

## Temporal variations of Eastern Black Sea aerosol

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Received: 24/05/2017, Accepted: 12/10/2017, Available online: 25/01/2018

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### Abstract

In this study, chemical composition of coarse (PM<sub>2.5-10</sub>) and fine (PM<sub>2.5</sub>) aerosols and their seasonal characteristics was used to investigate factors affecting seasonal variations in concentrations of species. Concentrations of 17 trace elements and SO<sub>4</sub><sup>2-</sup> were determined in coarse and fine aerosol samples collected at a high altitude (1115 m above sea level) site (Torul, 40°32'34"N 39°16'57"E) between March 2011 to November 2012 on the Eastern Black Sea region of Turkey. The samples were analyzed by energy dispersive x-ray fluorescence (EDXRF) using an Oxford ED-2000 Spectrometer. Measured concentrations varied between approximately 0.40 ± 0.7 ng m<sup>-3</sup> for As and 2070 ± 1270 ng m<sup>-3</sup> for SO<sub>4</sub><sup>2-</sup>. Soil-derived elements, Al, Si, K, Ca, Ti, V and Fe, had higher concentrations in the coarse fraction as expected. The results indicated that concentrations of elements showed well-defined seasonal variations. Crustal elements showed higher concentration in summer. Na, which is an element generally associated with sea salt had also higher concentrations in summer season, suggesting a strong crustal contribution to Na concentration at our station. Anthropogenic elements As, Zn, Pb and Cr had comparable concentrations in both seasons. Cu, Ni, and V, had higher concentrations in winter season due to sources close to sampling point. Crustal enrichment factors of Ni, Cu, Cr, As, Pb, Zn and SO<sub>4</sub><sup>2-</sup> varied between 12 for Ni and 800 for SO<sub>4</sub><sup>2-</sup>. Upper atmospheric flow climatology showed that most frequent flow direction was the sector between West and North, indicating the regions between these wind sectors are the potential source regions for the observed levels of species.

**Keywords:** Trace elements, Aerosol, Temporal variations, EDXRF

### 1. Introduction

Aerosols in the atmosphere originate from both from natural (wind-blown, sea spray, frost fires) and anthropogenic (fuel and biomass burning, industrial processes, traffic emissions) sources (Güllü *et al.*, 2005; Tokgöz, 2013). Global aerosols production estimates suggest that since they interact with solar radiation (IPCC, 2001) and effect micro-meteorological processes (Bhaskar and Mehta, 2010), aerosols may affect Earth's energy

balance and hence the climate (Öztürk *et al.*, 2012; Tecer *et al.*, 2012). Therefore, accurate data on the quantity and characteristics of pollutants at the source and receptor sites are required in order to assess perturbations in the biogeochemical cycles of trace elements (Rasmussen, 1998).

Aerosol composition is highly variable in space and time because of the diverse sources (Rostogi and Sarin, 2009). Temporal variations of concentrations depend on several factors including; their sources, transport pattern, and meteorological factors. Since most of these patterns change in time, chemical composition of atmospheric aerosol show short and long term variations (Solomon *et al.*, 1996).

Seasonal variations of particulate matter and factors controlling these variations have been reported in many studies (Carmichael *et al.*, 1996; Güllü *et al.*, 1998; Khillare *et al.*, 2004; Hueglin *et al.*, 2005; Kulshrestha *et al.*, 2009; Cheung *et al.*, 2011; Öztürk *et al.*, 2012; Zhang *et al.*, 2014). These studies have revealed that the seasonal variations of species measured in particulate matter depend on one or more factors of flow frequency from different wind directions (Güllü *et al.*, 1998; Zhang *et al.*, 2014), source type (Hueglin *et al.*, 2005; Kulshrestha *et al.*, 2009), particle scavenging (Öztürk *et al.*, 2012; Zhang *et al.*, 2014) and meteorology (Khillare *et al.*, 2004; Kulshrestha *et al.*, 2009). Several studies showed that the concentration of crustal elements is generally higher in the summer season than those on winter (Güllü *et al.*, 1998; Chakraborty and Gupta, 2010; Alharbi *et al.*, 2015), indicating the enhanced resuspension of soil particles during dry summer months. On the contrary, different seasonal variations in concentrations of crustal elements have been observed depending on the site location and meteorological properties such as wind speed, temperature and humidity (Kulshrestha *et al.*, 2009). Effect of particle scavenging on seasonal variations of species was also investigated (Güllü *et al.*, 1998; Karakaş *et al.*, 2004). Güllü *et al.*, (1998) concluded that the seasonal variations of species were mostly affected by particle scavenging rather than variation in upper atmospheric motions, since variations in the upper atmospheric motions were not large enough to cause

substantial seasonal variations in concentrations of measured species.

