CHEMICAL CHARACTERIZATION OF MICRONUTRIENTS IN THE ATMOSPHERIC PARTICLES

OVER THE EASTERN MEDITERRANEAN:

BIO-AVAILABILITY

AND

IMPACT OF ATMOSPHERIC INPUTS ON MARINE PRODUCTIVITY

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CHEMICAL CHARACTERIZATION OF MICRONUTRIENTS IN THE ATMOSPHERIC PARTICLES OVER THE EASTERN MEDITERRANEAN: BIOAVAILABILITY AND IMPACT OF ATMOSPHERIC INPUTS ON MARINE PRODUCTIVITY

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ABSTRACT

CHEMICAL CHARACTERIZATION OF MICRONUTRIENTS IN THE ATMOSPHERIC PARTICLES OVER THE EASTERN MEDITERRANEAN: BIOAVAILABILITY AND IMPACT OF ATMOSPHERIC INPUTS ON MARINE PRODUCTIVITY

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Bulk aerosol samples were collected using a high volume sampler at a rural site (Erdemli) on the coast of Eastern Mediterranean. The sampling was carried out on a daily basis between April 1 – 30 2015 and July 20 – August 20, 2015, and intermittently before April (n=68). The sampling periods were chosen to reflect the aerosol population such as, Saharan dust dominated, mixed and anthropogenic dominated. In addition to high-volume sampling, wet deposition samples were also collected covering the same period and the samples were segregated by size via filtration. An acid digestion scheme was applied to samples for total concentrations. For speciation of elements, a preconcentration setting of serially connected cationic and anionic exchange columns was applied to selected samples. Samples were selected according to their air mass back trajectory history to reflect their sources and origins. All samples were analysed with ICPMS for the elements of interest (Al, Fe, Mn, Co, Cr, Ni, V, Ca, Cu, Zn, As, Cd, Pb and P)

Clear reciprocal relationship was established between dust episodes and elements of crustal origin. Soluble fractions of elements were separated from total concentration, and anionic and cationic forms of soluble part was determined to assess their bioavailability, as anionic forms of trace elements are generally associated with organic complexation. It has been observed that major fraction of soluble Al is found in anionic form, while the concentration of anionic soluble Fe is 1.2 times greater than of cationic Fe. It has been established that contribution of polyphosphates to water soluble phospates can reach up to 20%. The two main sources of phosphorus was determined to be mineral dust and agriculture, accounting for 34 and 33 % of total concentration, respectively.

Surface waters which were obtained from both coastal and open waters were treated with atmospheric dust of two different compositions. In the course of experiments, chlorophyll-a was recorded to increase in all treatments while phosphorus was assimilated from the medium down to 0,3 nM. Results of the atmospheric dust addition experiments confirmed the effect of aerosols, as Chl-a concentration increased up to 4-fold with regard to controls, in both coastal and open water samples alike.

Keywords: Eastern Mediterranean, atmospheric aerosols, marine productivity, micronutrients.

ÖZ

DOĞU AKDENİZ ATMOSFERİK PARÇACIKLARINDA MİKRO BESİN TUZLARININ KİMYASAL KARAKTERİZASYONU: BİYOKULLANILABİLİRLİK VE ATMOSFERİK GİRDİNİN DENİZSEL ÜRETKENLİĞE ETKİLERİ

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Doğu Akdeniz kıyısında bulunan Erdemli yakınlarındaki kırsal örnekleme alanında yüksek debili örnekleyici kullanılarak aerosol örneklemesi yapıldı. Örnekleme 1 – 30 Nisan 2015 ile 20 Temmuz – 20 Ağustos 2015 tarihleri arasında ve Nisan öncesindeki dönemde aralıklı olarak gerçekleştirildi (n=68). Örnekleme dönemleri Sahra kökenli, antropojenik kökenli, ya da kaynak bakımından karışık aerosol popülasyonlarını yansıtmak üzere seçildi. Yüksek debili örneklemeye ek olarak, aynı dönemi kapsayan yaş çökel örneklemesi yapıldı ve örnekler filtreleme yoluyla tanecik boyutlarına göre ayrıldı. Asit ile kimyasal özütleme şeması toplam derişimlerin tayini için tüm örneklere uygulandı. Anyonik ve katyonik değişim kolonlarının seri olarak bağlanmasından mürekkep bir prekonsantrasyon düzeneği ise seçilmiş örneklerin türleştirilmesinde kullanıldı. Örnekler geri yörünge tarihlerine bakılarak, farklı kaynak ve kökenleri temsil edecek biçimde seçildi. Tüm örneklerde ilgili elementlerin (Al, Fe, Mn, Co, Cr, Ni, V, Ca, Cu, Zn, As, Cd, Pb and P) analizleri ICPMS ile yapıldı.

Toz olayları ile toprak kökenli elementler arasında açık bir mütekabiliyet ilişkisi olduğu tespit edilmiştir. Elementlerin çözünebilir kısımları toplam derişimden ayrılmış, anyonik form genel olarak organik komplekslerle ilişkilendirildiğinden çözünebilir kısmın anyonik ve katyonik formlarının oranları biyokullanılabilirliğini değerlendirmek üzere tayin edilmiştir. Alüminyum iz metalinin büyük bir kısmı anyonik forumda gözlenirken demirin anyonik formunun katyonik formuna kıyasla

1.2 kat daha yüksek olduğu görülmüştür. Polifosfatların suda-çözünebilir fosfatlara % 20’ler seviyesinde katkı yapabileceği anlaşılmış, aerosol fosforun mineral toz (% 34) ve tarımsal (% 33) olmak üzere başlıca iki ana kaynağı olduğu anlaşılmıştır.

Hem Kıyı hem de Açık istasyonlardan elde edilen yüzey sularına iki değişik içeriğe sahip toz eklenmiştir. Deneyler süresince klorofil miktarının artış sergilediği gözlenirken fosforun ortamdan çekilerek 0,3 nM seviyelerine düştüğü tespit edilmiştir. Yapılan atmosferik toz ekleme deneylerinin sonuçları, toz eklenen hem kıyı hem de açık su örneklerinde kontrol gruplarına kıyasla 4 kata kadar Chl-a artışı göstererek aerosollerin denizsel üretime etkisini teyit etmiştir.

Anahtar Kelimeler: Doğu Akdeniz, atmosferik aerosoller, denizsel üretim, mikro besin tuzları.

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1 INTRODUCTION

1.1 Aim of the Study

Earth’s ocean, covering more than two thirds of the Earth’s surface is an undeniable source for human existence. It is estimated that the economic contribution of the ocean to the global economy is about $ 24 trillion, and annual wealth it provides amounts to an approximate $ 2.5 trillion (WWF, 2015). Besides the economic and social importance, oceans absorbs about one third of the human originated carbondioxide emission and produce roughly the half of the oxygen in the atmosphere.

Aprroximately % 25 of the World’s ocean is characterized as High Nutrient Low Chlorophyll (HNLC) areas (Boyd et al., 2007) while a striking % 60 is considered Low Nutrient Low Chlorophyll (LNLC) area (Guieu et al., 2010). It has been well established through the iron fertilization studies carried out in the 1990s and 2000s that HNLC regions of ocean principally lack the essential micronutrients such as iron and other trace elements in order to sustain marine phytoplankton growth (Martin, 1990; Martin et al., 1990, 1994; Coale et al., 1998; Landry et al., 2000). Thus, long range transport of aerosol particles to the marine environment has potential to modify the nutrient cycles in marine ecosystem and moreover has a direct effect on radiative forcing, when these two factors combined, effect of dust can be a significant component of climate change in a global scale. (Martin et al., 1990; Martinez-Garcia et al., 2011). The studies carried out in the HNLC and LNLC regions of the oceans during the last twenty years have shown that input of micro- and macronutrients to the marine ecosystem has been strongly affected by atmospheric aerosols and under certain seasonal and geographical conditions, atmospheric input becomes the predominant source of nutrients (Herut et al., 1999; Kubilay et al., 2000; Markaki et al., 2003; Koçak et al., 2010).

