

The dominant contribution on wet deposition of water-soluble main ions in the South-Eastern Adriatic region

Research Article

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Abstract: The results of content of water-soluble ions measured in 604 samples of precipitation collected in South-Eastern Adriatic region during 6 years have been analyzed. The HYSPLIT model was used to study the air mass paths. Although the ion concentrations of investigated ions in precipitation of air masses from the continental parts of Europe were significant, the total wet deposition is dominated by precipitation coming over the Mediterranean Sea. The sea salt components are significantly correlated. The correlations between Ca^{2+} and Mg^{2+} , Ca^{2+} and SO_4^{2-} and Ca^{2+} and K^+ indicate the main terrigenous ions.

Keywords: *Precipitation chemistry • Mediterranean basin • a main influence*
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1. Introduction

One of the processes for removing the gaseous and particle pollutants from the atmosphere is atmospheric deposition. The temporal and spatial evolution of atmospheric chemistry could be traced by studying the chemical composition of rain and associated wet deposition [1], being the gases and particles that are captured by clouds and rain droplets. Wet and dry depositions play an essential role in controlling the concentration of biogeochemical elements in the atmosphere and in acting as a source of nutrients for the biological system. The chemical content of precipitation integrates numerous physical and chemical mechanisms. Moreover, the identification of chemical and physical characteristics of rainwater helps in evaluating the influence of the different sources and interactions of

gases and particles emitted by various ecosystems more or less disturbed by human activities [2].

Strong acidic aerosols can be directly emitted by coal and oil burning power plants and other industrial activities as primary acid aerosols. Ambient NH_3 produced by agricultural and industrial activities reacts rapidly with acidic sulfates resulting in neutral and partially neutralized ammonium salts $(\text{NH}_4)\text{HSO}_4$, $(\text{NH}_4)_2\text{H}(\text{SO}_4)$, and $(\text{NH}_4)_2\text{SO}_4$ [3].

The main natural sources of ammonia are aerobic biological sources in soil, breakdown of aminoacids in organic waste material, while the anthropogenic sources are coal and fuel oil combustion and waste treatment. Moreover, there are significant sources of ammonia from agriculture and global livestock farming as well as from the oceans due to decay of N-containing organic compounds [4,5].

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The dust transported from North Africa (Sahara and Sahel deserts) is one of the major natural sources of particulate matter (PM) in the atmosphere of Southern Europe, as satellite observations, modelling and ground-base measurements have shown [6-8]. The seaside of Montenegro has a Mediterranean climate and is under the influence of marine aerosol containing Na^+ , Cl^- , Mg^{2+} , K^+ and SO_4^{2-} .

Water soluble ions are continuously removed from the atmosphere by dry and wet deposition processes. Although wet deposition is very efficient, it is sporadic in nature.

The aim of this work was identification of contribution of air masses originated from various European parts as well as from Northern Africa on the water soluble ions wet deposition measured in Herceg Novi, Montenegro. Also an effort was made to estimate the possible sources of the ions of interest from identified regions. In order to study the air origin for the city of Herceg Novi ($42^\circ 27' \text{N}$, $18^\circ 33' \text{E}$), the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model is used. The HYSPLIT model [9,10] is a complete system for computing simple air parcel trajectories to complex dispersion and deposition simulations [11-13]. The dispersion of a pollutant is calculated by assuming either puff or particle dispersion. In the puff model, puffs expand until they exceed the size of the meteorological grid cell (either horizontally or vertically) and then split into several new puffs, each with its share of the pollutant mass. In the particle model, a fixed number of particles are advected about the model domain by the mean wind field and spread by a turbulent component. The model's default configuration assumes a 3-dimensional particle distribution (horizontal and vertical) [9].

2. Experimental procedure

By means of the HYSPLIT model using the CDC1 global reanalysis meteorological data, three-day backward trajectories ending at the mentioned measuring site at 500, 1000, and 1500 m were calculated for days with minimal precipitation of 0.5 mm. Backward trajectories were computed for a time period of 72 h before the time each sample was collected at a start time of 00:00 local time. Since it was found that a 72-hour time period allowed us to adequately identify precipitation source areas for most of the samples. In order to determine the air mass source and history for the precipitation events sampled for this study, an air mass backward trajectory model was run for each of the 604 samples. Air mass trajectories were classified into six trajectory (588 cases)

