SO_4^{2-}) and organic (HCOO^- and $\text{C}_2\text{O}_4^{2-}$) anions, thereby suggesting that at least some of these species might have common biomass burning sources (Ianniello et al., 2011, and references therein). However, in the case of SO_4^{2-} and NO_3^- the most likely explanation would rather be the use of both coal and wood for burning, as well as the effect of the mixing layer depth.

In the ambient atmosphere, inorganic ammonium salts such as NH_4HSO_4 , $(\text{NH}_4)_2\text{SO}_4$, NH_4NO_3 , and NH_4Cl are known to be produced by gas-to-particle conversion processes. In the present work, from the ionic balance analysis the NH_4^+ ion was assigned as the most critical parameter in the chemical composition analysis of aerosol particles (with 274 analysed samples, i.e. about one-quarter of the total, being highly deficient in cations). Figure 7a, b present the relationship between the molar concentrations of fine-

particulate NH_4^+ (i.e. from raw IC data and also in the total form estimated under the assumptions from Arsene et al., 2011) and that of particulate SO_4^{2-} for both the cold (Fig. 7a) and warm (Fig. 7b) seasons. Correlations between particulate NH_4^+ and SO_4^{2-} are statistically significant in both cases (detailed statistics in Table S5).

During cold and warm seasons, the $[\text{NH}_4^+]/(2 \times [\text{SO}_4^{2-}])$ molar ratio was either ~ 1 (raw IC data) or $(\text{NH}_4^+(\text{total})$ values) equal to 1.76 (cold season) and 1.02 (warm season). These data suggest the existence of enough NH_3 for the complete neutralization of H_2SO_4 , and also a predominance of particulate $(\text{NH}_4)_2\text{SO}_4$ in agreement with the observations of Ianniello et al. (2011). Moreover, as shown in Table 4, for particulate SO_4^{2-} and NH_4^+ (total) the correlation was statistically significant (with Pearson coefficients of 0.96, $p < 0.001$ for the cold season and 0.97, $p < 0.001$ for the warm season), thereby suggesting that $(\text{NH}_4)_2\text{SO}_4$ could be formed from $\text{H}_2\text{SO}_4(\text{g})$ and $\text{NH}_3(\text{g})$ in either case. However, the 1.76 value for the $[\text{NH}_4^+](\text{total})/(2 \times [\text{SO}_4^{2-}])$ molar ratio during the cold season will indicate that there should still be

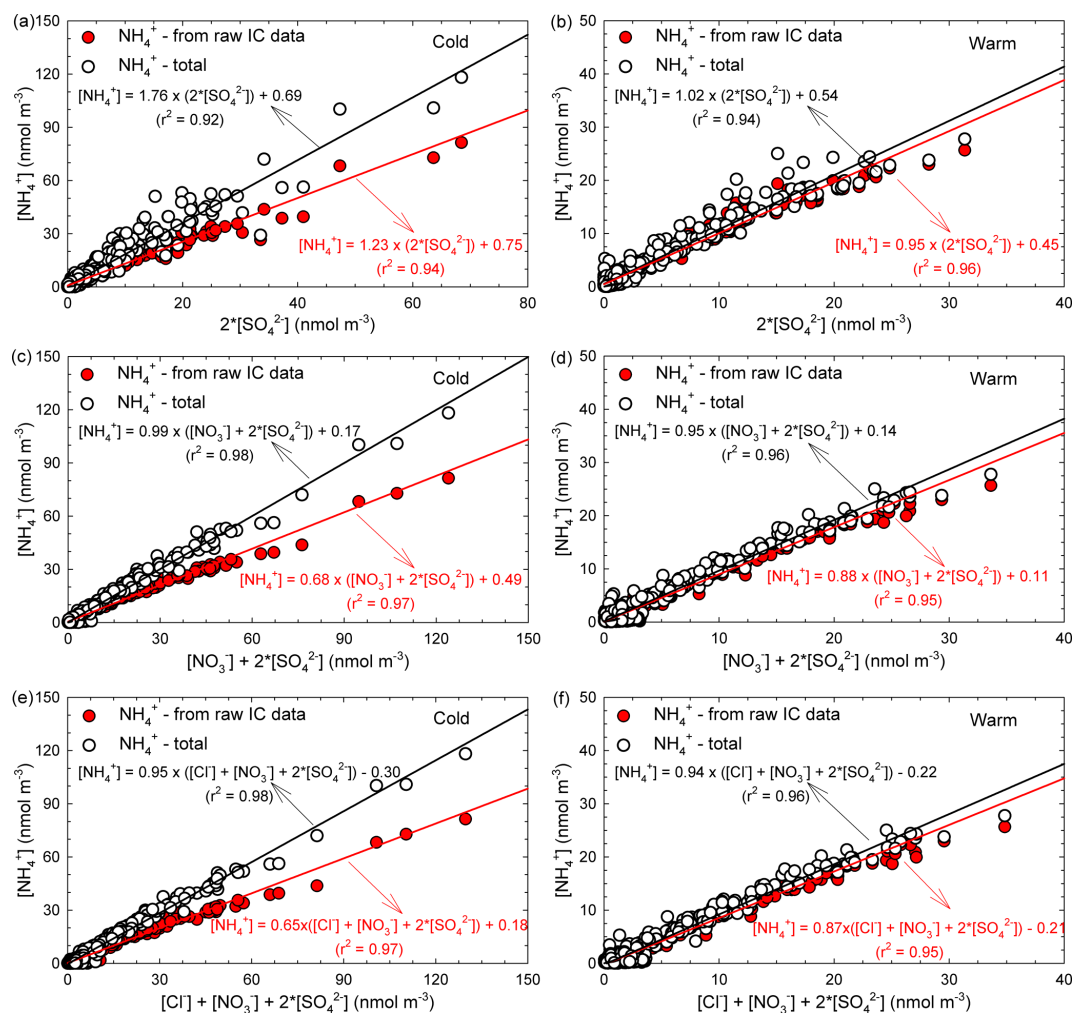


Figure 7. Regression analysis of the $[\text{NH}_4^+]$ vs. $(2 \times [\text{SO}_4^{2-}])$ (a, b), $[\text{NH}_4^+]$ vs. $([\text{NO}_3^-] + 2 \times [\text{SO}_4^{2-}])$ (c, d), and $[\text{NH}_4^+]$ vs. $([\text{Cl}^-] + [\text{NO}_3^-] + 2 \times [\text{SO}_4^{2-}])$ (e, f) dependences specific to PM_{2.5} particles.

particulate NH_4^+ potentially available for combination with other anions (or the existence of enough excess ammonia to neutralize acidic species such as HNO_3 and HCl). Zhao et al. (2016) report a $[\text{NH}_4^+] / (2 \times [\text{SO}_4^{2-}])$ molar ratio of 1.54 ($R^2 = 0.63$), indicating the complete neutralization of H_2SO_4 and a predominance of $(\text{NH}_4)_2\text{SO}_4$ in sulfate salts during the cold season.

Unfortunately, at present, no measured NH_3 values are available for the site of interest but it is still believed that, in the atmosphere of Iasi, sufficient gas-phase NH_3 occurs to promote both the homogeneous and heterogeneous formation of nitrate salts in the collected aerosol particles. The NH_4NO_3 formation routes might involve either the homogeneous reaction between gaseous HNO_3 and NH_3 (Ianniello et al., 2011) or the heterogeneous reaction between NH_3 and the products formed upon hydrolysis of N_2O_5 that could be present on the surface of the pre-existing moist aerosols under relatively high humidity (Pathak et al., 2011; Shon et al.,

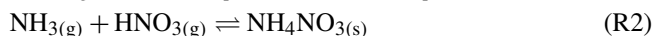
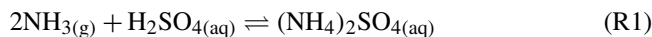
2013). Actually, gaseous NH_3 can influence both the inorganic ions and the aqueous-phase H^+ distribution in aerosols. The concentration of H^+ in aqueous aerosols is mainly determined by the balance of the acidic ionic components with the basic ones. During both cold and warm seasons, about half or slightly more than half of the collected samples were found to be alkaline with pH values fluctuating between 7 and 8. The remaining samples were acidic and with pH values ranging mainly from 1 to 3. Zhao et al. (2016) report that, on average, a +25 % perturbation in the NH_3 level could lead to a 0.14 unit pH increase, and a – 25 % perturbation could cause a 0.23 unit pH decrease. They concluded that sufficient NH_3 was frequently present in the wintertime atmosphere, and also that the fine collected particulates were almost fully neutralized by NH_3 .