The aforementioned studies have emhpasized that atmospheric input impacts macronutrient and trace elements cycles and can modify phytoplankton composition and biotic processes such as marine primary production. In addition to their biogeochemical impacts, atmospheric aerosols can also modify the radiative budget of the world by absorbing, refracting and scattering the sunlight and reflecting radiation from the Earth's surface (Charlson et al., 1987; IPCC, 2007). Radiative forcing generated by the atmospheric aerosols were calculated to be -1.2 W m^{-2}, and be able to companstate about half of the radiative forcing caused by greenhouse gases (2.63±0.26 W m^{-2}) (IPCC, 2007). Moreover, aerosols play an importan role in water vapor nucleation; they influence formation, size and other properties of cloud droplets, which in turn affects the radiative properties and distribution of rain clouds (Ramanathan et al.; 2001). They provide a reaction surface for phase transformation of many chemical species; during their long range transport, they can interact with nitrous, sulfurous and organic species (particle, liquid and gas) (Mamane and Gottlied, 1989, 1992) which in turn, alter and affect the physical (such as optical) and chemical (such as solubility) properties of aerosol particles (Spokes et al., 1994; Arimoto, 2001).

It has also been demonstrated that aerosols can provide K, P, N, Fe and other trace elements to land and marine ecosystems (Avila et al., 1998; Guerzoni et al., 1999). Atmospheric Fe input to the marine ecosystem can enhance marine primary production in especially HNLC regions and play an importan role on CO_2 export to the ocean (Coale et al. 1998; Bakker et al., 2001). In this way, atmospheric trace element input can play a key role in sustaining marine production, wherein the marine production is limited by micro- or macronutrients. There are two possible outcomes of atmospheric input in marine ecosystems. If marine production is not limited by any of the essential nutrients, the ecosystem will not respond to the atmospheric input and no net change in primary production, phytoplankton biomass, species composition, atmospheric CO_2 uptake or abundance of biogenic sulfurous compounds will be observed. On the other hand, in a nutrient limited marine region (such as the Eastern Mediterranean), the ecosystem will respond to the atmospheric nutrient input, and changes in markers such as primary production rate, phytoplankton biomass, biological species composition, atmospheric CO_2 absorption, chl-a concentration will be observed. An increase in the primary producers will also have economic implications as it will support the biomass increase in higher trophic levels such as fish.

The present study aims to (i) identify temporal variability of aerosol trace metal composition on both seasonal and daily scales, (ii) determine the origin and source areas of atmospheric aerosols by applying air mass back trajectory, positive matrix factorization, and assess the influence of different sources (such as mineral dust events and anthropogenic activities) over the general chracteristics of aerosols in the Eastern Mediterranean, (iii) carry out the speciation of water-soluble fraction of trace metals and phosphorus species in atmospheric particles, dry and wet deposition modes, in order to determine their ‘bioavailability’ in marine systems and (iv) evaluate the impact of atmospheric deposition on the ecosystem of the Eastern Mediterranean surface waters by adding compositionally different atmospheric samples in a controlled experimental environment, i.e., performing a microcosm dust addition experiment.

1.2 Overview

Considering the nutrient abundance and primary production, the Mediterranean sea is extremely oligotrophic. The anti-estuarine circulation between Atlantic ocean and the Mediterranean can be the reason behind the observed oligotrophy; the nutrient-rich deep waters are discharged to the Northern Atlantic through Gibraltar while the limited nutrients in the surface water coming in from the Atlantic Ocean are rapidly assimilated and nutrient-poor water is transported eastward (Hamad et al., 2005). In addition, the impact of riverine input is limited to coastal areas. The annual primary productivity of the Mediterranean Sea is about half of the ultra-oligotrophic Sargasso Sea (Krom et al., 2004; Pitta et al., 2005). As can be seen in the satellite image in Figure 1.2.1, the productivity of the Mediterranean is extremely low compared to the North Atlantic and Black Sea, and the production decreases in the eastward direction. In accordance with these fact, uniquely high N/P ratio becomes higher from the west (22) to the east (25-28) (Krom et al., 1991; Yılmaz and Tuğrul, 1998), indicating a more severe P deficiency in the Eastern Mediterranean.

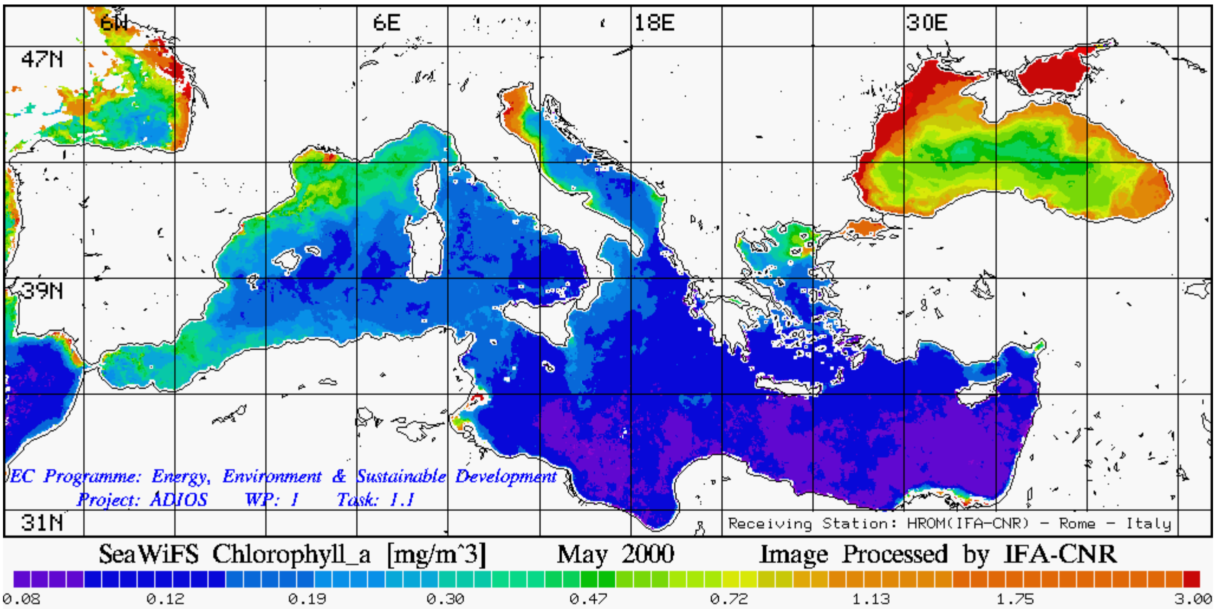


Figure 1.2.1 Sea WiFS satellite image showing average chl-a concentration in May 2000 (Santoleri et. al., 2016).

The Mediterranean is one of the highest mineral dust receiving region in the world (Guerzoni et al., 1999; Kubilay et al., 1995, 2000; Koçak et al., 2004a), due to its proximity to the arid and desert areas of North Africa and the Middle East. Hence, it has been emphasized that the nutrients (P, Fe and other essential trace elements) carried by long range transport mechanisms and introduced to the surface waters can caues biogeochemical changes (Herut et al., 1999; Markaki et al., 2003; Carbo et al., 2005). For example, dust addition experiment carried out by Herut et al. (2005) demonstrated that introduction of mineral dust may increase chl-a and primary production rate up to 5 times.

