

# CHEMICAL COMPOSITION OF PRECIPITATION IN THE EASTERN MEDITERRANEAN ATMOSPHERE

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## ABSTRACT

Short and long-term variations in chemical composition of precipitation in the Eastern Mediterranean was investigated by analyzing approximately 500 daily, wet-only precipitation samples collected between 1992-2000 at a rural station on the Mediterranean coast of Turkey. Collected samples were analyzed for major ions and trace elements. Concentrations of anthropogenic species in rain water, such as  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , Zn, Cu, Pb are comparable to the concentrations reported for regions that affected from anthropogenic emissions. Although the concentrations of ions responsible for the acidity in precipitation is relatively high, pH of the rain water was 5.1 indicating extensive neutralization of acidity in rain. Alkaline soil was found to be responsible for the neutralization. Measured ions and elements showed well defined seasonal variations. Concentrations of crustal elements were high in summer and concentrations of marine elements were high in winter season due to season dependent generation mechanisms. Seasonal variations in the concentrations of anthropogenic species were not as pronounced as those observed in crustal and marine elements and ions. Sulfate concentration showed a statistically significant decrease between 1992 and 2000, but similar decrease was not observed in concentrations of  $\text{NO}_3^-$  and other anthropogenic species. Wet deposition fluxes of measured parameters showed seasonal cycles that are consistent with rainfall pattern in the region.

## INTRODUCTION

Chemical composition of precipitation has often been used to typify atmospheric quality around a sampling area. The sources for the ions and trace elements are a combination of marine, crustal and anthropogenic influences, and relative contribution of each influence dependent on the distance and importance of the source and climatological conditions of the region. Significant amount of study have been completed to find the characteristics of precipitation chemistry of Mediterranean atmosphere till now; Reference [8], [7], [4], [12], [5], [1] and [16] can be considered among these studies.

If the pollutants leading to acid rain are absent in the atmosphere, the pH of the precipitation of the clean atmosphere is slightly acidic due to dissolution of  $\text{CO}_2$  in rainwater [6]. A previously performed study revealed that pH of the Eastern Mediterranean is around 5.2 although the concentrations of major acid forming ions, sulfate and nitrate, were comparable with the values obtained for the regions with similar characteristics (i.e. emission profile, meteorology etc.) [2]. The obtained high pH value was attributed to the neutralization of acidity in precipitation by  $\text{CaCO}_3$  that is found in the local soil in considerable amount and also imported to the region with the Saharan incursions and  $\text{NH}_3$  from the fertilizer application or emission from the barns [1]. However, the role of  $\text{NH}_3$  in the neutralization process was found to be small as compared to the  $\text{CaCO}_3$ . In addition to crustal material,

Mediterranean region is a receipt of acid carrying air masses originating from south-eastern Europe including industrialized countries such as Italy [15].

After the protocol on the S emissions came into force in 1988 and revised further in 1994, there have been reductions in SO<sub>2</sub> emissions by more than one third in Europe. As a result of this, a declining trend in S deposition has been observed in Europe. Although NO<sub>x</sub> protocol took effect in 1988, reductions in NO<sub>x</sub> emissions have not been similarly successful [10].

The aim of this study is to find the chemical composition of the precipitation samples collected between 1992 and 2000 at a rural station located on the coast of Eastern Mediterranean. In addition to this, seasonal behaviors of the pollutants and the sources that have influenced the chemical composition of the precipitation have been discussed.

## EXPERIMENTAL

Only a brief description of experimental techniques will be presented in this manuscript, because detailed description of methods used for sampling and analysis are given elsewhere [1].

Daily, wet-only rain samples were collected between 1992 and 2000 at a rural station on the Mediterranean coast of Turkey at approximately 20 km west of Antalya (30.34 E, 36.47 N). The sampling station is located on a rock structure at a height of 20 m above the sea level. A total of 500 wet deposition samples were collected in the sampling period.

Two rain samplers were installed on the sampling platform. The first sampler used for the analysis of trace metals and major cations and the second sampler, which was used to collect samples for analysis of Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and NH<sub>4</sub><sup>+</sup>.

Collected samples were stored at 4°C until they were shipped to the central laboratory in Ankara. Their volume and pH were determined in a class-100 clean area. The volume of the samples was measured using calibrated sampling bottles. The pH of the collected samples was determined using a Radiometer PHM 80 portable pH meter equipped with a combination glass electrode.