A modeling study conducted by Pervin (1991), has shown that the most of the  $\text{SO}_4^{2-}$  concentration at the Eastern Black Sea region of Turkey was originating from distant sources, and showing that the contribution of Turkey was very small. However, studies conducted in the Black Sea region of Turkey are scarce (Hacisalihoğlu *et al.*, 1992; Karakaş *et al.*, 2004; Doğan *et al.*, 2010; Tecer *et al.*, 2012). In this study size-distributed aerosol samples, ( $\text{PM}_{2.5-10}$  and  $\text{PM}_{2.5}$ ), were collected at a high altitude rural station located Eastern part of Black Sea region of Turkey. The station was established at a relatively pristine site, where there are no significant local sources, to investigate the factors affecting seasonal variations in concentrations of elements. This paper presents seasonal patterns in Eastern Black Sea aerosol.

## 2. Methodology

The sampling station was located at a log storage area of the Ministry of Forestry, which was located at approximately 5 km to southwest of the Torul village at the Eastern Black Sea coast of Turkey ( $40^\circ 32' 34''\text{N}$ ,  $39^\circ 16' 57''\text{E}$ ). Sampling station was surrounded by barren land. Altitude of the station was 1115 m above sea level. The station was approximately 70 km from the coastline and shown in Figure 1. Sampling was performed between March 2011 and December 2012. The sample collection period was 24 h for all collected samples and sampling were interrupted only to change filters. In total, 270 daily coarse and fine aerosol samples were collected.

Coarse ( $\text{PM}_{2.5-10}$ ) and fine ( $\text{PM}_{2.5}$ ) aerosol samples were collected on polycarbonate (Nuclepore) filters using Gent Stacked Filter Unit (SFU) (Hopke *et al.*, 1997). The SFU was operated at a fixed flow rate of  $16.7 \text{ l min}^{-1}$ . The initial and second filters were 47 mm in diameter with pore sizes of 8 and  $0.4 \mu\text{m}$ , respectively. Coarse and fine fractions of the aerosol were collected separately on these filters. The flow through filters will result in the collection of the particles with diameters larger than  $2.2 \mu\text{m}$  on the initial filter (coarse fraction). Those with diameters smaller than  $2.2 \mu\text{m}$  pass through the initial filter and were held on the backup filter (fine fraction).

Before and after sampling, coarse and fine filters were desiccated in a constant humidity chamber for 24 h to reach a constant humidity and weighed using microbalance (Sartorius, Model MC-5). Mass concentrations of fine and coarse particles were determined gravimetrically from the difference in filter weights before and after sampling.

Samples were analyzed using an energy dispersive X-Ray Spectrometer (EDXRF) (Oxford, model ED-2000) for trace elements including Na, Mg, Al, Si, S, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Ba and Pb at Sarayköy research center of the Turkish Atomic Energy Agency (TAEK). An Ag anode X-ray tube with maximum current of  $1000 \mu\text{A}$  and with maximum voltage of 50 kV was used as a source of excitation. The EDXRF was calibrated with spiked synthetic standards and accuracy of results were tested by running NIST SRM 2783 (Air Particulate Matter on Filter Media). More detailed description of the analytical system and blank levels are given elsewhere in Balcilar *et al.*, (2014).



Figure 1. Location of the sampling location

## 3. Results and discussions

Median values of measured species in the coarse and fine fraction aerosols are plotted in Figure 2. Concentrations in the data set varied between  $0.40 \pm 0.7 \text{ ng m}^{-3}$  for As and  $2070 \pm 1270 \text{ ng m}^{-3}$  for  $\text{SO}_4^{2-}$ . Karakaş, (1999) reported

background values at central Black Sea region of Turkey for As and  $\text{SO}_4^{2-}$  as  $1.6 \pm 1.6 \text{ ng m}^{-3}$  and  $4900 \pm 2900 \text{ ng m}^{-3}$ , respectively. Concentration of Na, a good marker element for sea salt, was fairly low compared to Na concentrations reported in Turkish coastal studies. Concentration of Na is

highly dependent on the distance between sampling station and coastline, which was 70 km in our case. Its concentration was higher in the coarse fraction. Although most of the coarse sea-salt particles deposit during 70 km transport from coast to our station, non-sea-salt Na comes from soil particles, which are also coarse. Therefore, occurrence of Na in coarse fraction is not surprising.