Natural and anthropogenic aerosols can be transported for thousands of kilometers, through countries and continents by the atmosphere and can contribute to atmospheric particle loading on a global scale. Human originated pollutants were determined in both northern (Tuomi et al., 2003) and the southern (Lowenthal et al., 2000) polar regions, and it is understood that pollutants add to a significant amount of the total aerosol budget. On the other hand, it has been demonstrated that Saharan mineral dust can and does influence, via long range tranport, the North Atlantic (Carlson and Prospero, 1972), Europe (Borbely-Kiss et al., 1999), the Western Mediterranean (Loye-Pilot et al., 1986; Rodriguez et al., 2001), the Eastern Mediterranean (Kubilay and Saydam, 1995; Kubilay et al., 2000; Herut et al., 2001; Koçak et al., 2004a)

In the case of the Mediterranean, Kubilay et al. (2000) showed that North African dust is transported by cyclone systems, and dominate the region in the transitional seasons of spring and autumn. The study of Lelieveld et al. (2002) demonstrated how anthropogenic aerosols affect the Mediterranean basin in summer period. According to this research, boundary layer of the Mediterranean atmosphere is exposed to the influences from Europe, while pollutants originating from Asia and even North America can be traced in the middle and the upper troposphere in the region. It should be emphasized that high concentrations of anthropogenic pollutants are chiefly associated with industrial European countries such as Ukraine, Russia, Greece, France, Spain and Turkey (Güllü et al., 2005), while mineral dust is characteristically associated with Libya, Algeria, Mali, Mauritania, Western Sahara and Bodele (Koçak et al., 2009)

For this research, atmospheric samples were collected in the atmospheric sampling tower stationed in the Middle East Technical University Institute of Marine Science campus, in the vicinity of Erdemli. The atmospheric samples can be classified into three sub-categories as (a) aerosol, (b) wet deposition (rainwater) (c) dry deposition. The aerosol samples were collected on a daily basis while rainwater samples were episodic. The frequency of dry deposition samples was 1 to 2 weeks. However, dry deposition samples were found to be contaminated by animals (insects and birds mostly) and were proven unsuccessful through the analyses therefore they were not used in the study. For the dust addition experiment, near surface water (depth: 10 m) samples were taken from both coastal and open stations.

1.3 Literature Review

During the last thirty years, atmospheric aerosol studies increasingly gain importance and precedence, expanding the collective knowledge on the subject. These studies cover many different regions and areas of the globe. The researchers investigated the long range transport of aerosols (Carlson and Prospero, 1972) and their impact atmospheric chemistry (Mamane and Gottlied, 1989; Dentener et al., 1996), global and regional climate change (IPCC, 2007), biogeochemical cycles (Bakker et al., 2001) and public health (Salma et al., 2002). Both in the Eastern Mediterranean and the other regions of the world, many scientific studies regarding the elemental and water-soluble contents, size distribution, temporal variability, transport and origin of atmospheric particles have been carried out (Prospero, 1981;

Arimoto et al., 1989; Kubilay and Saydam, 1995; Güllü et al., 1998; Al-Momani et al., 1998; Özsoy and Saydam, 2001; Mace et al., 2003; Kindap et al., 2006; Kuloğlu and Tuncel., 2005; Türküm et al., 2008; Doğan et al., 2008; Yatkın and Bayram, 2008; Karaca et al., 2009; Tecer et al., 2012). In these researches, it can be seen that atmospheric particle samples are typically collected via cellulose, quartz, PTFE or polycarbonate filters, either as size-segregated or in bulk. It can be also seen that a common procedure for dry and wet deposition is filtration of samples through filters with pore size of 0,45 µm or 0,2 µm. Total element concentrations are usually determined by dissolving elements in the solvent phase, and this is typically achieved through nitric and hydrofluoric acid digestion. Once the samples are dissolved, elemental analysis is commonly carried out by the use of atomic absorption spectrometry (AAS), inductively coupled plasma mass spectroscopy (ICPMS). On the other hand, even though separation of soluble fractions by anionic and cationic ion exchanger recins is a well established technique used in river and sea researches (Jiann and Presley, 2002; Wen et al., 2006), application of this method is limited in the Mediterranean. Nimmo and Chester (1993) performed speciation of Co and Ni in the rainwater samples collected from Western Mediterranean by using Cathode Stripping Voltametry (CSV) and found out that % 25 and % 44 of soluble Ni and Co are bound to organic ligands, respectively. Aerosol addition experiments focus on the possible impacts of dust on marine production (Herut et al., 2005) while limited studies have demonstrated the possible toxic and deteriorating effects of atmospheric particles on phytoplankton communities (Paytan et al., 2009). Regarding the origin and source of phosphorus, Graham and Duce assert that “Phosphorus may be injected into the atmosphere on soil particles as a result of erosion by wind, in spores, fungi and pollen that result from biological activity, on sea-salt particles derived from oceans and as emissions due to man's industrial and agricultural activities” (1979). Moreoveri polyphosphates such as tripolyphosphate and trimetaphosphate are known to found in bacteria (Graham and Duce, 1981).

2 MATERIALS AND METHODS

2.1 Sampling Site

2.1.1 Atmospheric Sampling Site

Aerosol filter, wet and dry deposition samples were collected on top of the sampling tower which is 22 m tall, and 10 m away from the sea, located in Middle East Technical University Institute of Marine Science (METU-IMS) Campus (36° 33' 54" N and 34° 15' 18" E) (Figure 2.1). The average proximity of sampling site to the major pollutants is 10-50 km, thus, site is classified as rural (Putaud et al., 2002). The immediate vicinity of the station is densely populated with cultivation areas; typically lemon groves and greenhouses. Mersin, with an approximate population of 800000, is 45 km to the northeast and hosts soda, chromium and fertilizer industries (Kubilay and Saydam, 1995; M. Koçak et al., 2012). The climate displays Mediterranean characteristics, with temperate winters and dry, hot summers. Seasons vary notably in length. For instance, relatively long springs are characterized by changeable weather and North African cyclones (Kubilay et al, 2000), while considerably shorter autumns exhibits similarly unsettled weather (Brody and Nestor, 1980).

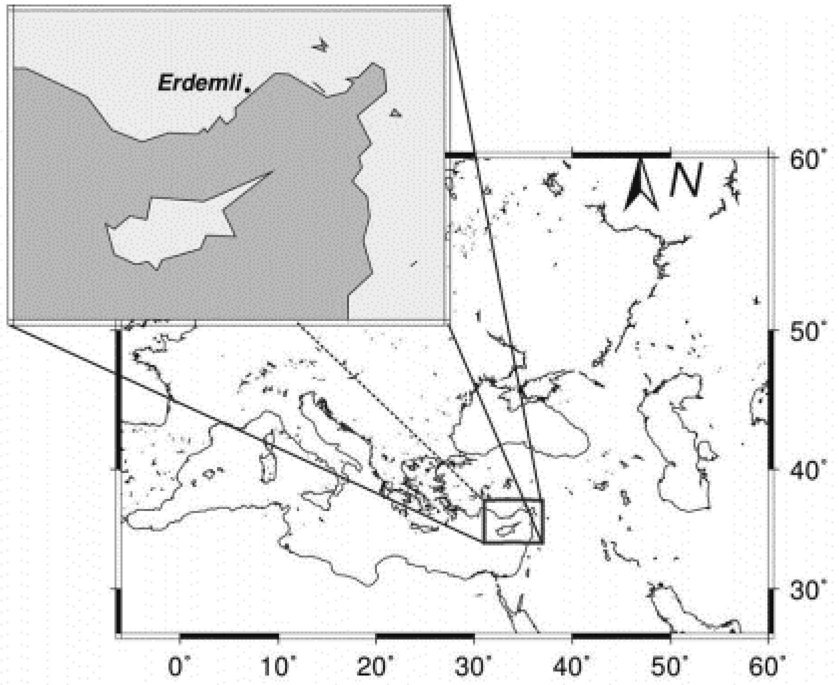


Figure 2.1.1 Geographical position of the sampling site within the Eastern Mediterranean area.