Figure 7c, d, e, f show the relationships between the fine-particulate molar concentrations of (i) NH_4^+ and the sum of SO_4^{2-} and NO_3^- (Fig. 7c, d), and (ii) NH_4^+ and the sum of

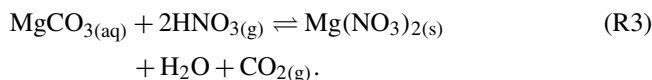
SO_4^{2-} , NO_3^- , and Cl^- (Fig. 7e, f), for both cold and warm seasons. From details given in Fig. 7c, d, e, f it can be easily observed that NH_4^+ , with both calculation methods (IC and total), was in deficit over the cold and warm seasons. Under these circumstances, it is believed that both particulate NO_3^- and Cl^- could be associated with other alkaline species or be part of acidic aerosol. Because the neutralizing capacity of NH_4^+ toward SO_4^{2-} , NO_3^- and Cl^- acidic species might give a rough indication on the potential particle acidity (Li et al., 2015); from Fig. 7c, d, e, f it is quite clear that at the study site, if NH_4^+ derived from raw IC data is used, the neutralization ratios in the investigated particles are less than unity. This suggests that the atmospheric particles are most likely acidic, and also that a more complex chemistry involving the HNO_3 and HCl species is ongoing. However, when NH_4^+ (total) is used, the neutralization ratio approaches 1 and suggests a possibly complete neutralization of particle acidity. From details in Fig. 7e, f it can be easily seen that actually the available NH_4^+ is not enough to compensate for other species. However, it should be noted that Cl^- does not significantly influence the neutralization of particle acidity. In a study performed by Zhao et al. (2016) the authors reported a $[\text{NH}_4^+]/(2 \times [\text{SO}_4^{2-}] + [\text{NO}_3^-])$ molar ratio of 0.86 ($R^2 = 0.78$) and an $[\text{NH}_4^+]/(2 \times [\text{SO}_4^{2-}] + [\text{NO}_3^-] + [\text{Cl}^-])$ molar ratio of 0.60 ($R^2 = 0.86$). Details presented in Fig. 7c, d clearly show that when NH_4^+ (total) is taken into account, a complete neutralization of H_2SO_4 and HNO_3 can be achieved during the cold season (Fig. 7c). In contrast, during the warm season (Fig. 7d) the molar ratio is slightly lower than 1 (i.e. 0.95). According to Seinfeld and Pandis (1998), during the warm season the high temperature and the low RH would be favourable for NH_4^+ to reach a minimum concentration because it is mainly transformed into NH_3 . Actually, temperature values above 25°C , such as those often encountered at the investigated site over the warm season, are known to prevent formation of particulate NH_4NO_3 (Adams et al., 1999). Under these circumstances, a considerable decrease in the $[\text{NH}_4^+](\text{total})/([\text{NO}_3^-] + 2 \times [\text{SO}_4^{2-}])$ molar ratio is to be expected during the warm season. The cold season temperature and RH at the investigated site were, respectively, $5.3 \pm 3.9^\circ\text{C}$ and $(65.3 \pm 12.8)\%$. Coherently, the data presented in Table 4 show that the $(\text{NO}_3^-, \text{NH}_4^+(\text{total}))$ pair has a significant correlation (Pearson coefficient of 0.98, $p < 0.001$) only during the cold season, while during the warm season (temperature and RH of, respectively, $18.9 \pm 3.8^\circ\text{C}$ and $40.5 \pm 7.7\%$) the correlation is very poor as increasing temperature and decreasing RH limit the production of the NH_4NO_3 aerosol (Matsumoto and Tanaka, 1996; Utsunomiya and Wakamatsu, 1996; Alastuey et al., 2004).

In the atmosphere, both H_2SO_4 and HNO_3 are known to compete for the reaction with NH_3 to form $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 . As presented in Sect. 3.2.2, at the investigated site a reduction in both in NO_3^- and SO_4^{2-} was observed over the

warm season and this may cause a further increase in gas-phase NH_3 . It is also interesting to observe that the reaction rate constant of $(\text{NH}_4)_2\text{SO}_4$ aerosol formation is similar to the rate constant of NH_4NO_3 formation (Harrison and Kitto, 1992; Pandolfi et al., 2012; Behera et al., 2013), and both are much higher than the rate constant between NH_3 and HCl (Behera and Sharma, 2012). This issue probably dictates the competition of any of the particulate SO_4^{2-} , NO_3^- , and Cl^- for the available NH_4^+ . Usually, when a sufficient amount of NH_3 is available for neutralization of H_2SO_4 and HNO_3 , fine-mode $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 will be formed via Reactions (R1) (Cziczo et al., 1997; Zhang et al., 2015) and (R2) (Fountoukis and Nenes, 2007; Zhang et al., 2015).



In contrast, in NH_3 -limited environments, coarse-mode NO_3^- is formed through Reaction (R3) involving Mg^{2+} (but not Ca^{2+}):



During the warm season, however, higher concentrations of $(\text{NH}_4)_2\text{SO}_4$ compared to NH_4NO_3 are expected because $(\text{NH}_4)_2\text{SO}_4$ is less volatile than NH_4NO_3 (Utsunomiya and Wakamatsu, 1996). Moreover, NH_4NO_3 will be formed only when excess NH_3 is available to react with HNO_3 . A modelling study by Backes et al. (2016) suggests that a reduction of the total $\text{PM}_{2.5}$ concentrations in north-western Europe, mainly due to reduced formation of NH_4NO_3 . However, the NH_3 concentration in the atmosphere over Europe seems to be high enough to saturate the reaction forming $(\text{NH}_4)_2\text{SO}_4$ particles, even in a scenario of reduced NH_3 levels, while on the contrary it is not high enough to saturate the reaction with HNO_3 to form NH_4NO_3 particles. A reduced formation of NH_4NO_3 particles may lead to an increase in gas-phase HNO_3 during winter. In our study, results from the ISORROPIA-II thermodynamic model foresee an increase in gas-phase HNO_3 at higher RH values during the cold season. Higher levels of gas-phase HNO_3 may increase its condensation onto existing particles such as sodium chloride (NaCl), and the replacement of Cl^- with NO_3^- may enhance the concentration of HCl in the atmosphere (similar processes are described in Arsene et al., 2011).

In the atmosphere, additional non-volatile species containing nitrate and chloride might also be present; thus we investigated the potential of fine-particulate NO_3^- and Cl^- to be chemically bound to Ca^{2+} , Mg^{2+} , K^+ , or Na^+ . The free NO_3^- and Cl^- concentrations, defined as the fractions of excess nitrate and chloride that are not bound to alkali or alkaline earth metals, were estimated for both

the cold and warm seasons according to the concept described in Ianniello et al. (2011). Zero or negative values of free NO_3^- and Cl^- imply that NH_4NO_3 and NH_4Cl are not present. Estimated free NO_3^- and Cl^- concentrations showed similar contributions in both the $\text{PM}_{2.5}$ and PM_{10} fractions. Over the cold season we calculated $(6.5 \pm 7.9) \times 10^{-3} \mu\text{mol m}^{-3}$ ($0.4 \pm 0.5 \mu\text{g m}^{-3}$) for NO_3^- , and negative values for free Cl^- ; over the warm season we had $(1.6 \pm 1.8) \times 10^{-3} \mu\text{mol m}^{-3}$ ($0.1 \pm 0.1 \mu\text{g m}^{-3}$) for NO_3^- , and again negative values for free Cl^- (data provided as mean $\pm$ SD). This result suggests the potential presence of NH_4NO_3 , especially during the cold season, but it excludes the occurrence of NH_4Cl . During the cold season, particulate NO_3^- did not show correlation with either Ca^{2+} or Mg^{2+} , but it showed significant correlation with K^+ ($r = 0.85$, $p < 0.001$; see Table 4), which indicates the possible formation of the non-volatile KNO_3 salt along with NH_4NO_3 . Over the warm season, fine-particulate NO_3^- did not show correlation with K^+ , but it showed significant correlation with Na^+ and Mg^{2+} (respectively, $r = 0.71$, $p < 0.001$ and $r = 0.86$, $p < 0.001$), indicating possible formation of non-volatile NaNO_3 and $\text{Mg}(\text{NO}_3)_2$ but not of $\text{Ca}(\text{NO}_3)_2$ salts. Moreover, in the warm season the fine-particulate NO_3^- also showed statistically significant correlation with HCO_3^- ($r = 0.63$, $p < 0.001$), which suggests a prevalence of particulate NO_3^- formation via the mineral route over the homogeneous reactions. The interaction between NO_3^- and Mg^{2+} could increase in importance during the warm season because, as NH_4^+ is not available, neutralization of HNO_3 could occur on coarse soil particles rich in Mg^{2+} (Matsumoto and Tanaka, 1996; Utsunomiya and Wakamatsu, 1996; Alastuey et al., 2004).