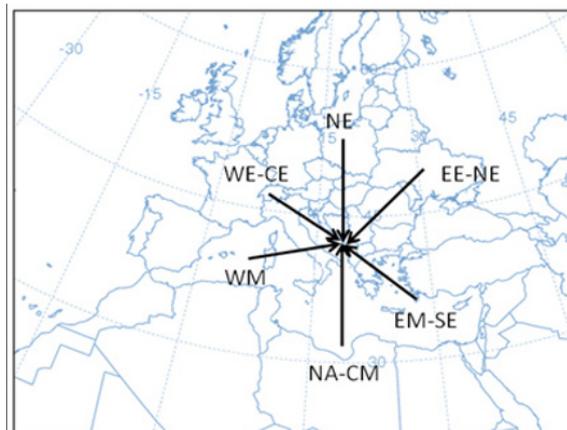


Figure 1. Classification of backward trajectories for Herceg Novi using HYSPLIT model: NE (Northern Europe), EE-NE (Eastern Europe-Northeastern Europe), EM-SE (Eastern Mediterranean-Southeastern Europe), NA-CM (Northern Africa-Central Mediterranean), WM (Western Mediterranean), and WE-CE (Western Europe-Central Europe).

categories by the direction of their approach to Herceg Novi (Fig. 1) and 16 cases are undefined.

The samples collection were made daily during 24 hours (from 8 am to 8 am the following day - meteorological time) in the period from January 1995 to December 2000. Only the samples collected during the rainy days at the measuring site were taken into account. The samples used were positioned at 1.5 m above the ground, they were opened (without coverage) and because of that the precipitation samples, except the wet deposition, contained some amount of dry deposition [13,14]. The amounts of anions in the precipitation were determined spectrophotometrically as follows: Cl^- by the mercury thiocyanate-iron method, NO_3^- by the Griess method and SO_4^{2-} by the barium perchlorate - Thorin method. The amount of NH_4^+ was determined spectrophotometrically by the Indophenol Blue method. The amounts of Na^+ and K^+ in the precipitation was determined by flame photometry and the amounts of Mg^{2+} and Ca^{2+} by atomic absorption spectrometry.

Detection limits ($\mu\text{eq L}^{-1}$), precisions (%) and accuracies (%) for Na^+ , Mg^{2+} , K^+ , Ca^{2+} , NH_4^+ , SO_4^{2-} , NO_3^- and Cl^- are given in Table 1. The precisions are expressed as the relative uncertainty (the standard deviation of the total data set divided by the average and multiplied by 100). The statistical way to present uncertainties was chosen because of the large number of data.

The Volume-Weighted Mean (VWM) concentrations of the ionic constituents measured in rainwater in South-East Adriatic coast region were calculated using the following equation:

Table 1. Detection limits, precisions and accuracies.

	Na ⁺	Mg ²⁺	K ⁺	Ca ²⁺	NH ₄ ⁺	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻
Detection limits (µeq L⁻¹)	2.2	0.2	0.1	5.0	1.1	2.1	1.6	0.6
Precisions (%)	4.7	4.5	1.9	12.4	9.1	1.2	1.2	0.8
Accuracies (%)	2.0	2.7	0.8	6.6	4.8	5.4	4.2	4.3

$$VWM(\mu\text{eqL}^{-1}) = \frac{\sum_{i=1}^{n=604} C_i P_i}{\sum_{i=1}^{n=604} P_i} \quad (1)$$

where C_i is the ion concentration for each species in $\mu\text{eq L}^{-1}$ and P_i the precipitation amount for each rainy event in mm. The Wet Deposition (WD) was calculated using the equation:

$$WD = VWM \times P \quad (2)$$

with VWM being the Volume-Weighted Mean concentration for each species and P the mean rainfall amount measured during the period of study [15].

3. Results and discussion

3.1. Backward trajectories

The air mass origin for each sampling day was studied by backward trajectories. The six origins of the air masses were defined (Fig. 1): Northern Europe (NE), Eastern Europe - North-Eastern Europe (EE-NE); Eastern Mediterranean - Southeastern Europe (EM-SE); Northern Africa-Central Mediterranean (NA-CM); Western Mediterranean (WM); Western Europe - Central Europe (WE-CE), while 16 cases remained undefined. The results shown in Fig. 2 indicate that the heights and frequencies of precipitation originated from air masses coming from Northern Europe and Eastern Europe - North-Eastern Europe are the lowest. On the other hand, the heights and frequencies of precipitation coming by air masses from the Western Mediterranean and Northern Africa and the Central Mediterranean are the highest.