Sulfate, NO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> ions were measured by ion chromatography using a Varian Model HPLC ion chromatograph coupled with VYDAC.302 IC anion exchange column. Ammonium ion was determined spectrophotometrically by Unicam 8625 UV-VIS spectrometer and other cations including Na<sup>+</sup>, K<sup>+</sup> and Ca<sup>2+</sup> were measured using a Perkin-Elmer model 1100B flame AES. Magnesium, Fe, Zn and Al were analyzed by flame AAS. Concentrations of Cu, Cd, Pb, Ni, Cr, V, and Mn in wet deposition samples were determined by a Perkin-Elmer HGA-700 electrothermal atomization system coupled to spectrophotometer.

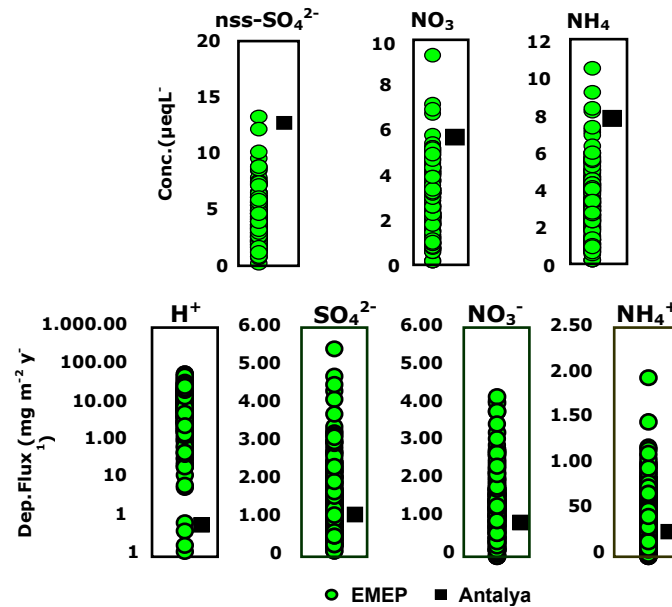
## RESULTS AND DISCUSSION

### *Composition of Rain*

Average and median concentrations of measured parameters and ranges observed between 1992 and 1993 are given in Table 1. As table reflects median concentrations vary between 0.4

**Table 1.** Average and median concentrations of elements and ions in the Eastern Mediterranean rain water

		Mean	Median	Range
pH		5.3 ± 0.81	5.3	6.9 – 3.0
SO <sub>4</sub> <sup>2-</sup>	mg/l	6.1 ± 10	3.2	97 – 0.30
NO <sub>3</sub> <sup>-</sup>	mg/l	3.4 ± 7.8	1.5	86 – 0.01
Cl	mg/l	22 ± 52	7.3	660 – 0.08
NH <sub>4</sub> <sup>+</sup>	mg/l	1.2 ± 1.3	0.77	8.9 – 0.01
Mg	mg/l	1,1 ± 1,4	0.5	8.6 – 0.01
Ca	mg/l	3.4 ± 4.5	2.1	38 – 0.10
K	mg/l	0.91 ± 2.0	0.34	16 – 0.03
Na	mg/l	6.5 ± 11	2.8	79 – 0.27
Cd	µg/l	1.4 ± 2.2	0.39	9.6 – 0.04
Cu	µg/l	27 ± 49	4.2	200 – 0.65
Pb	µg/l	17 ± 21	7.3	98 – 0.78
Al	µg/l	860 ± 1300	430	8400 - 30
Ni	µg/l	23 ± 25	14	160 – 1.3
Cr	µg/l	12 ± 13	7.9	66 – 0.42
Zn	µg/l	67 ± 71	42	410 – 3.0
Fe	µg/l	950 ± 1450	450	8700 - 87
V	µg/l	11 ± 17	3.1	73 – 0.87
Mn	µg/l	67 ± 51	50	240 - 30



**Figure 1.** Comparison of concentration and wet deposition fluxes of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{NH}_4^+$  with data reported from EMEP network

$\mu\text{gL}^{-1}$  for Cd and  $7.3 \text{ mgL}^{-1}$  for Cl. Another point that should be emphasized from the Table is that standard deviations are large. This is not due to the unsatisfactory sample collection or wrongly measurements of the samples but because of non-Gaussian distributions of elements and ions which is due to the daily varying meteorological conditions. Distributions of concentrations of measured parameters were tested using Chi-square test and found to be log-normal for most of the species. Concentrations of elements measured in Eastern Mediterranean were compared with similar data from over 100 EMEP stations covering whole Europe. Concentrations and wet deposition fluxes  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{NH}_4^+$  measured in this study and EMEP network are depicted in Figure 1.