From the literature it is known that species such as $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 , at room temperature, uptake water (deliquesce) at RH values of, respectively, $(79 \pm 1) \%$ and 39% (Cziczo et al., 1997). The $(\text{NH}_4)_2\text{SO}_4$ aerosol particles might remain in metastable or supersaturated state liquid phase until a very low RH (crystallization point, RH around 33%) is reached (only thereafter a solid might be formed). In contrast, for NH_4HSO_4 it has been shown that the solid phase is difficult to form. In the present work, it is very likely that only over July (RH of 32.95%), August (RH of 37.12%), and September (RH of 31.56%) could the formation of solid $(\text{NH}_4)_2\text{SO}_4$ or NH_4HSO_4 occur.

Pure NH_4NO_3 deliquesces at 62% RH and there is suggestion that sometimes even at 8% RH the crystallization point is not reached (Dougle et al., 1998). According to suggestions from the literature, only during months when the ambient RH is lower than the RH at deliquescence (RHD), is the NH_4NO_3 considered as a solid (Seinfeld and Pandis, 1998). In the present work, from March to October the ambient RH was always lower than the RHD and NH_4NO_3 could thus be assumed to be in equilibrium with the solid phase. Within all the other months, from the estimated RHD values there is the possibility that NH_4NO_3 is in equilibrium with

the aqueous phase and deliquescent particles. However, in the investigated site, solid NH_4NO_3 could be formed almost over the entire year due to either the very complex chemical composition of the collected particles or the abundant contribution of organic carbon to the particle mass concentration (Dougle et al., 1998). Formation of NH_4NO_3 over the warm season has also been reported by Ianniello et al. (2011) but under different conditions. For deliquesced particles it is suggested that most of the fine-particulate NO_3^- occurs as an internal mixture with SO_4^{2-} , and also that HNO_3 can easily be absorbed into the droplets (Huang et al., 2010). In specific circumstances, the fine-particulate NO_3^- can be formed from HNO_3 and NH_3 through heterogeneous reactions on fully neutralized fine-particulate SO_4^{2-} , which is abundant in urban areas (Stockwell et al., 2000). In the present work, a statistically significant correlation between SO_4^{2-} and NO_3^- was observed during the cold season in the $\text{PM}_{2.5}$ fraction ($r = 0.91$, $p < 0.001$). High concentrations of NO_3^- were found in the presence of elevated RH levels (significant correlation: $r = 0.84$, $p < 0.001$), while SO_4^{2-} concentrations were high over the entire RH range (non-significant correlation: $r = 0.44$, $p = 0.177$). These results can be interpreted as nitrate being produced on pre-existing sulfate aerosols, which could provide sufficient surface area and water content for the heterogeneous reactions to occur. Although the formation of fine-particulate NO_3^- can take place via Reaction (R2), in particular circumstances and especially at high RH values, the amounts of the gaseous precursors such as NH_3 and HNO_3 may have relatively little influence on the fine-particulate NO_3^- formation (Markovic et al., 2011).

The salt NH_4Cl is known to be 2–3 times more volatile than NH_4NO_3 , as HCl is more volatile than HNO_3 . Moreover, at $\text{RH} < 75\text{--}85 \%$, particulate NH_4Cl is in equilibrium with the gaseous compounds (Ianniello et al., 2011, and references therein). Coherently, during the cold season particulate NH_4^+ (total) showed a statistically significant correlation with particulate Cl^- (Pearson coefficient of 0.73 , $p < 0.001$), but during the warm season the correlation was very poor. Finally, only during the cold season were significant correlations between fine-particulate Cl^- and SO_4^{2-} (Pearson coefficient of 0.59 , $p < 0.001$) and between fine-particulate Cl^- and RH (Pearson coefficient of 0.71 , $p = 0.010$) observed. Usually, high concentrations of fine-particulate Cl^- and SO_4^{2-} were found at high levels of RH ($35\text{--}83 \%$). Under these circumstances, the amount of gaseous precursors is believed to have relatively little influence on the formation of fine-particulate Cl^- . If formed, NH_4Cl is most probably generated from HCl and NH_3 through heterogeneous reactions on neutralized sulfate particles. However, in the present work, estimation of free Cl^- suggests that no Cl^- was available to be bound with other chemical species (i.e. NH_4^+) apart from alkali or alkaline earth metals, thereby excluding a significant occurrence of NH_4Cl (especially over the warm season).

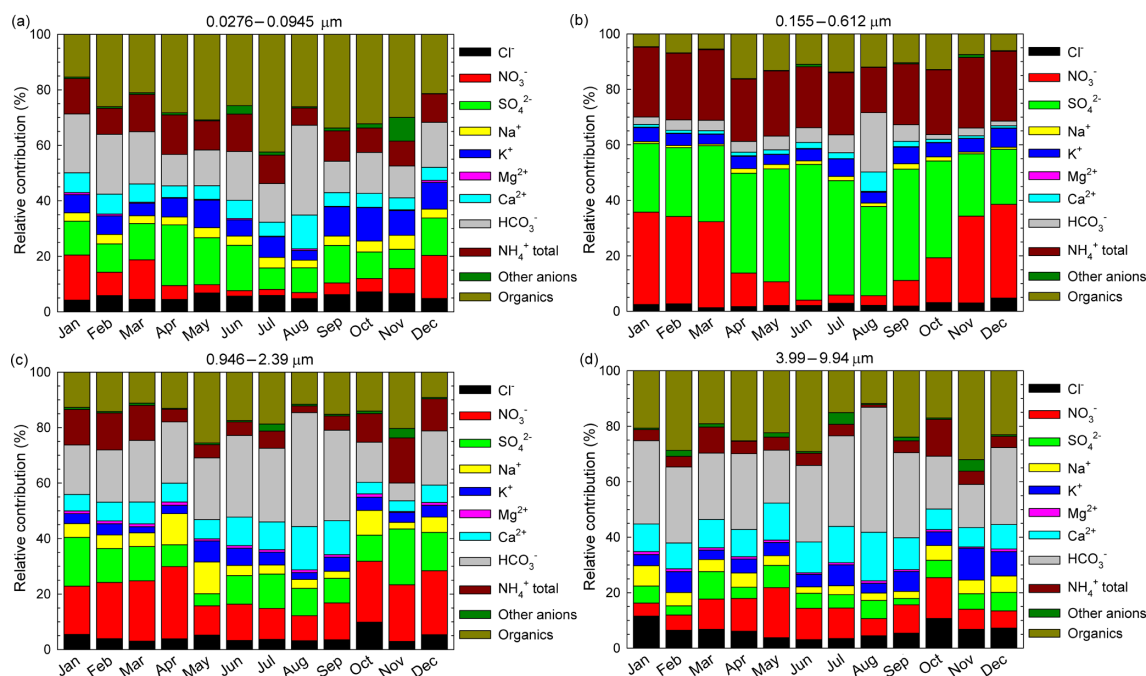


Figure 8. The relative contributions, as monthly averages, of identified and quantified water-soluble ions to total detected components in the 0.0276–0.0945 μm (a), 0.155–0.612 μm (b), 0.946–2.39 μm (c), and 3.99–9.94 μm (d) size range grouped fractions.

3.3 Relative ionic contribution in size-resolved aerosol particles from Iasi and potential influence of long-range transport phenomena on particle size distribution

Figure 8a, b, c, d present, as monthly averages, the relative contributions of identified and quantified water-soluble ions to total detected components in fractions grouped in four stages, i.e. 0.0276–0.0945 μm size range (Fig. 8a), 0.155–0.612 μm size range (Fig. 8b), 0.946–2.39 μm size range (Fig. 8c), and 3.99–9.94 μm size range (Fig. 8d). From details presented in Fig. 8a, for the 0.0276–0.0945 μm fraction there is an important contribution of formate, acetate, and oxalate that may actually indicate a possible important role of organic acids in secondary organic aerosol formation. Higher values of these components over the warm season may suggest an enhancement in the role of biogenic emission sources. Important contributions come from SO_4^{2-} , NH_4^+ (total), K^+ , and even (unexpectedly high) HCO_3^- . However, high particulate HCO_3^- is also evident for the 0.946–2.39 μm (Fig. 8c) and 3.99–9.94 μm size range (Fig. 8d) fractions. The 0.155–0.612 μm fraction (Fig. 8b) seems to be mainly constituted by SO_4^{2-} , NO_3^- , and NH_4^+ (total), with very small contributions from other ions.