Concentrations of soil-derived elements, including Al, Si, K, Ca, Ti, V and Fe were higher in the coarse fraction, because soil particles have a mass median diameter between 3.0 - 3.5  $\mu\text{m}$  (Kuloglu and Tuncel, 2005). Coarse-to-fine ratios of these elements varied between 1.2 for K and 3.1 for Ca.

Concentrations of elements with mixed natural and anthropogenic sources (residual fuel combustion, metal processing), such as Ti, V, Cr, Mn and Ni had comparable concentrations in coarse and fine fraction particles. Since parts of their concentrations are due to presence of coarse soil particles, this is an expected pattern for these elements.

Pollution-derived elements measured in this work, including  $\text{SO}_4^{2-}$ , Cu, Zn, As and Pb had higher concentration in fine fraction. Their coarse-to-fine median ratios varied between 0.2 for  $\text{SO}_4^{2-}$  ion and unity for As. Sulfate ion had smallest coarse-to-fine ratio, which is followed by Pb (C/F ratio is 0.5). Coarse to fine ratios of elements is a reflection

of their size distribution in the atmosphere. Lead and  $\text{SO}_4^{2-}$  were reported to have smallest mass median diameter (0.7  $\mu\text{m}$  for Pb and 0.5  $\mu\text{m}$  for  $\text{SO}_4^{2-}$ ) in an impactor study performed at the Eastern Mediterranean (Kuloglu and Tuncel, 2005).

Summer and winter season median values of measured species are shown in Figure 3. Summer, in this study, is the period between May and October and winter is the remainder of the year. This division is based on the rainfall amount, because rainfall is one of the most important parameters affecting seasonal variation in concentration of elements (Güllü *et al.*, 1998; 2005). In the Black Sea region, approximately 80% and 20% of the precipitation occurs in winter and summer months, respectively.

Summer-to-winter median concentration ratios of elements varied between 1.92 for Al and 0.08 for V. Elements with the highest summer-to-winter ratio were crustal elements and  $\text{SO}_4^{2-}$ . Higher concentrations of crustal elements during summer, is due to easier resuspension of soil particles during the dry summer season. Since soil is damp or ice covered in winter, resuspension of local soil is less likely. This scenario results in higher concentrations of soil-related elements in summer. Concentration of  $\text{SO}_4^{2-}$  was also higher in summer owing to higher solar flux, which leads to faster gas-phase oxidation of  $\text{SO}_2$ .