It is clear from the figure that concentrations of  $\text{nss-SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{NH}_4^+$  measured in the Eastern Mediterranean precipitation are among the highest reported in whole Europe. As the Figure 1 depicts, these concentrations higher than corresponding concentrations reported for regions with a known acid rain problem like New York for which  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  concentrations were found as  $68$  and  $45 \mu\text{eqL}^{-1}$  whilst the values found in this study are  $113$  and  $70 \mu\text{eqL}^{-1}$ , respectively [11].

Anomalously high  $\text{SO}_4^{2-}$  ion concentrations in the Eastern Mediterranean aerosol was well documented previously [14], [9]. The Figure 1 demonstrates that  $\text{SO}_4^{2-}$  concentrations are also high in precipitation.

Another interesting feature in the Figure 1 can be drawn. Previous studies have demonstrated that although aerosol  $\text{SO}_4^{2-}$  concentrations are high in the Eastern Mediterranean, concentrations of other anthropogenic ions such as  $\text{NO}_3^-$  and  $\text{NH}_4^+$  in aerosols are not correspondingly high. Nevertheless, concentrations of these ions in precipitation are as high as  $\text{SO}_4^{2-}$ . This may be due to the incomplete sampling of aerosol  $\text{NO}_3^-$  by filters.

### ***Neutralization of Acidity***

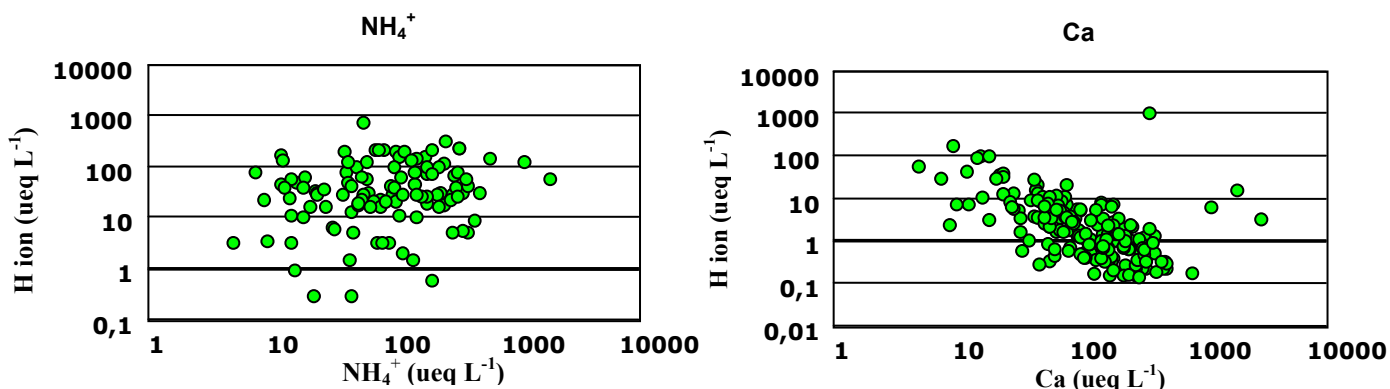
As stated in previous section considerably high concentrations of acidifying ions  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  in precipitation were detected in this study which generally implies fairly low pH in precipitation. However, pH of the rainwater collected over a long period of time in this study is not acidic and average pH is found as 5.2. Approximately 35 % of the rain events sampled had  $\text{pH} < 5.0$  and can be considered as acidic. Most of the acidic pH events occurred in winter season which is due to the scarcity of the ions taking part in the neutralization process.

The main theme of precipitation chemistry in the Eastern Mediterranean is the extensive neutralization of acidity. The relation between free acidity in precipitation and neutralizing agents  $\text{NH}_4^+$  and  $\text{Ca}^{2+}$  ions are given in Figure 2.

There is a significant correlation between H ion and Ca, suggesting that, unlike most part of the world,  $\text{CaCO}_3$  is primary neutralizing agent in the Eastern Mediterranean. The most common alkaline species which can neutralize rainwater acidity are  $\text{NH}_3$  and  $\text{CaCO}_3$ . For the areas where agricultural activities are high  $\text{NH}_3$  from the fertilizer can be main neutralizing agent. However,  $\text{CaCO}_3$  is more important neutralizing agent since the local soil is rich in  $\text{CaCO}_3$  and Saharan incursions bring considerable amount of  $\text{CaCO}_3$  rich soil to the region [2]. Quantitative neutralization of acidity by calcite is frequent in Mediterranean Sea [13].