The highest absolute frequency was observed for precipitation from the Western Mediterranean (110 cases). Also, the highest daily precipitations were registered for air masses from Africa and Central Mediterranean (220 mm) and from the Western Mediterranean (180 mm).

The relative frequency (Fig. 3) of the total number of days with precipitation greater than or equal to 0.5 mm (Fig. 3a) is caused by two prevailing cyclonic circulations: from the Western Mediterranean, WM, (36.6%) and from the Central Mediterranean, A-CM,

(30.6%). In the latter case, 82.6% was influenced by the vicinity of Africa.

Next, the relative frequency of days with precipitation less than 10 mm (Fig. 3b), and greater than or equal to 10 mm (Fig. 3c) were analyzed. This threshold is selected since precipitation exceeding 10 mm is a heavy precipitation event- one most likely to cause flash flooding. Again, circulations from Western and Central Mediterranean were dominant. The relative frequency of days with very intensive precipitation (76.4%) was greater than the relative frequency of those with precipitation less than 10 mm (59.1%) for the air mass formed in the Western and Central Mediterranean. However, the relative frequency of days with precipitation less than 10 mm was almost 20% for circulation from the East (EE-NEE and EM-SEE) and less than 10% for precipitation exceeding 10 mm.

Many authors pointed out that cyclones tend to develop in the Mediterranean basin. The geography of the region, namely the high orography skirting the Mediterranean Sea and the existence of inland seas, determines the relatively small areas where cyclogenesis tends to occur [16,17]. In the winter this is essentially along the strongly baroclinic Northern coast: in the lee of the Alps when an upper trough is blocked by the mountains; over the Aegean and Black Seas when an upper trough moves over the relatively warm water basins. In spring, the strengthening of the meridional temperature gradient along the Northern African coast favors the development of Saharan depressions. These tend to occur on the lee side of the Atlas Mountains, within a region of very weak static stability. Thermal forcing does play an increased role in the genesis and maintenance of Mediterranean lows in spring and, particularly, in summer [17]. Maheras *et al.* [18] and Anagnostopoulou *et al.* [19] also studied the cyclonic occurrence in three regions of enhanced cyclonic activity: Gulf of Genoa (Western Mediterranean), Southern Italy (Central Mediterranean) and Cyprus. They found that for the Genoa region the cyclone pressure minimum is located over the gulf, while for the cyclones that occur in Southern Italy, the pressure minimum is rather broad, especially in winter, covering a wide region including the Adriatic Sea.