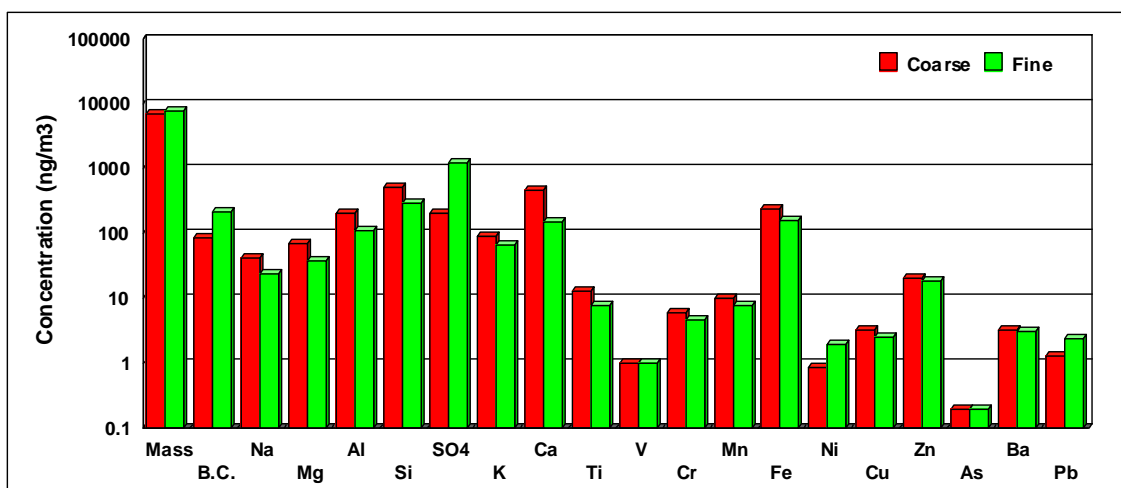


Figure 2. Median values of measured species in the Eastern Black Sea

Sodium is frequently used as marker element to quantify sea salt contribution to aerosol mass. Since more active storm activity over the sea generates higher quantities of sea salt during the winter season, higher concentrations of sea-salt elements are expected in the winter season. However, summer-to-winter median concentration ratio for Na, in this study, was 1.6, which is comparable to corresponding ratios observed in crustal elements. Higher Na concentrations during summer season are probably due to approximately 70 km distance between the coastline and our station. Since sea salt particles are coarse they are quickly scavenged from atmosphere within few kms from coastline and crustal contribution start to dominate Na concentrations at distances far from the coastline. A crude calculation using Al-to-Na ratio in Mason's (1966) crustal compilation, Al and Na concentrations in our samples

demonstrated that, on the average, more than 90% of observed Na concentration at Torul station could be accounted for by crustal aerosol, which explains higher concentrations of Na recorded in summer season.

Elements with mixed origin, like K, Ti and anthropogenic elements, such as As, Zn, Pb and Cr had comparable concentration in summer and winter seasons. This pattern is not unique and reported in many studies around the Black Sea and Eastern Mediterranean (Güllü *et al.*, 2005) and Black Sea (Karakas *et al.*, 2004; Tokgöz and Tuncel, 2015) basins. The only exceptions to this general pattern were observed in concentrations of Cu, Ni, and V, which have higher concentrations in winter season. This unexpected pattern could be an artifact for V because it was measured in only few samples during summer period,

but the pattern was real for Cu and Ni. Particle scavenging by rain is probably the most important factor affecting seasonal variations in concentrations of elements. Particles are scavenged from atmosphere more effectively in winter with frequent rain events during their transport from their source regions to Eastern Black Sea, which results in higher concentrations of elements in summer. Elements that have nearby sources are not affected from scavenging as much and can have relatively high concentrations in winter season as well. Thus, higher

concentrations of Ni and Cu in winter can be attributed to their local sources. Smelters at Samsun, Murgul (Artvin), Georgia and Ukraine (Dzubay and Stevens, 1984) may be the nearby sources that can affect seasonal variation in concentrations of these elements. Rain scavenging was shown to be the main reason determining seasonal variation in concentrations of elements at Eastern Mediterranean as well (Karakaş *et al.*, 2004; Doğan *et al.*, 2008; Koçak *et al.*, 2007).