The seasonal variation observed mainly for SO_4^{2-} and NO_3^- might suggest an enhancement of photo-oxidative processes over the warm season. The 0.946–2.39 μm (Fig. 8c) and 3.99–9.94 μm size range (Fig. 8d) fractions have a non-homogeneous chemical composition dominated mainly by

HCO_3^- , NO_3^- , and organics. Among all the analysed ions in the investigated period, in the PM_{10} fraction SO_4^{2-} was the most abundant with $(26.0 \pm 4.3)\%$, followed by NO_3^- $(26.0 \pm 10.7\%)$, NH_4^+ (total) $(15.0 \pm 3.4\%)$, organics including acetate, formate, and oxalate $(12.2 \pm 3.7\%)$, and HCO_3^- $(10 \pm 7.7\%)$. Similarly, in the $\text{PM}_{2.5}$ fraction SO_4^{2-} was again the most abundant $(28.9 \pm 5.6\%)$ followed by NO_3^- $(19.6 \pm 12.1\%)$, NH_4^+ (total) $(16.6 \pm 3.2\%)$, organics including acetate, formate, and oxalate $(11.4 \pm 4.0\%)$, and HCO_3^- $(8.0 \pm 6.8\%)$. In both the PM_{10} and $\text{PM}_{2.5}$ fractions, the largest contribution of SO_4^{2-} was observed in June 2016 with, respectively, $(34.6 \pm 10.9\%)$ and $(40.8 \pm 11.0\%)$. During the cold season, particulate SO_4^{2-} and NO_3^- contributions were, respectively, $(23.6 \pm 2.3\%)$ and $(28.6 \pm 4.9\%)$ for PM_{10} and $(25.5 \pm 2.9\%)$ and $(30.1 \pm 5.8\%)$ for $\text{PM}_{2.5}$. During the warm season, the SO_4^{2-} and NO_3^- contributions were, respectively, $(28.5 \pm 4.7\%)$ and $(10.1 \pm 4.8\%)$ for PM_{10} and $(32.4 \pm 5.6\%)$ and $(9.2 \pm 5.4\%)$ for $\text{PM}_{2.5}$. Wonaschutz et al. (2015) report NO_3^- contributions of 31.3 % during winter and 6.9 % during summer for Vienna (Austria).

Particulate Ca^{2+} and HCO_3^- , as dust tracer ions, contributed significantly, especially over the warm season $(43.8 \pm 11.2\%$ in PM_{10} and $37.8 \pm 12.3\%$ in $\text{PM}_{2.5}$ in August 2016), suggesting that Ca^{2+} and HCO_3^- mostly originate from soil dust resuspension during the dry season. In 2016, spring was the season with predominant air masses undertaking long-range transport from the S-SE sector (see Fig. 1), thereby suggesting the presence of sea spray aerosols from the Black Sea or other marine areas. The highest contribu-

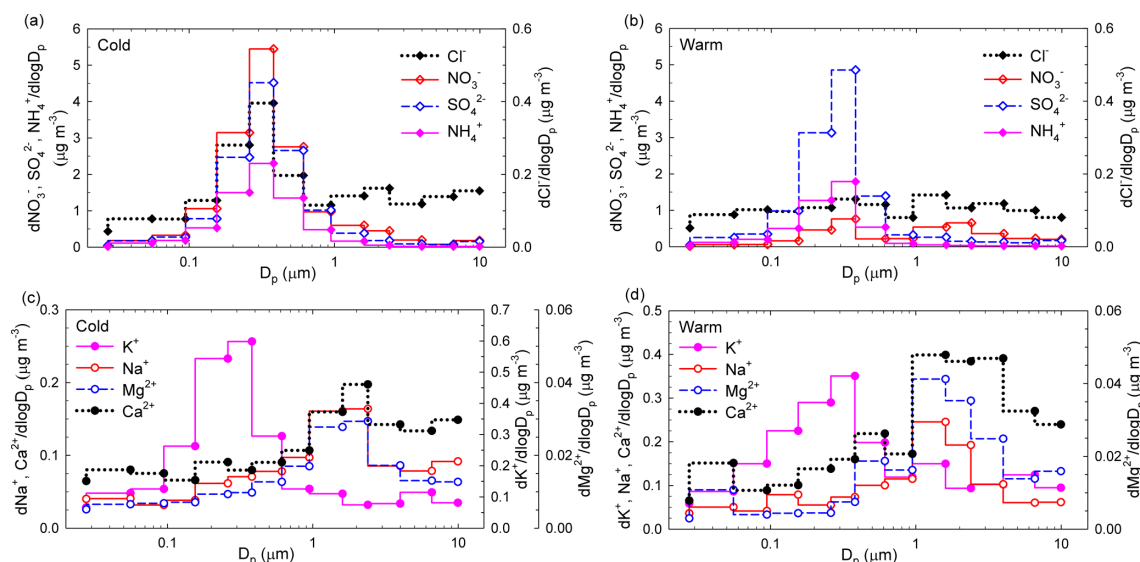


Figure 9. Size distributions of seasonal averaged mass concentrations for Cl^- , NO_3^- , SO_4^{2-} , and NH_4^+ (a, b) and K^+ , Na^+ , Mg^{2+} , and Ca^{2+} (c, d) ions in atmospheric aerosols from Iasi, during both the cold season and the warm season, respectively.

tions from sea spray aerosol tracers (i.e. Na^+ and Mg^{2+} ; Ma-siol et al., 2012) were actually recorded in April (5.8 % for Na^+ and 0.7 % for Mg^{2+}). Although the most abundant ions are SO_4^{2-} , NO_3^- , and NH_4^+ (total), organics (including acetate, formate, and oxalate) might also bring significant contributions ((17.3 ± 4.4) % in PM_{10} and 18.2 ± 5.1 % in $\text{PM}_{2.5}$ in July 2016, much higher than that reported by Arsene et al., 2011, for Iasi). The difference might reflect either an inversion of the photochemistry taking place at the investigated location, or differences in the sampling efficiency between the two studies.

Figure 9a, b, c, d show the size distributions of seasonal averaged mass concentrations for Cl^- , NO_3^- , SO_4^{2-} , and NH_4^+ (Fig. 9a, b) and K^+ , Na^+ , Mg^{2+} , and Ca^{2+} (Fig. 9c, d). While during the cold season NO_3^- , SO_4^{2-} , NH_4^+ , and K^+ reside mainly in the fine mode with maxima at ~381 nm, all the other ions (i.e. Cl^- , Na^+ , Mg^{2+} , Ca^{2+}) have major contributions in the super-micron mode (maxima between 1.6 and 2.39 μm). Over the cold season, clear evidence was obtained of the occurrence of chloride in a bimodal distribution. During the warm season only SO_4^{2-} and K^+ presented clear maxima at 381 nm, while all the other identified or quantified species had more important contributions in the super-micron mode. For SO_4^{2-} , a larger modal diameter in the cold season compared to the warm season is most likely due to hygroscopic growth under high RH and/or to increased secondary aerosol production (lower temperatures facilitate condensation). Secondary aerosol mass from aqueous-phase reactions may also play a role (Wonaschutz et al., 2015). The maxima observed in the coarse mode could also be explained considering that heterogeneous chemistry on dust particles

might act as a source for some particulate species (Wang et al., 2012).

While particulate NO_3^- over the cold season presented monomodal distributions in the sub-micron size range (maxima at 381 nm), over the warm season a second mode was observed with maxima in the 1.60–2.39 μm size range. Such a size distribution suggests that NO_3^- during the warm season is produced by adsorption of HNO_3 on sea salt and soil particles (Park et al., 2004). According to Karydis et al. (2016), particulate NO_3^- is not only associated with NH_4^+ in the fine mode. Light metal ions such as Ca^{2+} , Mg^{2+} , Na^+ , and K^+ , which mainly occur in the coarse mode, can be associated with NO_3^- and affect its partitioning into the aerosol phase. Dust effects on the distribution of particulate species might include a decrease in fine-mode NH_4^+ and a shift of particulate NO_3^- from the fine to the coarse mode (Wang et al., 2012). In addition, the presence of significant levels of NO_3^- , Cl^- , Mg^{2+} , Ca^{2+} , and Na^+ in the coarse fraction might suggest that NO_3^- possibly originates upon reaction of HNO_3 with MgCO_3 , CaCO_3 , or NaCl . Similar patterns were identified in Vienna, Austria (Wonaschutz et al., 2015), and in Prague, Czech Republic (Schwarz et al., 2012). Significant amounts of particulate NO_3^- formed upon reaction of HNO_3 with CaCO_3 on soil-derived particles have also been observed and reported (Yao et al., 2003; Sharma et al., 2007). Moreover, sea salt aerosols may also undergo chemical transformation of NaCl into NaNO_3 during transport (Schwarz et al., 2012).