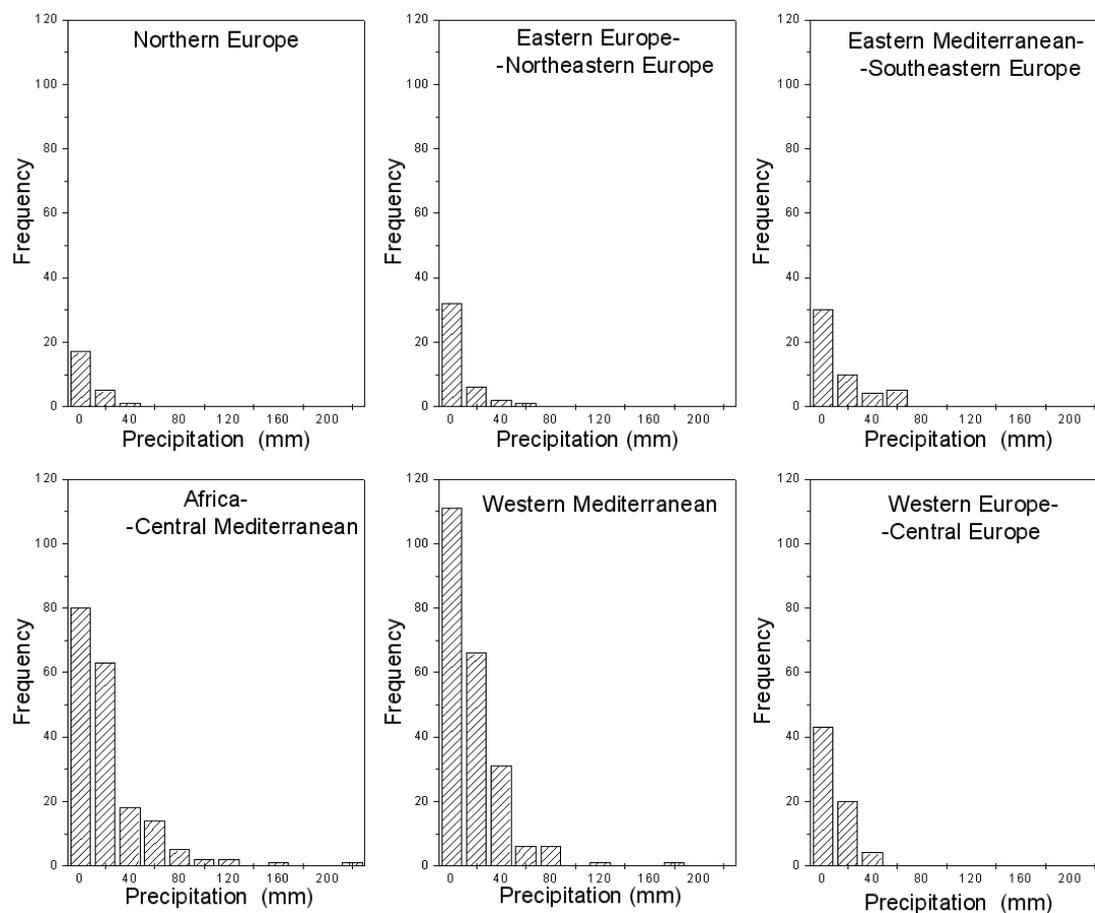


Figure 2. Frequencies of precipitation (mm) of air masses from various directions.

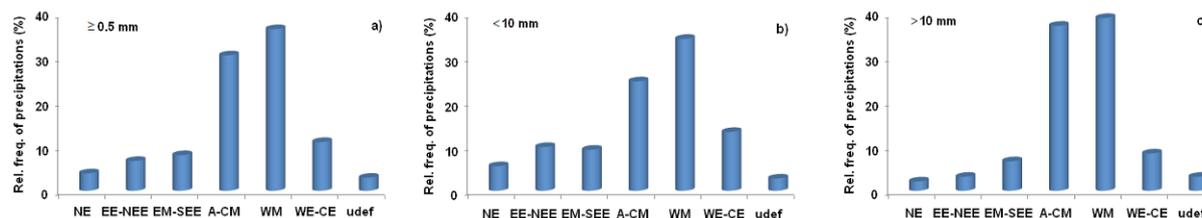


Figure 3. Relative frequency of the total number of days with precipitation a) greater than or equal to 0.5 mm, b) precipitation less than 10 mm and c) precipitation greater than or equal to 10 mm for Herceg Novi.

3.2. Chemical composition

The mean values and standard deviations (σ) of the daily temperatures, precipitation, pH and concentrations of the main ions in the precipitation measured in the South-Eastern part of the Adriatic Sea for 604 samples of precipitation divided according to years are given in Table 2.

The order of the volume-weighted mean concentrations (meq L^{-1}) of ion species in precipitation in 1995 were as follows: $\text{Na}^+ > \text{Cl}^- > \text{SO}_4^{2-} > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{NH}_4^+ > \text{NO}_3^- > \text{K}^+$; in 1996: $\text{Na}^+ > \text{Cl}^- > \text{SO}_4^{2-} > \text{Ca}^{2+} > \text{NO}_3^- > \text{Mg}^{2+} > \text{NH}_4^+ > \text{K}^+$; in 1997: $\text{K}^+ > \text{Ca}^{2+} > \text{Na}^+ > \text{Cl}^- >$

$\text{SO}_4^{2-} > \text{Mg}^{2+} > \text{NO}_3^- > \text{NH}_4^+$; in 1998: $\text{Na}^+ > \text{Cl}^- > \text{Ca}^{2+} > \text{SO}_4^{2-} > \text{NO}_3^- > \text{Mg}^{2+} > \text{NH}_4^+ > \text{K}^+$; in 1999: $\text{Cl}^- > \text{Mg}^{2+} > \text{Na}^+ > \text{Ca}^{2+} > \text{SO}_4^{2-} > \text{NO}_3^- > \text{NH}_4^+ > \text{K}^+$ and in 2000: $\text{SO}_4^{2-} > \text{Cl}^- > \text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{NO}_3^- > \text{NH}_4^+ > \text{K}^+$.

Volume weighted yearly average concentrations of measured ions at our station are mainly in accordance with results in near the region within yearly variation [20]. Generally VWM of SO_4^{2-} is higher than these measured in wet-only precipitation in a Mediterranean coastal site in Patras in Greece, while VWM of Ca^{2+} in 1995 and 1996 is lower, but the values obtained in 1998, 1999 and 2000 are in accordance with results for Patras.