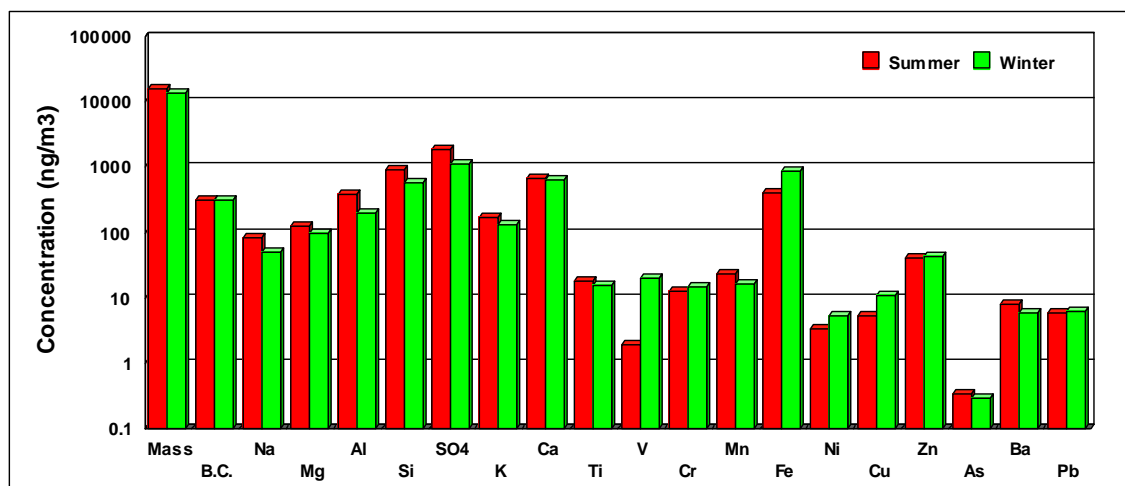


Figure 3. Summer and winter season median values of species

### 3.1. Crustal enrichment factors of elements

Chemical composition of the aerosols in the atmosphere is controlled by mixing of various natural and anthropogenic components and the extent to which the mixing occurs will vary both in space and time. Enrichment factors (EF), which provide qualitative information on the crustal and non-crustal components in aerosol population (Zoller *et al.*, 1974) are generally calculated relative to soil composition as soil is the most common component in aerosol population, EF can also be calculated relative to any source for which a reliable reference element is available.

Crustal Enrichment factor (EFC) of an element can be calculated using the following relation (Eqn. 1):

$$EFC = \frac{(C_x/C_{Al})_{sample}}{(C_x/C_{Al})_{soil}} \quad (1)$$

Where  $(C_x/C_{Al})_{sample}$  is the ratio of the concentration of the test element ( $C_x$ ) to that of Al in the sample.  $(C_x/C_{Al})_{soil}$  is the same ratio in soil. Aluminum is a generally used as crustal reference element, because its main source in aerosol is the crustal material (except for very small areas around Al plants) and it can be measured reliably using variety of analytical techniques. Other crustal markers, such as Fe, Sc, rare earths etc can also be used as crustal reference element. However, they are not as widely used either because they may have non-crustal sources (like Fe) or their measurements in atmospheric aerosol are not as easy as measurement of Al (like Sc, rare earth element). Global compilations of soil composition are used

to calculate  $(C_x/C_{Al})_{soil}$  in the relation. The EF values calculated in this work are based on the data given for the mean abundances of elements in the Earth's crust by Mason (1966). Since composition of local soil around the sampling point may be different from that of Mason's (1966) compilation, elements with EFC values < 10 are not considered as enriched. The EFC value of 1.0 (or <10) indicates that source of the element is exclusively crustal material. EFC values > 10 indicate enrichment and non-crustal source for the test element.

Enrichment factor of elements in, summer and winter seasons are given in Figure 4. Elements Fe, Na, Ti, Mg, K, V, Ba, Ca and Mn had enrichment factors <10 in both summer and winter seasons, indicating that there is no source other than crustal material for these elements.

Ni, Cu, Cr, As, Pb, Zn and  $SO_4^{2-}$  had enrichment factors between 12 for Ni and 800 for  $SO_4^{2-}$ . These are well documented anthropogenic elements and their enrichments are not surprising (Ho *et al.*, 2003; Kim *et al.*, 2009; Tecer *et al.*, 2012). In order to distinguish the natural and anthropogenic sources of the enriched elements, enrichment factor (EF) diagrams which are the log-log plots of crustal enrichment factors of elements vs. Al concentrations were generated. The EFC - Al plots of selected enriched elements are given Figure 5.

The EFC of crustal elements does not change with changes in Al concentrations resulting in a horizontal line in the EF diagram. The EF diagram of Ti is given in Figure 5 as an example.



Among those moderately and highly enriched elements namely, Cr and SO<sub>4</sub><sup>2-</sup> also given in Figure 5, indicating these elements have sources other than crustal dust. The EFC

values of these elements decrease with increasing Al concentration.