The size distributions of particulate K^+ reflect the occurrence of one dominant fine mode (with maxima at 381 nm) during both the cold and the warm seasons and of a second, less important mode during the warm season (with maxima

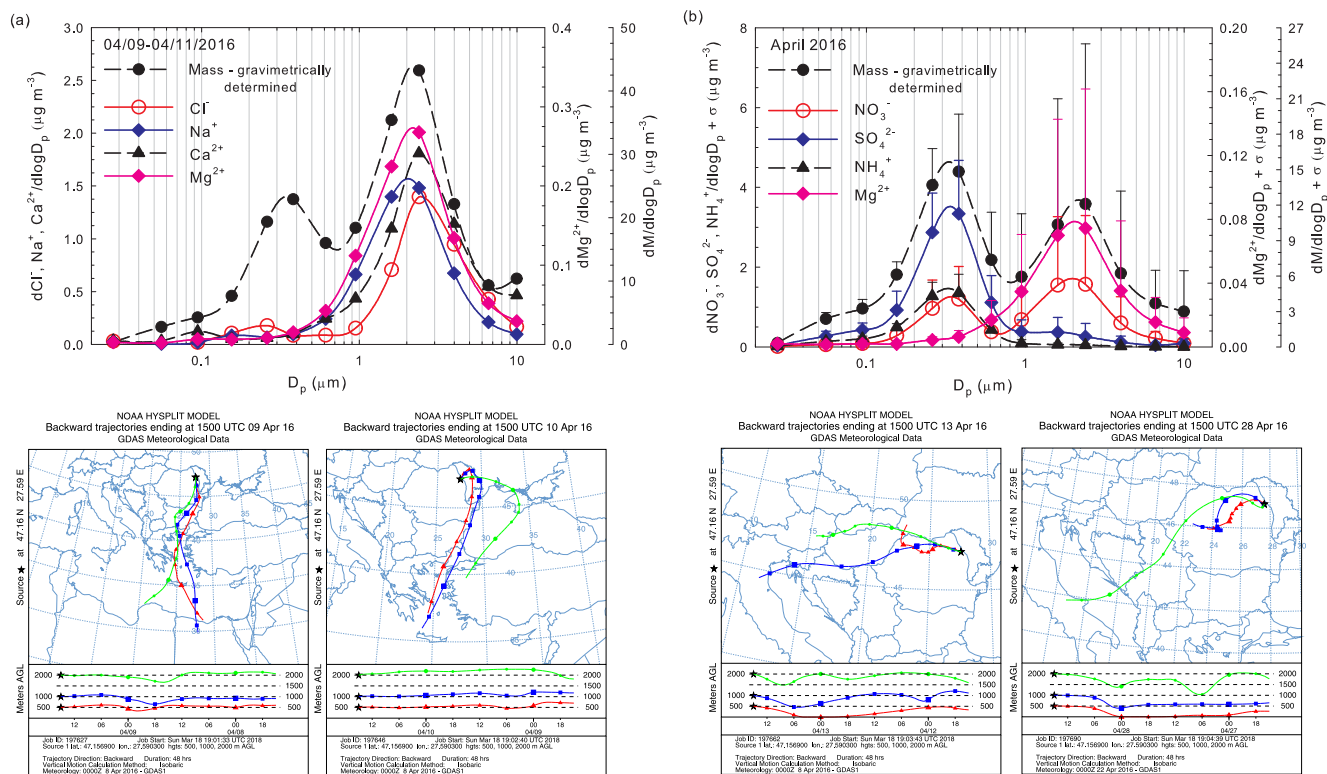


Figure 10. Evidence of long-range transport contributions from Saharan dust within the size distribution of particulate Na^+ , Ca^{2+} , Mg^{2+} , Cl^- ions, and aerosol mass (a) and of air mass buoyancy phenomena within the size distribution of particulate NH_4^+ , NO_3^- , SO_4^{2-} , Mg^{2+} ions, and aerosol mass (b).

in the 0.946–1.6 μm range). Such behaviour most likely reflects contributions from biomass burning over the entire year (Schmidl et al., 2008; Pachon et al., 2013). For both Ca^{2+} and Mg^{2+} ions, clear monomodal mass distributions with maxima in the 1.6 to 2.39 μm size range were observed over the investigated period. Over the warm season, Ca^{2+} accounts for $(7.0 \pm 2.9)\%$ of the PM_{10} fraction and for $(5.5 \pm 2.9)\%$ of the $\text{PM}_{2.5}$ fraction, while over the cold season it accounts for only $(3.0 \pm 0.6)\%$ of the PM_{10} and $(2.2 \pm 0.5)\%$ of the $\text{PM}_{2.5}$ fraction. These observations indicate that the impact from soil dust resuspension could be more important during the warm (dry) season. Mineral dust may also explain the higher coarse fraction of Mg^{2+} (mineral source being MgCO_3).

Clear evidence was obtained in this work that air mass origin highly influences the aerosol chemical composition at the investigated site. Annual averaged sector contributions, in terms of PM long-range transport, are shown in Fig. S2 while the seasonal contributions of PM and particulate inorganic and organic ions associated with different air mass origins are reported as radar charts in Fig. S3 (within Sect. S10). Figure S4 (within Sect. S10) highlights the percentage distributions for the identified and quantified ions and the gaseous concentrations of NH_3 , HNO_3 , and HCl for selected investigated events, predicted by ISORROPIA-II. Wonschutz et

al. (2015) suggested that in Vienna, Austria, air mass origin is the most important factor for bulk PM concentrations, chemical composition of the coarse fraction ($> 1.5 \mu\text{m}$), and mass size distribution, while it is less important for the chemical composition of the fine fraction ($< 1.5 \mu\text{m}$). Although Iasi is located far from the Mediterranean or Black Sea, over the warm season the sea salt chloride contribution to the aerosol budget in the area is not entirely excluded (Arsene et al., 2011). Moreover, dust particles originating from the Sahara are acknowledged as travelling across the tropical Atlantic Ocean ($10\text{--}90 \mu\text{g m}^{-3}$) and across the Mediterranean, affecting air quality in southern Europe ($10\text{--}60 \mu\text{g m}^{-3}$) (Karydis et al., 2016). In the present work, particulate Na^+ and Cl^- ions as tracers of sea salt aerosols (Tositti et al., 2014) were mainly observed in conditions predominated by contributions from air masses arriving in Iasi from the S-SE direction. However, one of the most interesting collected events was that of 9–11 April 2016. For this event, the PM_{10} fraction mass concentration was as high as $43.9 \mu\text{g m}^{-3}$, a value which is about 2 times higher than the average of the total events. These conditions were highly influenced by air masses originating from both the Saharan desert and the Mediterranean Sea. As shown in Fig. 10a, the size distributions of particulate Na^+ , Ca^{2+} , Mg^{2+} , Cl^- ions, and their mass concentrations present a highly dominating mode with

maxima at 2.39 μm . For this event, the (Ca^{2+} , Mg^{2+}) and (Na^+ , Cl^-) pairs showed statistically significant correlations (respectively, $r = 0.94$, $p < 0.001$ and $r = 0.85$, $p < 0.001$), suggesting common contributions from mineral Saharan dust (Ca^{2+} , Mg^{2+}) and from sea salt marine aerosols (Na^+ , Cl^-). Moreover, Fig. 10a clearly shows that Na^+ , Ca^{2+} , Mg^{2+} , and Cl^- make a very significant contribution to the total aerosol mass in the super-micron mode, with the maxima at 2.39 μm .

In April 2016, an interesting behaviour was also observed for the averaged mass size distributions of particulate NH_4^+ , NO_3^- , SO_4^{2-} , and Mg^{2+} (Fig. 10b). This month is highly affected by the atmospheric air mass buoyancy phenomenon, as shown by trajectory analysis for selected events and, while particulate NH_4^+ and SO_4^{2-} mainly resided in the fine mode with clear maxima at 381 nm, NO_3^- and Mg^{2+} also presented a predominant mode in the 1.6–2.39 μm fraction. Such distributions, corroborated with meteorological conditions, would actually suggest a possible heterogeneous formation route for SO_4^{2-} (Wang et al., 2012). In contrast, the adsorption of HNO_3 on mineral dust and sea salt particles (Karydis et al., 2016) would become more important for NO_3^- .

4 Conclusions

The atmospheric concentrations of particulate species including acetate, formate, fluoride, chloride, nitrite, nitrate, phosphate, sulfate, oxalate, sodium, potassium, ammonium, magnesium, and calcium were measured over 2016 at an urban site in Iasi, north-eastern Romania. The measurements were carried out using a cascade Dekati low-pressure impactor (DLPI), performing aerosol size classification in 13 specific fractions evenly distributed over the 0.0276–9.94 μm size range.

The entire data set was analysed to investigate the seasonal variations in fine-particulate species and the meteorological effects and to examine the contributions of local and regional sources. ISORROPIA-II thermodynamic model runs were used to estimate the pH values of the collected atmospheric particles, as on the present database it was the best method to analyse particle acidity.

Within the aerosol mass concentration, the identified ions' mass brings contributions as high as 40.6 % with the rest being unaccounted for yet. Fine-particulate Cl^- , NO_3^- , NH_4^+ , and K^+ exhibited clear seasonal variations with minima during the warm season, mainly due to cold season enhancement in the emission sources, changes in the mixing layer depth, and specific meteorological conditions (e.g. higher RH values prevailing in Iasi during the cold season). Fine-particulate SO_4^{2-} did not show much variation with respect to seasons. The measured concentrations of NH_4^+ and NO_3^- in fine-mode ($\text{PM}_{2.5}$) aerosols were in reasonably good agreement with modelled values for the cold season but not for the warm season. This observation reflects the susceptibility of NH_4NO_3 aerosols to be lost due to volatility.