Table 2. Average yearly values of measured parameters.

Year	1995		1996		1997		1998		1999		2000	
No. of events	119		124		77		105		103		79	
	Mean ± σ		Mean ± σ		Mean ± σ		Mean ± σ		Mean ± σ		Mean ± σ	
Daily t (C°)	14.5 ± 5.1		14.2 ± 4.7		14.5 ± 4.1		16.1 ± 5.2		14.9 ± 5.4		15.1 ± 4.8	
Precip.(mm)	14.8 ± 18.3		19.7 ± 29.8		18.4 ± 21.2		17.8 ± 25.3		13.8 ± 14.1		16.8 ± 21.1	
pH	6.24 ± 0.71		6.35 ± 0.85		6.10 ± 0.71		6.39 ± 0.69		6.28 ± 0.79		6.04 ± 0.66	
EC (µs/cm)	91.7 ± 120.7		96.2 ± 195.5		90.3 ± 118.2		91.6 ± 161.0		87.4 ± 146.4		99.5 ± 116.7	
	Mean ± σ	VWM	Mean ± σ	VWM	Mean ± σ	VWM	Mean ± σ	VWM	Mean ± σ	VWM	Mean ± σ	VWM
SO ₄ ²⁻ (µeq L ⁻¹)	137.3 ± 134.7	89.9	140.6 ± 143.1	105.4	147.1 ± 142.2	112.10	134.6 ± 169.2	75.1	114.3 ± 86.5	94.53	193.7 ± 296.6	115.7
NO ₃ ⁻ (µeq L ⁻¹)	36.8 ± 18.7	31.0	50.4 ± 16.9	44.6	53.9 ± 38.1	40.30	46.4 ± 17.9	39.1	54.2 ± 17.3	51.72	49.8 ± 50.6	31.7
NH ₄ ⁺ (µeq L ⁻¹)	51.3 ± 36.5	39.1	55.8 ± 40.8	39.8	48.6 ± 42.8	28.20	30.5 ± 26.4	21.4	34.0 ± 31.6	27.78	44.6 ± 42.9	27.3
Na ⁺ (µeq L ⁻¹)	164.6 ± 103.8	131.8	157.5 ± 87.4	174.9	174.1 ± 100.1	147.62	148.6 ± 83.8	107.3	131.5 ± 76.9	111.02	163.8 ± 92.0	106.6
Mg ²⁺ (µeq L ⁻¹)	48.7 ± 49.5	39.4	32.0 ± 38.8	42.5	82.9 ± 104.6	84.29	65.8 ± 79.1	35.9	133.2 ± 429.3	114.76	166.6 ± 622.8	81.3
Ca ²⁺ (µeq L ⁻¹)	93.3 ± 85.4	62.1	79.9 ± 78.9	61.0	296.8 ± 336.6	189.57	166.5 ± 208.8	82.2	125.9 ± 121.4	97.08	185.6 ± 200.1	97.3
Cl ⁻ (µeq L ⁻¹)	116.2 ± 63.4	105.5	115.5 ± 70.4	124.5	122.0 ± 77.4	113.22	119.6 ± 74.8	93.1	136.8 ± 83.9	140.10	163.6 ± 79.6	113.0
K ⁺ (µeq L ⁻¹)	19.2 ± 16.5	13.5	11.6 ± 14.5	12.3	285.3 ± 1834.7	197.26	23.6 ± 52.8	8.7	21.0 ± 37.9	16.82	23.3 ± 26.4	13.7

The anthropogenic effect to all the constituents is confirmed by the study of the ionic ratios and the correlation analysis [21], while the marine effect of the rainwater chemistry in Thessaloniki is obvious for the cases of Cl⁻ and Mg²⁺. Terrestrial sources contribute on regional and sub-regional scale in addition to the local emissions.

3.3. Analysis of correlations

The coefficients of correlations were calculated for each sub-data set obtained by division according to the origin of the air masses. The Spearman coefficients of correlations are given in Table 3.

The best correlations, especially in air masses over the Mediterranean, were found between all cations except ammonium. The best correlations between SO₄²⁻ and NH₄⁺ are found in air masses coming from the Northern and Eastern parts of Europe in which no correlations are found between SO₄²⁻ and NO₃⁻. However, significant correlations at the confidence level of 99.9% between SO₄²⁻ and NO₃⁻ are found in air masses coming from the Western part of Europe and from North Africa. From totally of 604 examined events, just 23 events from the Northern and 41 events from the Eastern parts of Europe could interrupt these correlations (Table 3).