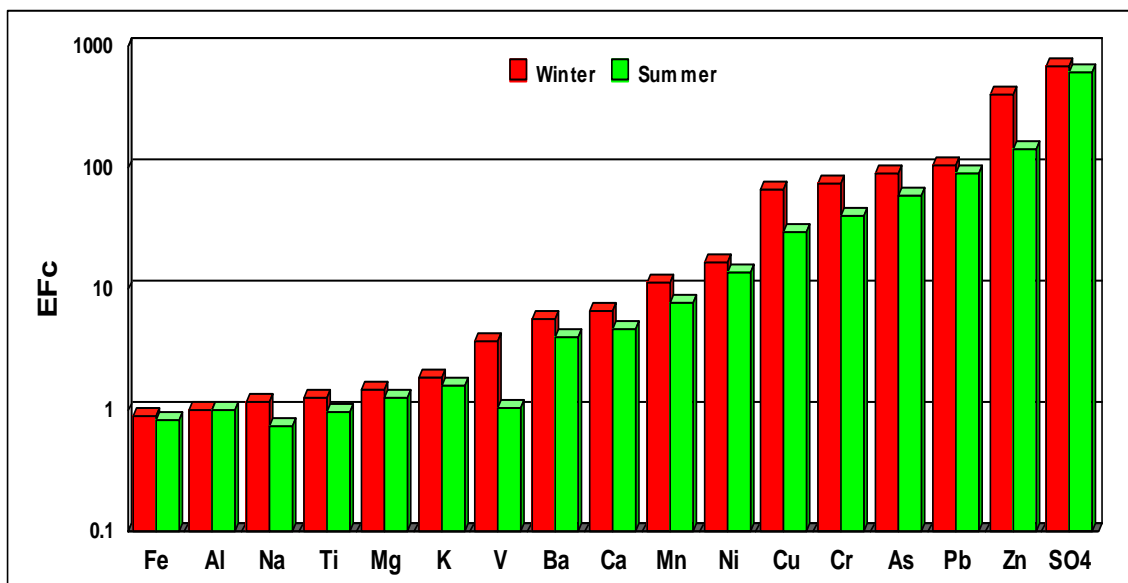


Figure 4. Seasonal crustal enrichment factors

3.2. Flow climatology

In order to assess long range transport of pollutants to the Eastern Black Sea atmosphere, both emission strength and frequency of flow from source regions are important for

the contribution of sources to measured concentrations of elements at the receptor. Therefore, it is essential to know flow frequencies at different wind sectors, which is also called flow climatology, to apportion sources at the sampling location.