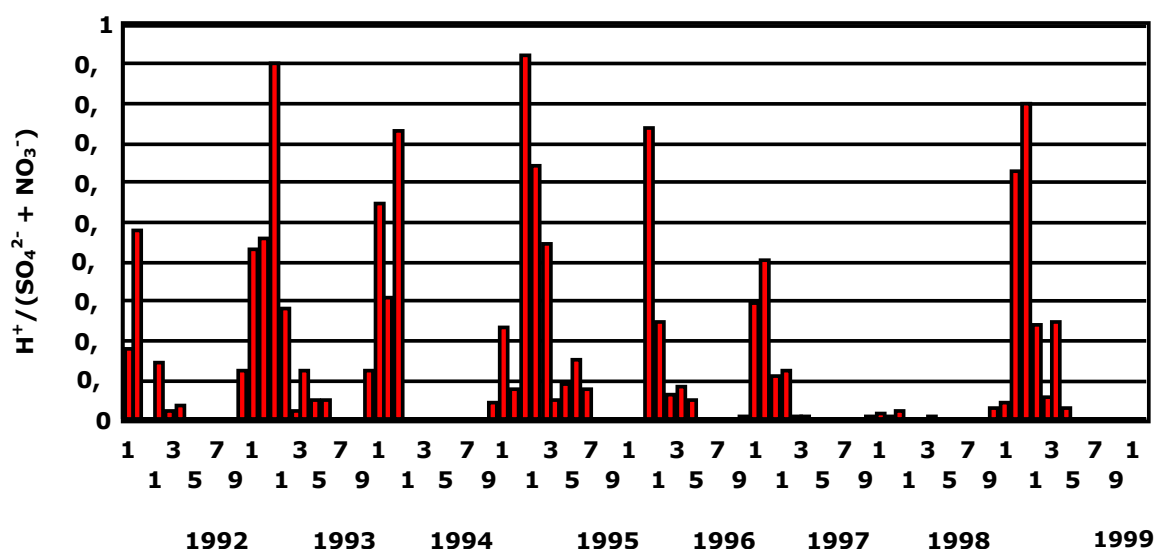
The equivalent ration of H ion concentration to the sum of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  concentrations ( $\text{H}/(\text{SO}_4^{2-} + \text{NO}_3^-)$ ) is a good indicator of the degree of neutralization in rain water. The ratio is

expected to be unity if there is no neutralization and deviation from unity indicates the degree of neutralization [3].



**Figure 2.** Relation between free acidity and  $\text{NH}_4^+$  and Ca concentrations in precipitation

To see the degree of neutralization, temporal variation of  $\text{H}/(\text{SO}_4^{2-} + \text{NO}_3^-)$  ratio between 1992 and 1999 is calculated and depicted in Figure 3. The ratio show highly seasonal pattern. It is close zero in summer indicating very extensive neutralization, but it is high in winter suggesting more acidic precipitation in winter.



**Figure 3.** Temporal variation of  $\text{H}/(\text{SO}_4^{2-} + \text{NO}_3^-)$  ratio between 1992 and 1999

This seasonal pattern in the neutralization process is consistent with the higher abundance of  $\text{CaCO}_3$  in the atmosphere during summer season. In the winter, wet soil conditions suppresses resuspension of soil particles resulting in low concentrations of soil and soil related elements in the atmosphere, as will be discussed in the subsequent section. However, in the summer season soil is dry and soil particles can easily become airborne even at mild wind speed.

Monthly average concentrations of selected elements and ions measured in this study are given in Figure 4. Most of the ions show well-defined seasonal variations.

Hydrogen ion concentration is high in winter and decrease to very low levels in summer, due to season dependent neutralization discussed previously.

Concentrations of marine elements Na and Cl, which is not shown in the Figure 4 have higher concentrations in winter. Sea salt aerosol is generated by bubble bursting in the immediate vicinity of the station. Higher wind speeds associated with frontal storms in winter generate high quantities of sea salt. Concentrations of these elements are low in summer due to milder winds.