2.1.2 Marine Sampling Site (For Bioassay)

Figure 2.2 shows the coastal (Depth: 100 m, 36.51 N, 34.29 E) and open (Depth: 200 m, 36.44 N, 34.34 E) stations from which the water samples that are used in. While coastal station is affected by riverine input at times, open station remains unaffected by such influences.

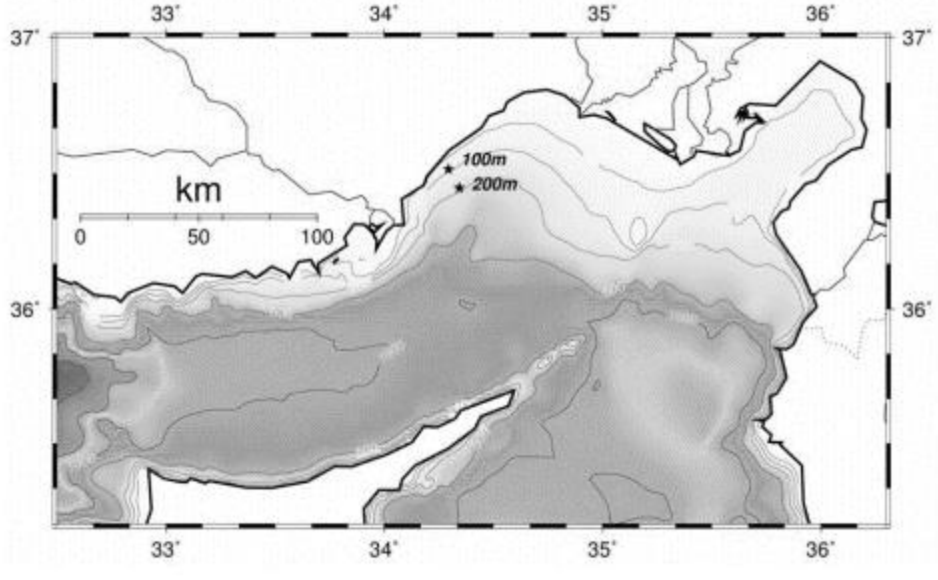


Figure 2.1.2 Geographical position of coastal and open stations from which the bioassay samples were taken.

2.2 Sample Collection

2.2.1 Collection of Atmospheric Samples

Collection of aerosol filters was carried out between February and August 2015. Samples were collected on a daily basis, and the sampling was only interrupted due to technical failures or periodical maintanence. Samples were collected by using a high volume sampler which obtains samples in bulk. Along with atmospheric aerosol samples, dry and wet deposition samples were also collected. With the high volume sampler the sampling was carried out for one month on a daily basis from April 1st to April 30th, 2015, and another month between July 20th and August 20th, 2015, In addition to these, sampling during February and March was carried out intermittently as to reflect dust events within this period (n=68). The samples collected for the study was given in Table 2.2.1.

Campaign for collection of dry and wet deposition samples spanned a greater period of time. The wet/dry deposition sampling covered the period from October 2014 to August 2015. Rain sampling was carried out after every rain event, while dry deposition sampling was done weekly or bi-weekly throughout the same period of time. As can be seen in the Table 2.2.1. 21 individual rain event were sampled in the period, while a great majority of the rain samples belonged to the time period between October 2014 to April 2015.

Table 2.2.1 Atmospheric samples collected for the study.

Sample /Analysis	January - March 2015	April 1-30 2015	July 20 – August 20 2015	Total
Bulk Aerosol Filter	8	30	30	68
Aerosol total trace metals	8	30	30	68
Phosphorus species	8	30	30	
Soluble fraction speciation	-	14	-	14
Wet Deposition	10	3	1	21*
Aerosol total trace metals	10	3	1	21*
Phosphorus species	10	3	1	21*
Soluble fraction	10	3	1	14

(a) Preparation of filters: Whatman-41 filters which were used with high volume sampler, were kept in %10 suprapur nitric acid for 24 h, in order to minimize trace metal blank contributions, and rinsed with Milli-Q water 3 times. The filters were then dried in a laminar flow hood. Polycarbonate filters (Whatman Track Etched d: 47mm) which were to be used in filtering dry and wet deposition samples were first washed with % 1 HNO_3 for 24 hours and washed with Milli-Q water 3 times. Afterwards, filters were equilibrated for at least 24 hours (at ~20 ˚C and ~% 50 relative humidity), weighed (with 0.01 mg sensitivity), labeled and stored in petri dishes.

(b) High Volume Sampler: Bulk aerosol sampling was carried out with high volume sampler (vacuum rate: 1 $m^3 min^{-1}$) and Whatman-41 filters (20 cm x 25 cm, cellulose nitrate). In order to reduce blank contributions, filters were treated with suprapur HNO_3 for 24 hours and washed with Milli-Q water 3 times. The filters were then placed in laminar flow hood to dry.

(c) Automatic Wet/Dry Atmospheric Deposition Sampler: Dry and wet deposition samples were collected with automatic dry/wet sampler (ARS1000, MTX, Italy) with a rain sensor, and 0.07 m^2 cylindirical plastic containers. Wet deposition samples were immediately collected after every rain event, while dry deposition samples were collected weekly with the help of 150 mL Milli-Q water (18.2 Ω). Both dry and wet deposition samples were immediately filtered through serially connected filters with pore sizes 2 and 0.4 μm. For comparison of trace metals with the subsamples obtained from 0.4 μm, an additional 0.05 μm filtration was applied to samples. However, since dry deposition sampling container was fully exposed to the external effects, they were contaminated (especially by birds and insects) beyond reparation. Thus data obtained from the analysis of dry deposition samples were dismissed and were not used in this research.

(d) Storing Samples After Collection: Aerosol samples were refrigerated to -20˚C immediately after collection and/or filtration, including dry and wet deposition samples.

2.2.2 Collection of Bioassay Samples

During the sea cruises samples were taken from both coastal and open stations at 10 m depth with the use of Niskin bottles. In order to carry out the atmospheric dust addition experiment, 400 L near surface water (depth: 10 m) was collected from both stations, and filtered with the zooplankton mesh with a pore size of 200 μm and directly transferred to the containers which were used throughout the experiment. In addition to the seawater samples, aerosol samples from two distinct periods of time were also collected to be used in the dust addition experiment. The dust samples to be used in the experiment was collected via pre-cleaned plastic trays, on the aforementioned tower. The first batch of dust was collected in the January 2015 and the second batch was collected in April 2015. First batch which was collected in the winter was darkish in color and of mixed origin, while the latter was of dominantly crustal origin and have a lighter shade as later chemical analysis indicated. Therefore the first batch of aerosol samples were named as Dark Brown (DB), and the nex batch Bright Brown (BB) and this labeling was applied throughout the experiment.

2.3 Sample Preparation

2.3.1 Atmospheric Samples

(a) Inductively Coupled Plasma Mass Spectroscopy (ICP-MS): In order to carry out trace metal measurements with the ICP-MS instrument, all samples require to be in solution phase. Two general procedures were applied for preparation of the samples for the ICP-MS. One is total acid digestion which is used to determine the total abundances of trace elements in the samples, and the other is the use of exchange columns for determination of soluble forms.