Clear evidences were obtained that NH_4^+ in $\text{PM}_{2.5}$ was primarily associated with SO_4^{2-} and NO_3^- . However, indirect ISORROPIA-II estimations showed that the atmosphere of Iasi might be ammonia rich during both cold and warm seasons, so that enough NH_3 would be present to neutralize the H_2SO_4 , HNO_3 , and HCl acidic components and to generate fine-particulate ammonium salts in the form of $(\text{NH}_4)_2\text{SO}_4$, NH_4NO_3 , and NH_4Cl . Significant amounts of fine-particulate NO_3^- were in fact detected during the cold season. The presence of possibly large amounts of NH_3 , the domination of $(\text{NH}_4)_2\text{SO}_4$ over NH_4NO_3 and NH_4Cl , and the high RH conditions in the cold season (likely leading to dissolution of a significant fraction of atmospheric HNO_3 and NH_3) are among the most important driving forces enhancing the fine-particulate NO_3^- and NH_4^+ distribution at the investigated site.

Most probably, gaseous NH_3 is not only a precursor of NH_4^+ formation, but it also affects the occurrence of NO_3^- and eventually Cl^- in $\text{PM}_{2.5}$ via neutralization processes. The chemical composition database concerning $\text{PM}_{2.5}$ (and PM_{10}), combined with predictions from ISORROPIA-II run in the forward mode, allow us to suggest that NH_3 was most probably present at a sufficiently high concentration to promote fine-particle acidity neutralization during both the cold and the warm seasons. Although it is known that running ISORROPIA-II in the forward mode with only aerosol concentrations as input may result in a bias in the predicted pH due to the repartitioning of ammonia in the model, this approach was the only one that allowed for a reasonable interpretation of the obtained results.

Over the warm season, $\sim 35\%$ of the total analysed samples presented pH values in the very strong acidity fraction (0–3 pH units range), while over the cold season the fraction of samples in this pH range was $\sim 43\%$. However, while during the warm season $\sim 24\text{--}25\%$ of the acidic samples were in the 1–2 pH range (reflecting mainly contributions from very strong inorganic acids), over the cold season an $\sim 40\%$ fraction in the 1–3 pH range would reflect possible contributions from other acidic type species (i.e. organics). The observed changes in aerosol acidity could potentially impact the gas–particle partitioning of semi-volatile organic acids.

Data availability. Data are available upon request to the contact author Cecilia Arsene (carsene@uaic.ro).

The Supplement related to this article is available online at <https://doi.org/10.5194/acp-18-5879-2018-supplement>.

Competing interests. The authors declare that they have no conflict of interest.

Acknowledgements. The authors acknowledge the financial support provided by UEFISCDI within the PN-III-P4-ID-PCE-2016-0299 (AI-FORECAST), PN-II-PCE-2011-3-0471 (EVOLUTION-AIR), and PN-II-RU-TE-2014-4-2461 (SOS-AROMATIC) projects. The European Union's Horizon 2020 research and innovation programme, through the EUROCHAMP-2020 Infrastructure Activity Grant (grant agreement no. 730997) and Chemical On-Line cOmpoSition and Source Apportionment of fine aerosols COLOSSAL grant (CA16109), is gratefully acknowledged. The authors also acknowledge the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model and/or READY website (<http://www.ready.noaa.gov>) used in this publication.

Edited by: Leiming Zhang

Reviewed by: two anonymous referees

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Physico-chemical Behaviour of Newly Synthesized Macrocylic Compounds

A reality between expectations and experimental evidences

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Three newly synthesized macrocylic amidic compounds have been tested for their potential to act as chelators for various metals. Spectroscopic (Fourier-Transformed-Infrared-Spectroscopy, fluorescence, UV-Vis absorption) and electrometric (conductometry) techniques have been used to characterize the chelating potential of the newly synthesized macrocylic compounds towards metals such as Ag, Al, Ca, Cd(II), Co(II), Cr(III), Cu(II), Fe(III), Mg, Mn(II), Ni(II), Pb(II) and Zn. Experimental investigations have been undertaken at M:L or L:M ratios of 1:1, 1:2, 1:3 and 1:4. From the interest potential chelators only for one macrocylic amidic compound some experimental evidences have been obtained for its possible implication in silver ions chelation both in methanol (MeOH) and methanol-dimethyl sulphoxide (MeOH-DMSO) binary systems.

Keywords: macrocylic amidic compounds, chemosensors, silver ions, chelators

Nowadays researchers interest to develop new sensitive, selective and rapid methods for the determination and removal of toxic metals from the environment has enhanced [1]. Development and application of chemical sensors for the detection of heavy metal ions, even at trace levels, is a modern research topic [2-3]. Molecular receptors based on crown ethers are well known complexing agents especially for heavy metal cations [4-5]. In addition, macrocylic compounds containing azo moiety are another important class of molecular receptors [6-7]. Supramolecular chemistry offers wide possibilities for azobenzocrowns functionalization, lipophilic crowns being successfully applied as ionophores in order to obtain miniaturized ion-selective membrane electrodes [8]. Some azoaryl crown ethers may act as chelators with good selectivity for binding metal ions in solution and, usually, the cation-ligand interactions are well illustrated by changes in the UV-Vis spectra [9]. It has been shown that changing the structure of some azobenzocrown ethers may induce favourable processes responsible on the formation of compounds with chromoionophore and fluoroionophore properties [10]. Synthesis of amides-based supramolecular systems has been reported, neutral macrocylic amides showing anion binding properties [11]. Interactions occurring between electron donors and electron acceptor complementary groups, may lead to the formation of intramolecular charge transfer complexes. Influence of dimensionality and charge on anions binding of macrocylic amides was reported by Kang et al. [12]. In addition, these macrocylic amides can form complexes

with metal ions, such as Cd(II), Fe(III) and Cu(II), and therefore, they can be used for selective complexation of metal ions. Studies of cyclophane amides complexation of metal ions, Cu(II), Ni(II) and Cd(II) have been reported [13].

In the present work, three newly synthesized macrocylic amidic compounds (fig. 1a,b,c) have been tested for their potential to act as chelators for various metals.

Experimental part

Materials and methods

Chemicals

The compounds used in the present work as potential chelators, i.e. GZ-I ($C_{16}H_{20}N_2O_5$, M: 320 g/mol), GZ-II ($C_{15}H_{18}N_2O_5$, M: 306 g/mol) and GZ-III ($C_{16}H_{20}N_2O_5$, M: 320 g/mol), have been synthesized in the Organic Chemistry Laboratory. For the investigated compounds stock solutions of 1.0×10^{-3} and 5.0×10^{-3} mol L⁻¹ have been prepared by dissolving appropriate amounts into standard flasks of 25 mL. Methanol has been used for compounds dissolution and dilution to the mark. For the GZ-III compound a stock solution of 1.0×10^{-2} mol L⁻¹ was prepared in the same way, using as solvents either methanol (MeOH) or methanol-dimethyl sulphoxide (MeOH-DMSO) (1:1, v/v) mixture. Sodium citrate, with addition of suitable amounts of hydrochloric acid, was used to prepare buffer solutions with pH values of 2.8, 3.4, 4.8 and 7.0. Sodium hydroxide solutions in various concentrations, i.e. 10^{-1} mol L⁻¹ (pH 12.7), 10^{-2} mol L⁻¹ (pH 11.9), 10^{-3} mol L⁻¹ (pH 9.4) and 10^{-4}

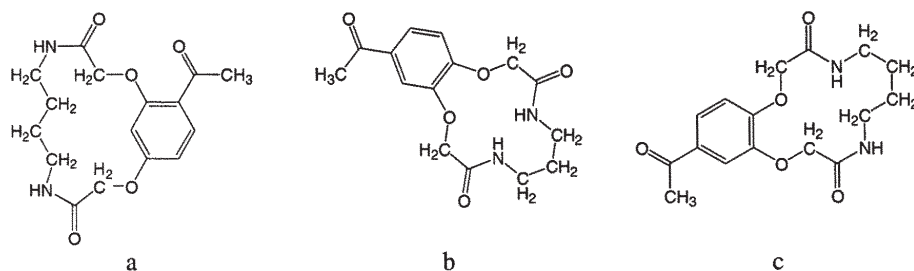


Fig. 1a,b,c: Chemical structures of the newly synthesized macrocylic compounds, i.e. GZ-I (a), GZ-II (b), and GZ-III (c), used in the present study