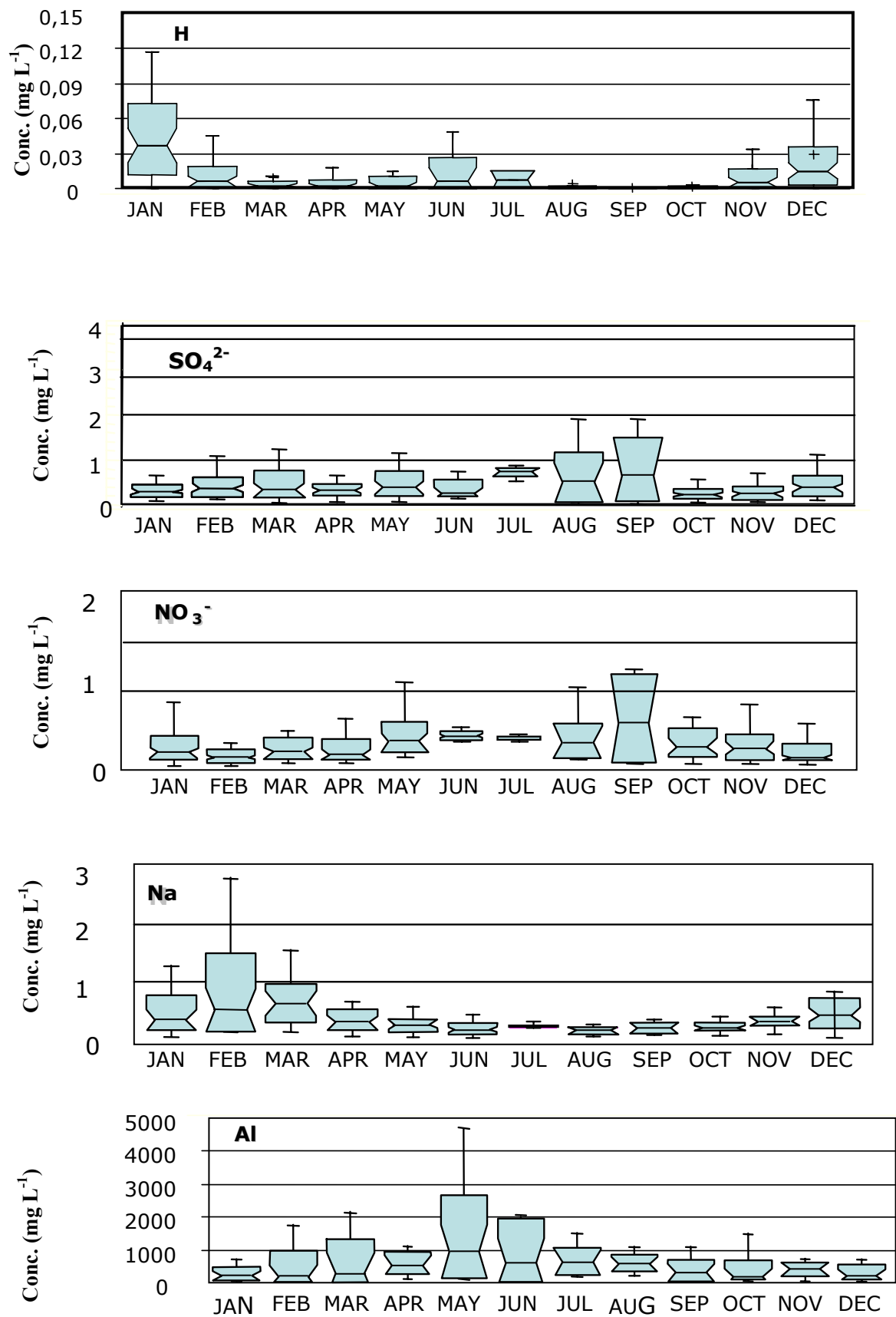
Concentrations of Al and other crustal elements such as Fe, Ca, Mn and V that are not shown in the figure are higher in summer season due to the abundance of airborne  $\text{CaCO}_3$  as discussed previously.

Concentrations of anthropogenic species depict two different seasonal behaviors. Sulfate,  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , Cd and Zn have higher concentrations in summer, whereas Pb has higher concentration in winter. Since these elements are transported to Eastern Mediterranean from distant source regions, they undergo more extensive wet scavenging during winter.

This can explain their observed high concentrations in summer. However, lead is an exception. Higher concentrations of this element in winter may be due to local sources of Pb. If Pb is emitted from local sources, as suspected, then its atmospheric concentrations would not be affected from rain scavenging as much as long-range transported species.

## CONCLUSION

The most significant finding of this study is high concentrations of acid forming sulfate and nitrate ions. Concentrations of these ions are among the highest reported values for Europe. Despite to this, the pH of the precipitation is not high as it is expected due to the extensive neutralization with the  $\text{CaCO}_3$  found abundantly as airborne. Crustal and marine elements show seasonal variation due to the different generation mechanism in summer and winter. Concentrations of crustal elements are high in summer since they can be easily uplifted by the action of wind and those of marine elements are high in winter due to increased occurrence of bubble bursting. Concentrations of anthropogenic elements like sulfate and nitrate transported to the region from distant sources are high in summer but low in winter due to the scavenging of the pollutants on the way to the sampling area by precipitation.



**Figure 4.** Monthly average concentration of selected elements and ions

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