The significant correlations are found between the main sea salt ions (Na⁺, Cl⁻, Mg²⁺). Generally, the correlations between Cl⁻ and Mg²⁺ are high in each of sub

data sets. Correlation between calcium (mainly derived from soil dust) and magnesium (mainly derived from sea salt) found in air masses coming over Mediterranean sea indicate joint transport of dust from land and marine aerosol. Being this correlation is lower in air masses coming from Northern Europe it could be concluded that the main source of magnesium is sea salt. The high correlation between Ca²⁺ and SO₄²⁻ in air masses coming from open sea (Northern Africa-Central Mediterranean and Western Mediterranean) points out that Sahara dust is the origin of CaSO₄. A significant correlation between these ions was also found in other air masses that could be consequences of re-suspension of previously settled CaSO₄ in the surroundings.

The analyses of correlations give significant and high coefficients of correlation between Ca²⁺ and Mg²⁺, Ca²⁺ and SO₄²⁻ and Ca²⁺ and K⁺ (Table 3). These correlations indicate that the main terrigenous ions were associated with formation of eolian particles which include gypsum (CaSO₄), calcite (CaCO₃) and dolomite (CaMg(CO₃)₂). The origin of potassium ion in rainwater is from washout of desert aerosol (from soil wind erosion), aerosols from combustion and biogenic aerosols [15].

3.4. Wet deposition

The calculated Volume Weighted Mean (VWM) and total Wet Deposition (WD) over the whole

Table 3. Spearman coefficients of correlations between species on 99% confidence levels (values in italic) and on 95% confidence levels.

		SO₄²⁻	NO₃⁻	NH₄⁺	Na⁺	Mg²⁺	Ca²⁺	Cl⁻	K⁺
Northern Europe	SO ₄ ²⁻	1.000							
	NO ₃ ⁻		1.000						
	NH ₄ ⁺	<i>0.610</i>		1.000					
	Na ⁺	0.490		<i>0.604</i>	1.000				
	Mg ²⁺					1.000			
	Ca ²⁺	0.588				0.507	1.000		
	Cl ⁻	0.473				0.626		1.000	
	K ⁺				<i>0.475</i>	<i>0.476</i>			1.000
Eastern Europe – North-Eastern Europe	SO ₄ ²⁻	1.000							
	NO ₃ ⁻		1.000						
	NH ₄ ⁺	<i>0.608</i>		1.000					
	Na ⁺	0.493			1.000				
	Mg ²⁺	0.570		0.357	0.687	1.000			
	Ca ²⁺	0.525			0.625	0.775	1.000		
	Cl ⁻	0.524	0.341	0.351	0.688	0.763	0.485	1.000	
	K ⁺	0.391			<i>0.473</i>	<i>0.468</i>	<i>0.573</i>	0.366	1.000
Eastern Mediterranean-South-Eastern Europe	SO ₄ ²⁻	1.000							
	NO ₃ ⁻	<i>0.382</i>	1.000						
	NH ₄ ⁺	<i>0.617</i>		1.000					
	Na ⁺	0.323			1.000				
	Mg ²⁺	0.346			0.792	1.000			
	Ca ²⁺	0.373			0.579	0.791	1.000		
	Cl ⁻	0.401		0.340	0.707	0.623	0.416	1.000	
	K ⁺	<i>0.443</i>		<i>0.513</i>	<i>0.486</i>	<i>0.618</i>	<i>0.692</i>	0.301	1.000
Africa-Central Mediterranean	SO ₄ ²⁻	1.000							
	NO ₃ ⁻	<i>0.455</i>	1.000						
	NH ₄ ⁺	<i>0.510</i>	<i>0.270</i>	1.000					
	Na ⁺	<i>0.560</i>		<i>0.254</i>	1.000				
	Mg ²⁺	<i>0.647</i>	<i>0.244</i>	<i>0.205</i>	0.778	1.000			
	Ca ²⁺	<i>0.579</i>	<i>0.338</i>	<i>0.228</i>	<i>0.493</i>	<i>0.637</i>	1.000		
	Cl ⁻	<i>0.575</i>	<i>0.225</i>	<i>0.224</i>	<i>0.750</i>	<i>0.721</i>	<i>0.374</i>	1.000	
	K ⁺	<i>0.631</i>	<i>0.250</i>	<i>0.376</i>	<i>0.514</i>	<i>0.676</i>	<i>0.556</i>	<i>0.481</i>	1.000
Western Mediterranean	SO ₄ ²⁻	1.000							
	NO ₃ ⁻	<i>0.474</i>	1.000						
	NH ₄ ⁺	<i>0.357</i>	<i>0.194</i>	1.000					
	Na ⁺	<i>0.563</i>	<i>0.215</i>		1.000				
	Mg ²⁺	<i>0.655</i>	<i>0.276</i>		<i>0.859</i>	1.000			
	Ca ²⁺	<i>0.621</i>	<i>0.313</i>	<i>0.183</i>	<i>0.570</i>	<i>0.692</i>	1.000		
	Cl ⁻	<i>0.432</i>	0.161		0.775	0.788	0.393	1.000	
	K ⁺	<i>0.636</i>	<i>0.291</i>	<i>0.286</i>	<i>0.601</i>	<i>0.686</i>	<i>0.658</i>	<i>0.461</i>	1.000
Western Europe – Central Europe	SO ₄ ²⁻	1.000							
	NO ₃ ⁻	0.297	1.000						
	NH ₄ ⁺	<i>0.403</i>		1.000					
	Na ⁺	<i>0.594</i>		<i>0.284</i>	1.000				
	Mg ²⁺	<i>0.549</i>			<i>0.853</i>	1.000			
	Ca ²⁺	<i>0.584</i>		<i>0.522</i>	<i>0.604</i>	<i>0.675</i>	1.000		
	Cl ⁻	0.328			0.763	0.739	0.291	1.000	
	K ⁺	<i>0.585</i>		<i>0.466</i>	<i>0.660</i>	<i>0.660</i>	<i>0.777</i>	<i>0.425</i>	1.000