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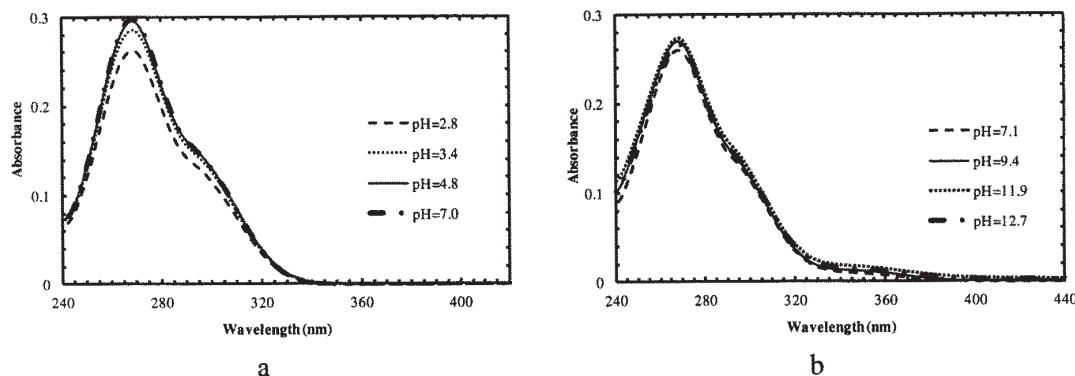


Fig. 2a,b. UV-Vis spectra recorded for GZ-III macrocyclic compound at various pH values, i.e. in citrate buffer (a) and sodium hydroxide (b) solutions

mol L⁻¹ (pH 7.1), were prepared by appropriate dilutions of concentrated NaOH solution (32%). A reference multi-element standard solution (1000 mg L⁻¹, Merck), containing Ag, Al, B, Ba, Bi, Ca, Cd(II), Co(II), Cr(III), Cu(II), Fe(III), Ga, In, K, Li, Mg, Mn(II), Na, Ni(II), Pb(II) Sr, Tl and Zn ions, was used to prepare by appropriate dilution a stock solution of 1.0×10^{-3} mol L⁻¹ reported at silver ions. Ultrapure water (18.2 MΩ.cm resistivity) has been used for appropriate standard dilution into a 25 mL standard flask. All chemicals, of highest available purity, were purchased from commercial sources and used without further purification.

Instrumentation

A double beam UV-Vis spectrophotometer (Specord 210 Plus, ANALYTIC JENA) was used for the absorbance measurements. Fluorescence measurements were performed on a FLS-920s spectrofluorometer (Edinburgh Instruments). pH measurements have been undertaken by using a pH meter HANNA HI, Model 4221. The conductivity measurements were performed on a digital HANNA HI conductivity apparatus, Model 4321, at 23.2 °C. IR absorption spectrum, for the crystals formed between GZ-III and Ag⁺, were recorded at room temperature, in KBr pellets, with a FTIR Vertex 70 spectrophotometer, with ATR and RAMAN II modules. Morphological details for the interest chemical structures (powder, crystals) were obtained by using a Scanning Electron Microscope (SEM), Model Quanta 250.

Measurement procedures

The influence of pH on the behaviour of the interest macrocyclic compounds has been investigated in a 10 mL final volume. Usually, 100 μL of 1.0×10^{-3} mol L⁻¹ ligand stock solution were added at 9.9 mL of citrate buffer solutions with various pH values. Similar procedure has been undertaken for solutions containing sodium hydroxide at various concentrations. Absorption spectra were recorded after appropriate homogenization. For the GZ-I and GZ-II compounds UV-Vis spectra in aqueous solutions were measured for M:L or L:M ratios of 1:1, 1:2, 1:3 and 1:4. Control samples have been used during the present investigations since methanol, used as solvent in particular situations, possesses specific absorption band in the interest UV-Vis region. Controls samples have been obtained by replacing with methanol in equivalent quantity the existent amount of the interest ligand.

Fluorescence measurements have been undertaken for the 1.0×10^{-2} mol L⁻¹ GZ-III solution and for the organic-aqueous mixture between GZ-III and Ag⁺ ions. Indications about a possible complexation between the GZ-III compound and Ag⁺ cations have been obtained by following the conductometric profile during titration with fixed titrant volume. The conductance of the interest mixture solution was measured after adding in a titration cell of a specific aliquot of Ag⁺ solution (1.0×10^{-1} mol L⁻¹)

followed by appropriate dilution with 30 mL of ultrapure water to ensure complete immersion of the electrode. The conductance of the solution in the cell was measured after each addition, of 500 μL of GZ-III solution, in a step-by-step procedure. For the GZ-III macrocyclic compound conductivity measurements were performed both in MeOH and MeOH-DMSO binary systems.

Results and discussions

pH influence on the macrocyclic compounds stability

Citrate buffer and sodium hydroxide solutions, with pH values between 2 and 13, have been used to study the influence of pH on the behaviour of the interest macrocyclic compounds. For the GZ-III macrocyclic compound the results are presented in figure 2a,b.

As can be seen in figure 2a, similar intensity at 268 nm and 295 nm of the absorption bands have been observed in the spectra of GZ-III in citrate buffer at pH 4.8 and 7. The absorption band with maximum intensity at 268 nm shows a low hypochromic effect at pH 3.4. The absorption band with maximum at 295 nm presents an observable hypochromic effect only for GZ-III spectrum recorded in citrate buffer at pH 2.8. As evident from figure 2b, identical absorption spectra have been recorded for GZ-III compound in various sodium hydroxide solutions. Taking into account the recorded experimental evidences, as shown in figure 2a,b, it seems that in the GZ-III macrocyclic amidic compound the atoms do not undertake any reorganization processes which could be responsible for changes in the profile of the absorption bands with maxima at 268 nm and 295 nm.

The GZ-I and GZ-II compounds potential to act as metal chelators

In order to investigate the potential of the GZ-I and GZ-II macrocyclic compounds to act as metal chelators a multi-element (ME) solution containing Ag, Al, Ca, Cd(II), Co(II), Cr(III), Cu(II), Fe(III), Mg, Mn(II), Ni(II), Pb(II) and Zn ions has been used during the present study. Absorbance spectra have been measured at various M:L ratios. Figure 3a,b shows the spectral features for GZ-I compound, while figure 4a,b shows similar experimental evidences for GZ-II compound.

Within these investigations it has observed that under 240 nm the spectra behaviour was strongly affected by the specific band of nitrate ion existent in the standard solution of the multi-element mixture (made in concentrated nitric acid). However, the intensity of the interest absorption bands showed a behaviour reflecting a direct proportionality with the multi-element variable quantity used both for GZ-I (fig. 3a) and GZ-II (fig. 4a) compounds. It has been also observed that increasing GZ-I and GZ-II compounds quantity induced a behaviour reflecting again the proportionality with the existent amount but with similar spectral features (fig. 3b and fig.

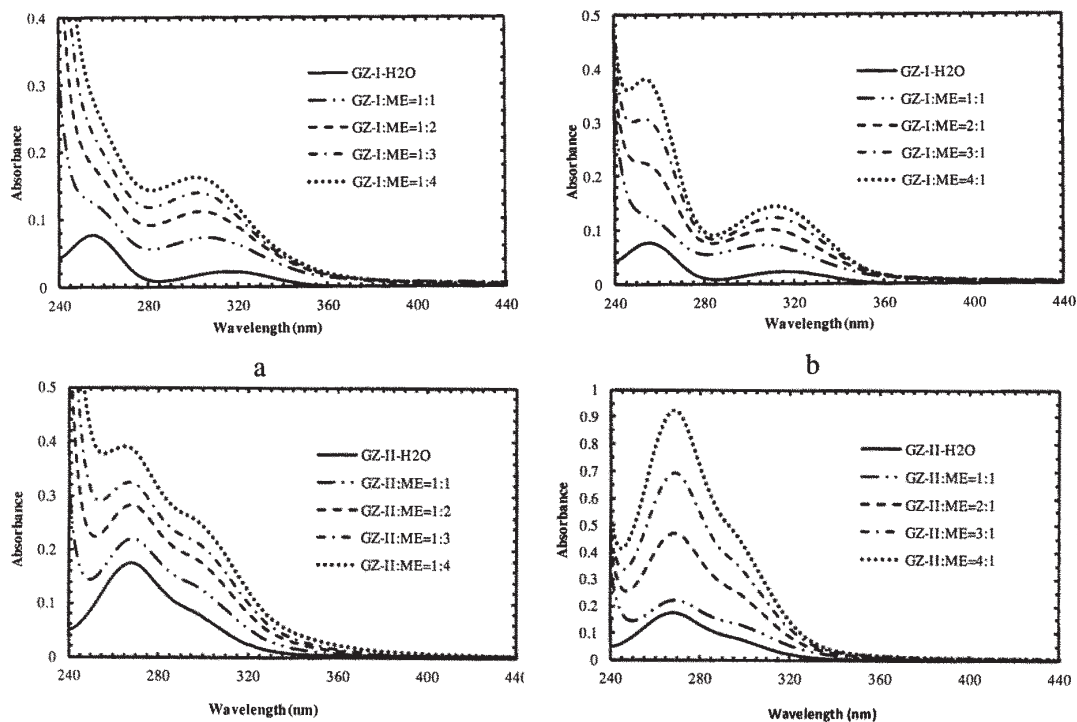


Fig. 3a,b The absorption spectra obtained for: (a) constant quantity of GZ-I macrocyclic compound and variable quantity of ME, (b) variable quantity of GZ-I macrocyclic compound and constant quantity of ME