(1) Total Acid Digestion: For determination of total metal concentrations, an open digestion scheme was adopted. 1/8 of each Whatman 41 filter was cut with the help of pre-cleaned nylon thread, and put in PTFE digestion vessels which were also pre-cleaned, acid washed, and subjected to reflux with concentrated HNO_3 for at least 24 hours, and then rinsed with deionized water. The deionized water used in the last step was, in addition, passed through serially connected columns packed with analytical grade Chelex 100 and AGMP-1 respectively, in order to achieve the minimum trace metal concentration. Into each vessel, 12 ml concentrated (%65 w/w) suprapur HNO_3 was added, and the containers were kept on a hot plate, temperature set to 120° C for 72 hours, with lids on. After the first 48 hours, 3 ml suprapur HF is added to containers in order to leach mineral lattices, and thus maximize recovery rates. In the final day, lids of the containers were removed to let evaporization. During the evaporization, into each container, 2 ml aliquots of HNO_3 were added three times to ensure the removal

of residual HF. When the acidic solution left in the vessels reduced to an approximate 2 ml, vessels were removed from heat, the solutions were transferred into pre-cleaned containers and diluted to 50 ml, with the aforementioned column-grade deionized water.

For analysis of particulate and colloidal fraction i.e., the material retained by polycarbonate filters, in the rainwater and dry deposition samples, the same acid digestion scheme was applied to the polycarbonate filters.

(2)Partitioning and fractionation of soluble species of trace elements: Separation of anionic and cationic species of soluble trace metals in rainwater and aerosol samples were achieved by a preconcentration method modified from Jiann and Presley method (2002), which utilizes serially connected columns couples packed with cation exchanger (Chelex 100) and anion exchanger (AGMP-1). Preparation of two resins are similar. Approximately 2 g of each resin were mixed with 2 N HNO_3 to form slurry, and then packed into the columns. Afterwards, 10 mL 1 M NH_4OH was passed through every column, in order to convert cation and anion exchangers into their NH_4^+ and OH^- forms, respectively. Columns then were connected serially end samples were passed through with a flow rate of 2 mL min^{-1}. After passing the liquid samples, columns were separeted again and each is washed with ammonium acetate (4 mL 1 M, 5 times) in order to remove the major ions such as Na, Ca, Mg, K. Finally, columns were treated with 7 ml 2 N HNO_3 to liberate ionic forms of trace metals from the columns, into aqueous phase.

High volume aerosol and wet deposition samples were subject to speciation. For wet deposition, 40 ml of filtrated rainwater samples were directly used. For high volume filter samples, 1/8 of each filter was extracted in 50 mL Milli-Q water. Rainwater samples and extracts from high volume samples alike were passed through columns as described.

2.3.2 Bioassay Samples

(a) Phytoplankton Pigment (HPLC): Samples which had been directly transferred from Niskin bottles were filtered from glass fiber (GF/F) filtres and kept at -20˚C until analysis. Filters were treated with acetone (%90 v/v) and grinded via ultrasonication, thus intracellular pigments are extracted from cells, to the liquid phase. The samples were kept in dark at +4 ˚C for at least 8 hours, and then centrifugated (5000 rpm).

(b) Flow Cytometry: Samples were transferred into dark glass 100 mL bottles and fixed with glutaraldehyde (1 mL, %25) immdiately, and analyses were performed within a few hours after sampling.

(c) Nutrients: Samples were stored at -20˚C in 100 ml LDPE bottles and thawed in the day of analysis.

(d) Inductively Coupled Plasma Mass Spectroscopy (ICP-MS): The samples to be assessed for their trace metal content and solubility were filtered with the use of 0.4 µm polycarbonate filters, separating soluble phase from particulate phase. The soluble fraction of the samples were then partitioned with columns as descoribed in section 2.3.1.a, (2).

2.4 Measurements

2.4.1 Inductively Coupled Plasma Mass Spectroscopy (ICP-MS)

Instrument consist of several parts: sample inroduction system, inductively coupled plasma, plasma interface, mass spectrometry, detector and computer. Sample introduction system which is comprised of an autosampler, pump, nebulizer and spray chamber convert liquid samples into droplets (diameters ranging between 1 and 10 µm) and convey it to the plasma interface. The sample droplets are then atomized by high energy argon plasma. Ions are extracted in the sample interface which consist of two nested Ni cones and accelerated in the quadripole area. The ions are separated in quadripole area depending on their mass/charge ratio before impacting on the detector. Perkin Elmer Nexion-350x Inductively Coupled Plasma Mass Spectroscopy instrument which was tested with TM-28.4 reference material was used in analyses. In Figure 2.4.1 detected and expected values for Al, Sb, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, V and Zn are given for comparison from the TM-28.4 tests. For all elements relative error was found to be below % 5 except Zn and Pb, which have a relative error of around % 10.

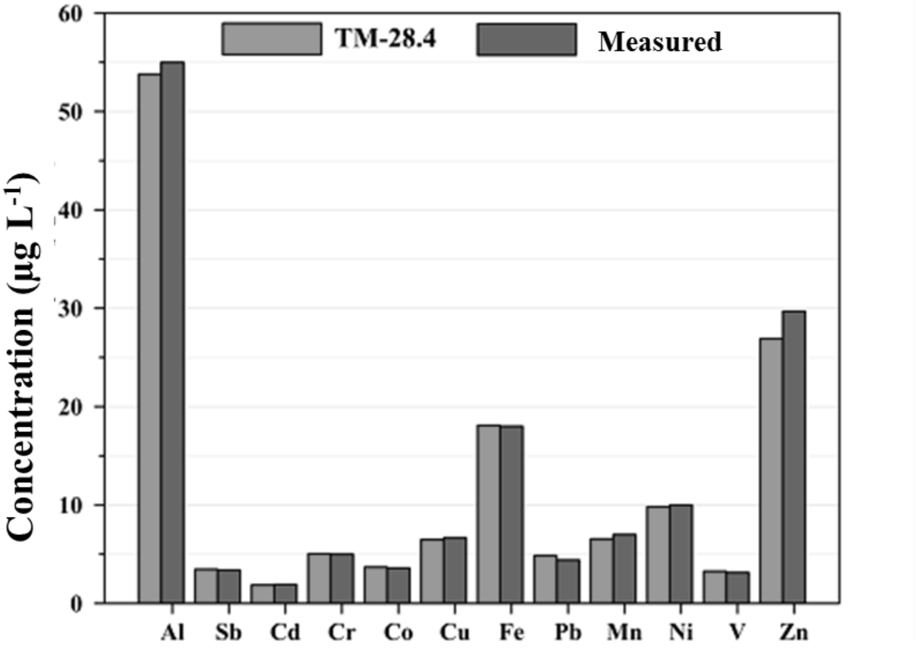


Figure 2.4.1 Measured and expected values of trace metals from TM-28.4 reference material.

Average blank values were substracted from determined sample concentrations. In Table 2.4.1 average blank values and detection limits (standard deviation*3) of bulk aesosol filters were given. The highest average blank values belonged to Al, Ca, Fe and Zn (25, 23, 16, and 7 ng m^{-3}, respectively), while their respective detection limits were found to be 17, 20, 10 and 7 ng m^{-3}. For elements Co and Cd, average blank contributions and detection limits were found to be compatable, and detection limit and blank contributions for both elements were determined to be 0.01 ng m^{-3}. For Mn, Cr, Cu, Ni and Pb were found to be less than 0.8 ng m^{-3}, while their limit of detection was about 0.4 ng m^{-3}. For the rest of the elements, it was observed that blank contributions were smaller than 0.05 ng m^{-3} while detection limit was about 0.05 ng m^{-3}.