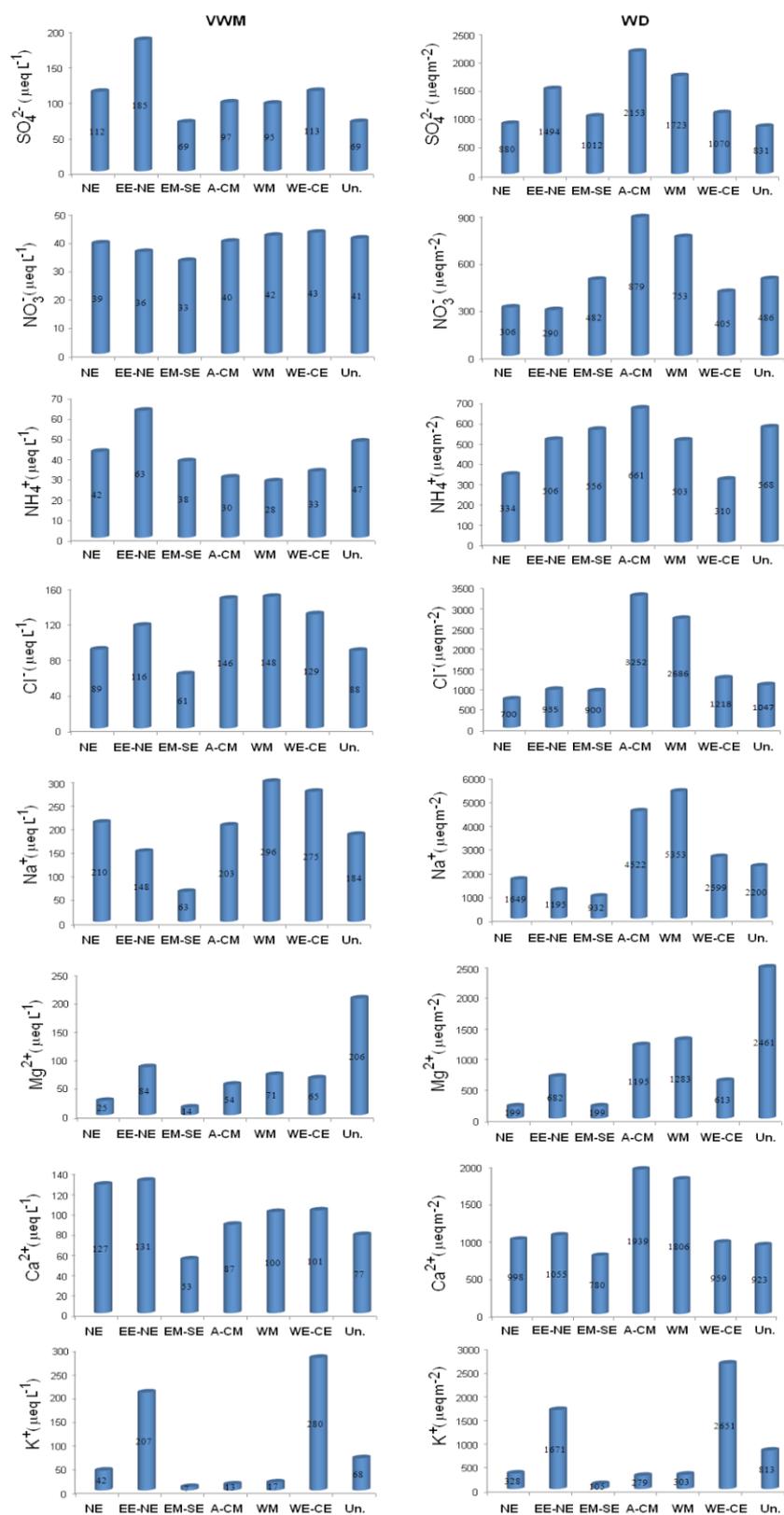


Figure 4. Average Volume-Weighted Mean and total Wet Deposition divided in six categories, plus undefined for the total period of investigation (1995 – 2000).

period of investigation are shown in Figs. 4a and 4b, respectively.

The highest values of VWM for: SO_4^{2-} ($185.0 \mu\text{eq L}^{-1}$), NH_4^+ ($62.7 \mu\text{eq L}^{-1}$), Mg^{2+} ($84.4 \mu\text{eq L}^{-1}$) were found in precipitation from air masses from Eastern Europe - Northeastern Europe (Fig. 3a). In precipitation from the Western Mediterranean and Western and Central Europe, the highest mean ion concentrations are for NO_3^- (41.6 and $42.8 \mu\text{eq L}^{-1}$, respectively) and for Na^+ (295.8 and $274.7 \mu\text{eq L}^{-1}$, respectively). The highest values of ion concentration of Cl^- ($148.4 \mu\text{eq L}^{-1}$) are from the Western Mediterranean and for K^+ ($280.2 \mu\text{eq L}^{-1}$) are from Western Europe and Central Europe.

The highest ion concentrations and Volume Weighted Mean (Fig. 4a) of SO_4^{2-} are found in the precipitation of air masses coming from Eastern and North-Eastern Europe, indicating anthropogenic sources that are consuming coal (coal fired power plants) and liquid fuels with a high content of sulfur and, old technologies without emission control that are still in use in this region. The total Wet Deposition (WD) (Fig. 3b) of SO_4^{2-} originating from Northern Europe ($880 \mu\text{eq m}^{-2}$) and Eastern – North-Eastern Europe ($1494 \mu\text{eq m}^{-2}$) is significant (Fig. 4b). Nevertheless, the most significant WD of SO_4^{2-} in the investigated region was caused by air masses coming from Africa and the Central