Fig. 4a,b. The absorption spectra obtained for: (a) constant quantity of GZ-II macrocyclic compound and variable quantity of ME, (b) variable quantity of GZ-II macrocyclic compound and constant quantity of ME

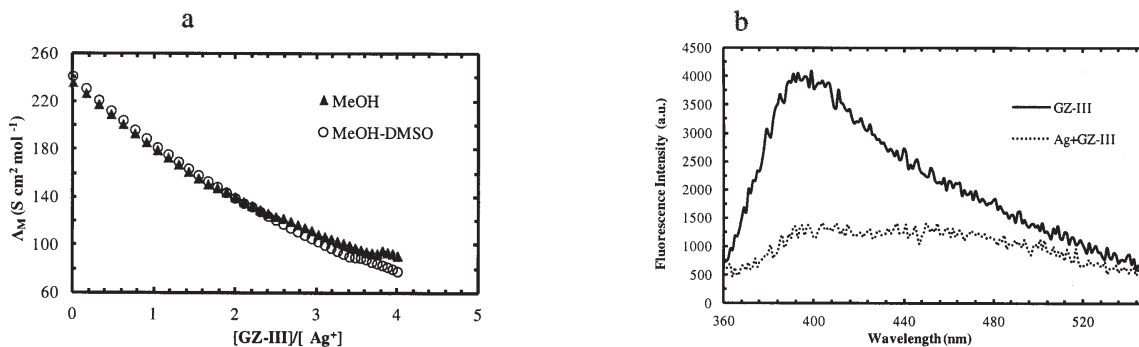


Fig. 5. Molar conductivity *vs.* mole ratio plots for GZ-III with Ag^+ complex in MeOH and in MeOH-DMSO binary systems

Fig. 6. Changes in the GZ-III macrocyclic compound (10 mM) fluorescence intensity upon addition of Ag^+ ions in a MeOH-DMSO binary systems

4b). The absorption spectra of the GZ-I and GZ-II compounds did not showed any observable changes in the spectral features recorded in the presence of the metals existent in the used multi-element reference material. It was concluded that these two macrocyclic compounds do not possess any potential to act as chelators for the existent metal ions.

Chemical behaviour of the GZ-III macrocyclic compound

Spectroscopic (FTIR, fluorescence) and electrometric (conductometry) techniques have been used to obtain experimental evidences for the possible implication of GZ-III macrocyclic compound in silver ions chelatzation.

Conductivity measurements

The conductometric profiles induced by a possible complexation between GZ-III macrocyclic compound with Ag^+ cations in both MeOH and MeOH-DMSO binary systems have been investigated. Changes of molar conductivity (Λ_m) *versus* the ligand and cation mole ratio, $[GZ-III]/[Ag^+]$, have been followed at 5 and 10 mM concentrations in GZ-III. As shown by figure 5, addition of GZ-III to Ag^+ cations in both MeOH and MeOH-DMSO binary systems resulted in a decrease in molar conductivity.

Such behaviour might indicate that the complex formed between GZ-III and silver ions is less mobile than the free solvated Ag^+ cations. Further experimental investigations revealed that DMSO addition did not induced a significant

influence on the species solvation in solution. The details presented in figure 5 show that the slope of each curve changes at the point where the ligand and cation mole ratio is about 3, which should be considered as an evidence for formation of a 1:3 $[Ag:GZ-III]$ complex. Similar assignment procedure for the formation of different complexes has been used in a study performed by Rounaghi et al. [14].

Fluorescence spectra

Fluorescence spectra have been measured in order to extract information about the potential of the interest compound, i.e. GZ-III, to present fluorescence. Details presented in figure 6 reveal that the GZ-III macrocyclic compound solvated in a MeOH-DMSO binary systems presents low intensity fluorescence emission. The presence of Ag^+ cations in the above presented system is suppressing fluorescence intensity, which might be a result induced by the formation of the complex with GZ-III compound.

IR Spectrum

For the GZ-III macrocyclic compound and the chemical structure obtained from a mixture between the GZ-III macrocyclic compound and Ag^+ ions, the IR spectra in the $1200-400\ cm^{-1}$ wavenumber region are presented in figure 7.

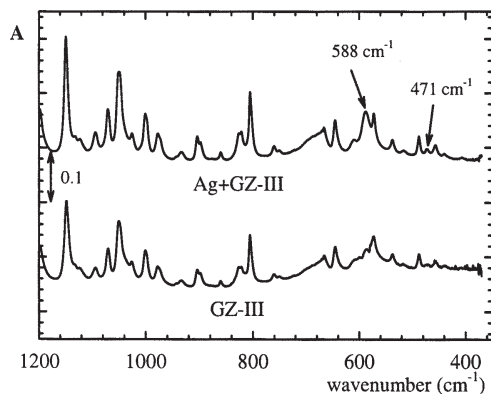


Fig. 7: IR spectrum of GZ-III macrocyclic compound and of the chemical structure resulted from a mixture between GZ-III macrocyclic compound and Ag^+ ions

The details presented in figure 7 reveal in some regions similar spectral characteristics but there are also two absorption bands with different behaviour. In the spectrum specific for the mixture between the GZ-III macrocyclic compound and silver ions the maxima observed at 471 and 588 cm^{-1} can be actually attributed to Ag-O and, respectively, Ag-N bonds vibrations [15-16]. These observations may indicate a possible coordination between the GZ-III compound with silver ions through the N and O atoms of the amidic groups.

SEM technique

Figure 8a shows the morphological details for GZ-III macrocyclic compound powder while figure 8b reveals the existence of some very fine acicular crystals obtained after drying to sec the organic-aqueous mixture between GZ-III and Ag^+ . The crystallization of the complex in the form of overlapping acicular crystals is very well illustrates by figure 8b. Unfortunately, at present it was not possible to isolate a single crystal, in order to use X-ray diffraction technique for establishing the structure of the newly formed compound.

Conclusions

The chemical behaviour of three newly synthesized macrocyclic compounds has been investigated in the present work especially due to the fact that their particular three-dimensional shape could provide suitable cavities for selective complexation of heavy metals. Various experimental approaches (spectrophotometry, fluorimetry, conductometry, microscopy) have been used in order to identify the potential of the interest macrocyclic compounds to bind some metal ions. The obtained results revealed that the GZ-I and GZ-II macrocyclic compounds do not have any potential to act as chelators for various metals in a spectacular opposition with the expectations from their chemical structures. Only for the GZ-III macrocyclic compound some experimental evidences have been obtained for its possible implication in chelating silver cations. For the GZ-III macrocyclic compound it has been observed that the pH do not influence its chemical behaviour. Further work should be undertaken to confirm

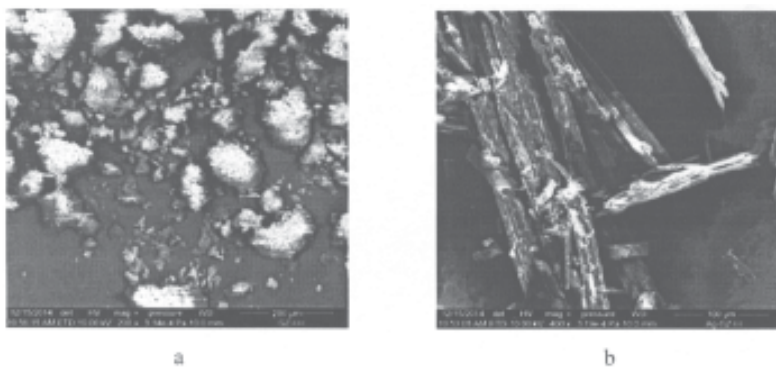


Fig. 8a,b. SEM details for GZ-III macrocyclic compound powder (a) and for the crystals formed between GZ-III and Ag^+ (b)

the present experimental observations and to investigate if or not the macrocyclic structure GZ-III can be used to develop a specific sensor for Ag^+ .

Acknowledgements: The author Zbancioc Ana Maria acknowledges to grant POSDRU/159/1.5/S/137750. PN-II-PCE-2011-3-0471 Project, No. 200/05.10.2011 is also acknowledged. CERNESIM Center is gratefully acknowledged for the infrastructure used in this work.

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Manuscript received: 23.01.2015