Table 2.4.1 Average blank values of trace elements and their detection limits (3×σ) given in ng m^{-3}

Element	Blank	LOD (3×σ)
Al	25.0	17.0
Fe	16.0	10.0
Ca	23.0	20.0
Mn	0.3	0.2
Cr	0.7	0.3
Co	0.01	0.01
Zn	7.0	7.0
V	0.03	0.02
Ni	0.3	0.2
Cu	0.4	0.3
Cd	0.01	0.01
Pb	0.2	0.1
As	0.03	0.02
P	0.04	0.03

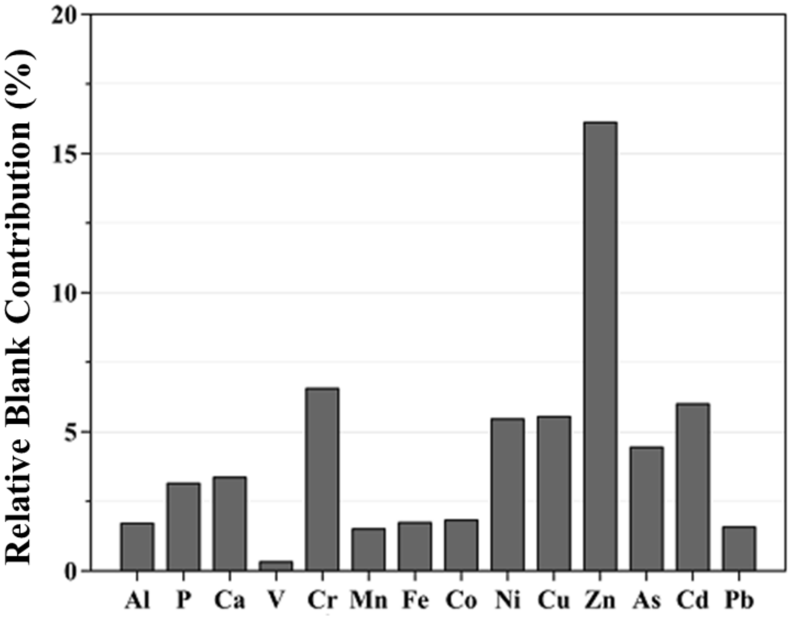


Figure 2.4.2 Relative blank contributions in high volume aerosol samples.

Figure 2.4.2 shows the relative blank contributions for trace elements determined in bulk aerosol samples. Blank contributions were found to be less than % 7, except for Zn. Relative contributions coming from blanks were calculated to be less than % 2 for Al, Fe, Co, Mn, Pb and V, and less than % 5 for Ca, As and P, and finally less than % 7 for Ni, Cu, Cd and Cr. In case of Zn, it was seen that blank contribution might reach up to % 20.

The accuracy of the ICP-MS measurements performed in this study was verified by using the certified reference material IAEA-433. Marine sediment reference material IAEA-433 was collected in 2002 off the Algerian coast of the Mediterranean Sea by International Atomic Energy Agency and afterwards it was deep-frozen, freeze-dried, then ground and sieved for use as an intercomparison material in trace metal analyses with similar matrices.

The certified reference material was measured along with the every batch of the digested bulk aerosol filter samples, dry and wet deposition filter samples, and dry – wet deposition liquid samples. In every batch, certified reference material IAEA-433 was also subjected to acid digestion identical to that of bulk aerosol and dry-wet deposition filter samples. In general, it was found out that measured values are in agreement with the reported values of IAEA-433. Analytical recoveries derived from obtained results, associated standard deviations and given certified values are presented in Table 2.4.2. As can be seen from Table 2.4.2. analytical recoveries of all elements except Cu is over % 80. Analytical recoveries for Fe, Co, Ni, and As were better than % 85, whereas for Mn, Zn, Cd, Pb the recoveries were higher than % 90. Only the recovery of Al concluded a result slightly higher than % 100, (% 102.0)

Table 2.4.2 Comparison between IAEA – 433 certified reference values and measured values.

	IAEA-433 certified values	IAEA-433 measured values	Recovery (%)
Al	78.2	79.78±6.53	102.0
V	0.16	0.130±0.014	81.3
Cr	0.136	0.112±0.0001	82.2
Mn	0.316	0.297±0.015	94.1
Fe	40.8	36.109±0.761	88.5
Co	0.0129	0.0111±0.0013	85.7
Ni	0.0394	0.033±0.005	84.7
Cu	0.0308	0.0230±0.0003	74.7
Zn	0.101	0.096±0.001	95.2
As	0.0189	0.0170±0.0004	89.7
Cd	0.000153	0.00015±0.00001	98.0
Pb	0.026	0.0245±0.0027	94.1

2.4.2 High Performance Liquid Chromatography (HPLC)

Pigment analyses regarding dust addition experiments were carried out using High Performance Liquid Chromotography (HPLC-Agilent 1100) with a C8 column. Centrifugated samples were drawn from sample containers, refiltered, 500 µl of each sample were transferred in vials, where it was mixed with 500 µl 1 M ammonium acetate. The samples were then introduced to the instrument via autosampler. One analysis took approximately 39 minutes. For the eluent phase, a solvent A (% 80 methanol + % 20 1 M ammonium acetate) and a solvent B (% 100 methanol) was used in changing ratios. Operation program of the HPLC is given at Table 2.4.2. According to table, mixing ratios throughout the experiment can be summarized as follows: (min; % Solvent A; % Solvent B) (0; 75; 25), (1; 50; 50), (20; 30; 70), (25; 0; 100), (32; 0; 100). For calibration, different standards for different pigments were used (for Chl-a, Chl-b: Sigma Chemicals; for carotenoids and Chl-c: VKI Water Quality Institute, Denmark). The pigment quantities then were used as indicator for the various phytoplankton taxa. (Table 2.4.3, Jeffrey et al. 1997).

Table 2.4.3 Operation program of the HPLC

Minute	% Solvent A	% Solvent B
0	75	25
1	50	50
20	30	70
25	0	100
39	0	100

Table 2.4.4 Categorization of phytoplankton according to indicator pigments.

Pigment	Phytoplankton Taxa
Fucoxanthin	Diatom
19’hexanolyxyfucoxanthin	Prymnesiophyceae
Peridinin	Dinoflagellates
Chlorophyll-b	Chlorophyes
Zeaxanthin	Cyanophyta
Buthanoloxy fucuxanthin	Chrysophyta
Divinyl chlorophyll-a	Prochlorophyceae

2.4.3 Ion Chromatography

For determination of soluble phosphate species, (phosphate, trimetaphosphate and tripolyphosphate) each bulk aerosol filter to be analyzed was thawed in the morning of analysis, 20 ml deionized water was added to the 1/8 of each filter, and for the extraction, they were subject to ultrasonication. After the extraction, extracts were transferred into 2 ml glass vials and analyses were performed with Dionex-5000 Ion Chromatography, with autosampler. For cationic species CS12A column coupled with 20mM methanesulfonic acid as eluent (flow rate: 1.0 mL/min, applied current: 59 mA, injection volume: 25µL) is used while analysis of anionic species was performed with AS11 column and 30mM NaOH as eluent (flow rate: 1.50 mL/min, applied current: 112 mA, injection volume: 200 µL). Both kinds of analyses were carried out at 30° C with suppressed conductivity detector.

2.4.4 Flow Cytometry

Flow cytometry method utilizes an array of laser optics, fluidics and detectors in order to measure light scatter and fluorescence emission from cells. The method allows to distinguish between, and determine the abundance of three major small sized phytoplankton taxa, namely *prochlorococcus*, *synechococcus* and *picoeukaryote* while excluding dead cells and cell debris. A 3-laser Apogee A450-micro Flow-system was employed for the analysis of bioassay samples.

The calibration of instrument were done by 1 µm synthetic particles and monoculture of *synechococcus.* Samples fixed with glutaraldehyde were poured in 1.5 mL eppendorf vials and then introduced to the instrument via autosampler with a flow rate of 60 µL min^{-1}. In order to tune out the background noise 39 was chosen as threshold value. The determination of particles were carried out through the attenuation of red and orange lasers with wavelengths 633 nm and 488 nm.