Mediterranean ($2152 \mu\text{eq m}^{-2}$) and Western Mediterranean ($1722 \mu\text{eq m}^{-2}$). The same trends are for other ions. In the region of the Central Mediterranean, there are several volcanoes, located in South Italy: Vesuvius, Etna and the permanent volcano Stromboli that are continuously emitting sulfur oxides as a natural emission sources. Also these volcanoes are emitting nitrogen oxides, chlorides *etc.*

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4. Conclusions

This study shows the dominant contribution on wet deposition of water soluble ions has air masses coming from Mediterranean. Precipitations from cyclones formed over the Western Mediterranean are the most frequent. The most frequent precipitation was coming in air masses from the Western Mediterranean and Africa and the Central Mediterranean, but the lowest frequency of events was from Northern Europe. Although the ion concentrations and VWM of Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , SO_4^{2-} , NO_3^- and NH_4^+ in precipitation of air masses from the continental parts of Europe are significant, the total WD is dominated by precipitation coming over the Mediterranean due to abundances of precipitation from this segment. The largest concentrations of SO_4^{2-} are in the precipitations of air masses coming from the North-Eastern regions of Europe where old technologies are located and heavy fuels with high contents of sulfur are used. The highest WD of SO_4^{2-} were found in precipitations of air masses coming from the Western Mediterranean caused by the highest abundances and frequencies of precipitations.

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