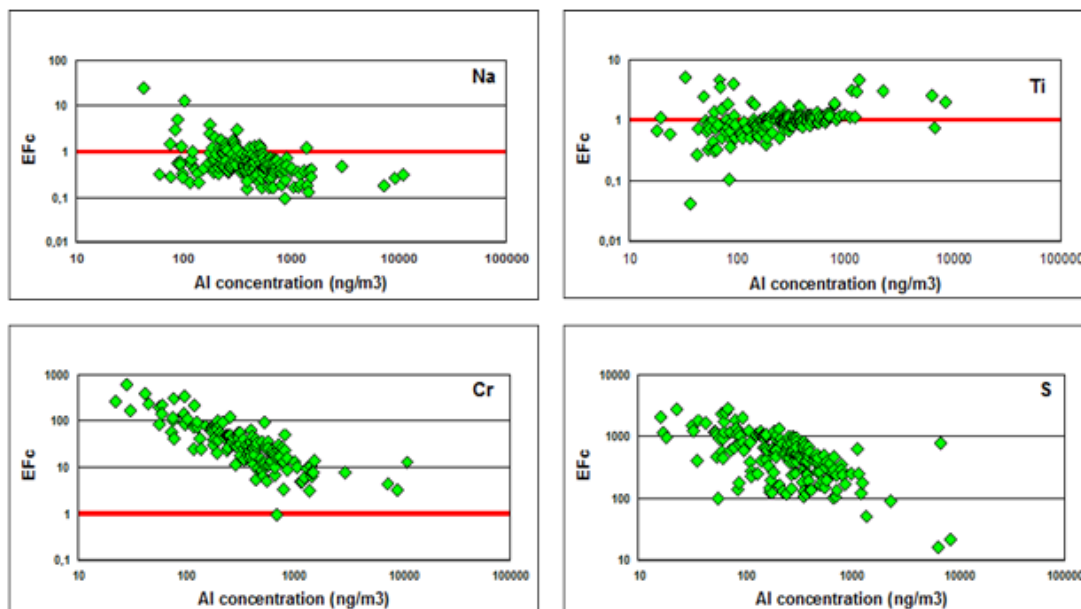


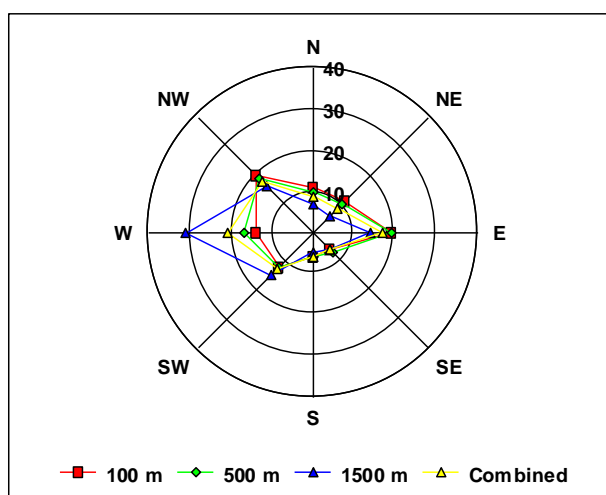
Figure 5. EFC versus Al concentrations of selected elements

In this study, the HYbrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) Version 4 (Stein *et al.*, 2015) model was used to determine flow frequencies at different wind sectors. Five-day back trajectories starting from the sampling station at 19:00 UTC at 3 different altitudes, namely 100, 500 and 1500 meter were calculated

for the years 2011 and 2012. Reanalysis meteorological data archive of the NOAA was used as input data for back trajectory calculations. Isentropic vertical motion method type was selected in the model calculation. Five-day long back trajectories were long enough to cover the major source regions that thought to be affecting Eastern Black

Sea atmosphere and they were not long enough to cause unreasonably high uncertainties. The trajectories were divided into hourly segments. As the trajectories were 5 day long, each trajectory was consisted of 120 segments. For each arrival heights 261 back trajectories were calculated. Calculated segments for 100, 500, 1500 meter were approximately 30000 and for combination of these 3 arrival height were approximately 95000.

The study domain was divided into 8 directional sectors as follows: North (N), North East (NE), East (E), South East (SE), South (S), South West (SW), West (W) and North West (NW). In order to understand flow pattern, each 1-hour segment obtained from back trajectories was assigned to a wind sector and the number of segments in each of the eight wind sectors were counted by using GIS software. The frequencies of airflow from each sector are presented in Figure 6.



**Figure 6.** Annual frequency of flow from each wind sector for 100, 500, 1500 m arrival height back trajectories and combined back trajectories (Numbers in the figure are the percent contribution of each sector)

The general pattern that is observed is higher contribution of W, NW and E sectors and particularly low contribution of SE and S sectors. Total contribution of W, NW and E is 56%. Such flow frequencies from these wind sectors reveal that countries such as Ukraine, Georgia and Russia are important source regions for the observed concentrations of pollutants (Tokgöz, 2013; Tokgöz *et al.*, 2012; Hacısalıhoğlu *et al.*, 1992; Dzubay and Stevens, 1984).

#### 4. Conclusions

Daily coarse (PM<sub>2.5-10</sub>) and fine (PM<sub>2.5</sub>) aerosol samples were collected between 2011 and 2012 at the Eastern Black Sea coast of Turkey, using a stack filter unit. Collected samples were analyzed for 17 elements, including Na, Mg, Al, Si, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Ba, Pb and SO<sub>4</sub><sup>2-</sup>. Most of the crustal elements occurred in coarse and most of the anthropogenic elements occurred in the fine fraction. Coarse-to-fine ratios of elements are related to their size distributions. Lead and SO<sub>4</sub><sup>2-</sup> are the species with the lowest C/F ratio and they are also the parameters with the smallest mass median diameters.

Concentrations of crustal elements are higher in summer season due to more effective resuspension of soil particles during dry summer months. Concentrations of anthropogenic elements were comparable in both seasons. Only concentrations of Cu and Ni were lower in summer season, which was explained by the presence particles from local sources.

Crustal enrichment factors of elements were <10 for soil-related elements and varied between 12 and 800 for elements with anthropogenic origin.

Upper atmospheric flow climatology showed that most frequent flow direction was the sector between W and N. Contribution of southern sectors to total flow was negligibly small.

#### Acknowledgement

This work was supported by the Scientific and Technological Research Council of Turkey (TUBITAK) Grant No 108Y306. We would like to thank General Directory of Forestry for allowing us to use their facilities for sampling.

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