2.4.5 Auto-Analyzer

For the measurement of nutrients (NO3-+NO2-, NH4+, Si(OH)4 ve o-PO43-) two channel Technicon A-II auto-analyzer is used. The method which allows continuous analysis with high sample volumes was developed by Technicon and accepted as a standart method. The detection limit of the method was determined to be 0.02, 0.05 and 0.1 µM for phosphate, nitrate (and ammonium) and silicate, respectively.

2.5 Calculations and Formulas

2.5.1 Calculation of the Concentrations of Water Soluble Species and Trace Elements

For C being concentration (ng m^{-3}) of the species in question, S and B, the observed concentrations (µg L^{-1}) in samples and blanks, respectively, D dilution factor (ml) and V is the total volume of the sample (m^{-3}), the concentration of a water soluble species can be expressed as:

$$C = \frac{S - B}{V} \times D$$

2.5.2 Calculation of Annual Nutrient Fluxes

For the calculation of atmospheric nutrient fluxes in dry and wet deposition modes, the studies of Herut et al. (1999, 2002) were predicated upon. For the wet deposition, the product of annual amount of precipitation (P_{annual}) and volume weighted mean concentration of the substance of interest (C_w) gives the annual wet flux (F_w).

$$F_w = P_{annual} \times C_w$$

Volume weighted mean concentrations of nutrient were calculated as follows:

$$C_w = \frac{\sum_{i=1}^{n} C_i \times Q_i}{\sum_{i=1}^{n} Q_i}$$

where, C_i is the concentration of the substance, and the Q_i is the amount of rainfall for the ith rain event.

Dry deposition flux (F_d) can be calculated as a product of species' settling velocity (V_d) and concentration (C_d). The unit of F_d is V_d and C_d are µmol m^{-2} y^{-1}, m y-1 and µmol m^{-3}, respectively.

2.5.3 Calculation of 3-Day Air Mass Back Trajectories

3-Day back trajectories of air masses reaching Erdemli station were calculated by HYSPLIT model (Hybrid Single Particle Langrangian Integrated Trajectory; Draxler and Rolph, 2003). For calculations NCEP/NCAR Reanalysis dataset was used (lateral resolution 2.5^{o}, 18 vertical levels). Vertical movement of air masses was determined based on the vertical velocities provided in the meteorological dataset. Cluster analysis was applied to back trajectories for categorization of air masses.

2.5.4 Calculation of Enrichment Factors

Enrichment factor is calculated as the ratio between the relative abundance of an element in aerosol and relative abundance of the same element in the Earth’s crust. For calculation of relative abundance of the element in question, a reference element of crustal origin must be chosen, thus, Al is used as reference in calculations. For the crustal ratios of the elements, past studies were used (Koçak et al., 2004a, Andreae et al., 2002, Wedepohl, 1995)

$$EF_{element} = \frac{\left(C_{element}/C_{ref}\right)_{aerosol}}{\left(C_{element}/C_{ref}\right)_{crust}}$$

3 RESULTS and DISCUSSION

3.1 Bulk Aerosol Filters: Trace Metal and Phosphorus Species

Arithmetic mean, standard deviation, minimum and maximum values and geometric means regarding bulk aerosol samples collected in April and July-August 2015 periods were presented in Table 3.1.1. As can be deduced from minimum and maximum values in the table, all trace metals exhibited dramatic daily variations. Similar variability has been reported for the Mediterranean region (Dulac et al., 1987; Bergametti et al., 1989; Kubilay and Saydam, 1995; Güllü et al., 1998).

As can be seen in Table 3.1.1,daily mean Al concentration in the station is 874 ng m^{-3}, with a standard deviation of 1116, implying great daily variability. The minimum and maxiumum observed values for Al (171 and 5901 ng m^{-3}) emphasize the dramatic daily variation of aerosol concentrations. The arithmetic and geometric means of Fe and Mn, two other predominantly crustal elements, are 783 and 588, and 16.6 and 12.2 ng $m^{-3,}$ respectively. Observed daily concentrations of the other trace elements Cr, Co, Zn, V, Ni, Cu, Cd, Pb and As are 7.09, 0.43, 36.4, 5.01, 4.79, 7.94, 0.18, 8.39 and 0.7 ng m^{-3}, respectively. The average daily concentration of total phosphorus is 1.51 ng m^{-3} with a standard deviation of 0.92 ng m^{-3} while its geometric mean was found to be 1.31 ng m^{-3}.

Factors affecting the concentration of trace metals in atmospheric aerosols can be summarized as follow: (i) origin of atmospheric particle, (ii) emission strenght of the source, (iii) proximity of sampling station to the source, (iv) history of air mass trajectories, (v) removal of particles, (vi) chemical transformation the particles undergo during long range transport. Arithmetic and geometric means usually gives an estimation regarding the distribution of dataset. In the case of a perfectly normal distribution, arithmetic and geometric mean of dataset are identical. However, as the dataset deviates from normal distrubition, these two values diverge. Previous research carried out in the region has been demonstrated that the concentrations of trace metals in atmospheric particles conform to log-normal distribution (Güllü et al., 1998; Koçak, 2004b). In figure 3.1.1. (a) and (b), expected (line) and observed (bars) (log-normal transformed) frequency (%) distributions of trace metals Al and Cd, which were chosen to represent aerosol populations of crustal and anthropogenic origin, respectively. Non-parametric Kolmogorov-Smirnov test demonstrates that trace metals exhibit lognormal distrubition with %95 (p<0.01) confidence level.

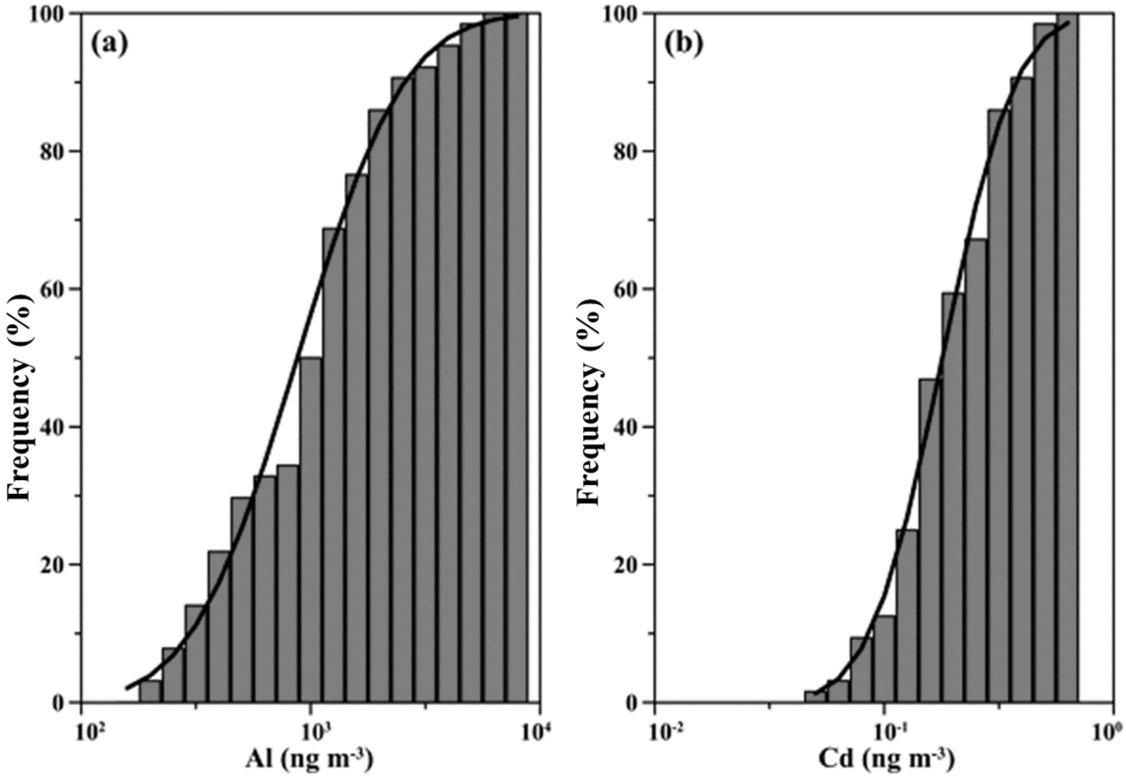


Figure 3.1.1 Expected and observed frequency distributions of log-transformed **(a)** Al (crustal) **(b)** Cd (anthropogenic) concentrations.

Element	Arithmetic Mean	Standard Deviation	Geometric Mean	Minimum	Maximum
Al	1224	1116	874.0	171.0	5901
Fe	783.0	651.0	588.0	131.0	3496
Ca	780.0	458.0	667.0	198.0	2349
Mn	16.6	12.0	12.9	2.56	63.0
Cr	10.2	12.5	7.09	1.84	74.4
Co	0.57	0.68	0.43	0.07	5.08
Zn	44.6	34.4	36.4	11.4	206
V	6.15	3.22	5.01	0.47	14.7
Ni	5.51	2.76	4.79	0.76	15.2
Cu	8.53	3.25	7.94	3.04	18.0
Cd	0.21	0.12	0.18	0.04	0.56
Pb	11.39	9.67	8.39	1.41	41.3
As	0.79	0.34	0.70	0.14	1.64
P	1.51	0.92	1.31	0.41	5.46

Table 3.1.1 Statistical summary of trace elements in aerosol samples (ng m^{-3}).

3.1.1 Comparison of Dataset with Literature

Before accounting for general trends and temporal variations in dataset, dataset acquired in this study will be compared with the previous studies, in order to investigate general characteristics. However, it should be emphasized that, comparisons as such face various diffculties and considerations, some of which are that sampling done for different studies cover different periods of time and that their sampling and analysis methodologies differ dramatically, etc. Considering trace metal concentrations presented in Table 3.1.2. following generalisations can be made:

(a) Lowest concentrations of elements of crustal origin such as Al and Fe were observed in polar regions and Pacific islands. Polar regions are relatively distant from the mineral dust belt, besides, the earth in the region is covered under ice, lowering the crustally originated aerosol concentrations. Even though islands in the Pacific are not covered with ice, their remoteness from arid and semi-arid regions resulted in low concentrations of crustal elements. Concentrations of crustal elements in the Eastern Mediterranean were observed to be 2 times higher than those of the Western Mediterranean. Main reason of this is the relative proximity of the Eastern Mediterranean stations to the Saharan and the Middle Eastern desert areas (Koçak et al., 2012, 2004b). In short, within the Mediterranean basin, mineral dust concentration displays a gradient, increasing from west to east. Trace metals concentrations observed in Erdemli were nearly 4 times greater than that of Amasra. This difference might be attributed to decay of mineral dust particle via wet and dry deposition while air flows from south to north (Koçak, 2006). The observed difference can be explained (up to % 30) by the fact that a 10 µm pre-impactor used in the sampling in Amasra (Karakaş, 1999). In addition, Fe and Al values observed in Sal, Cape Verde were twice greater than the Eastern Mediterranean values, which is in accordance with the direct exposure of the island to the Saharan dust events due to its geographical location.

(b) Lowest concentrations of elements of anthropogenic origin (Ni, Zn, Cu, Cd and Pb) were observed in Antarctica and the Pacific islands. These low concentrations in the aforementioned locations might closely be related with their remoteness to the pollutant sources. These elements also exhibited significant variability within the Mediterranean basin. Stations, especially island stations which were located far away from the industrial and urban regions were affected less by the pollutants. For instance, Cap Carbonara displayed the lowest Cd (0.03 ng m^{-3} concentration. The highest Zn and Pb concentrations were observed in Liverpool, which can be attributed to the typical urban feature of the station.

(c) Lead has been in decline since the nineties. Lead concentration was previously reported to have been decreased by % 25 from in the time period between the 1990s and early 2000s (Koçak et al., 2004b). The decline is observed to have continued in Erdemli, in a similar yet faster mode. Pb concentration was observed to have decreased threefold from 22 ng m^{-3} to 8 ng m^{-3} within the last decade (see Table 3.1.2). On the other hand, in comparison with the historical data (Koçak et al., 2004b) Cr, Ni, Zn and Cd concentrations were shown to be 1.5 times higher. However, when compared to Al, no dramatic change in their abundances was observed. For example, Cr/Al ratio is calculated as 0.0075 and 0.0080 for historical and new datasets, respectively.

(d) As for Mn, which is predominantly of mixed origin (affected by mineral dust and human activities alike) the Eastern Mediterranean values were found to be comparable with the values observed in Cap Ferrat and Tour de Valat. However, Mn/Al ratios differ significantly between two regions. The Mn/Al ratio was found to be 0.014 and 0.030 for the Eastern and Western Mediterranean, respectively.

Station	Al	Fe	Mn	Cr	Ni	Zn	Cu	Cd	Pb	References
MEDITERRANEAN										
Western Mediterranean										
Vignola	109	120	1.7	-	0.97	11.8	1.9	0.11	8.8	Sandori and Migon [1997]
Cap Ferrat	370	320	11	-	2.8	41	6.2	0.36	58	Chester et al. [1990]
Tour de Valat	380	275	13	-	-	60	3.8	0.51	56	Guieu et al. [1991]
Cap Carbonara	164	85	-	1.6	-	3.4	-	0.03	9.8	Guerzoni et al. [1997]
Blanes	-	-	-	-	5.5	50	7.9	0.6	50	Chester et al. [1992]
Eastern Mediterranean										
Tel Shikmona	720	798	14.5	2.9	-	85	5.4	0.19	33.6	Herut et al. [2001]
Erdemli	685	685	12.6	8.5	-	19	-	0.19	30	Kubilay and Saydam [1995]
Tel Shikmona	940	755	17.1	2.3	-	25.3	6.6	0.23	24.6	Koçak et al. [2004]
Erdemli	562	398	7.9	4.2	3.1	14.8	7.4	0.12	22.4	Koçak et al. [2004]
Antalya	307	230	6.2	2.9	2.6	7.5	-	-	33.2	Güllü et al. [1998]
Erdemli	874	588	12.9	7.0	4.8	26.5	7.9	0.18	8.4	This study
BLACK SEA										
Amasra	210	200	8.7	-	1.1	10	41	0.21	12	Karakaş [1999]
IRISH SEA										
Liverpool	317	340	8.4	2.1	3.0	36	21	-	43	Chester et al. [2000]
PACIFIC										
Enewetak	21	17	0.3	-	-	0.17	0.04	-	0.12	Arimoto et al. [1989]
Samoa	0.7	0.2	0.04	-	-	0.06	0.01	-	0.02	Arimoto et al. [1989]
ATLANTIC										
Sal	1600	960	13	3.1	-	-	1.7	-	-	Prospero [1981]
POLES										
Arctic	35	-	1.2	-	-	18.7	12.8	-	-	Toumi et al. [2003]
Antarctica	1.9	-	-	0.11	0.08	0.13	0.14	0.001	0.04	Mishra et al. [2004]

Table 3.1.2 A literature review of aerosol trace metals geometric means (ng m^{-3})

3.1.2 Daily Variability

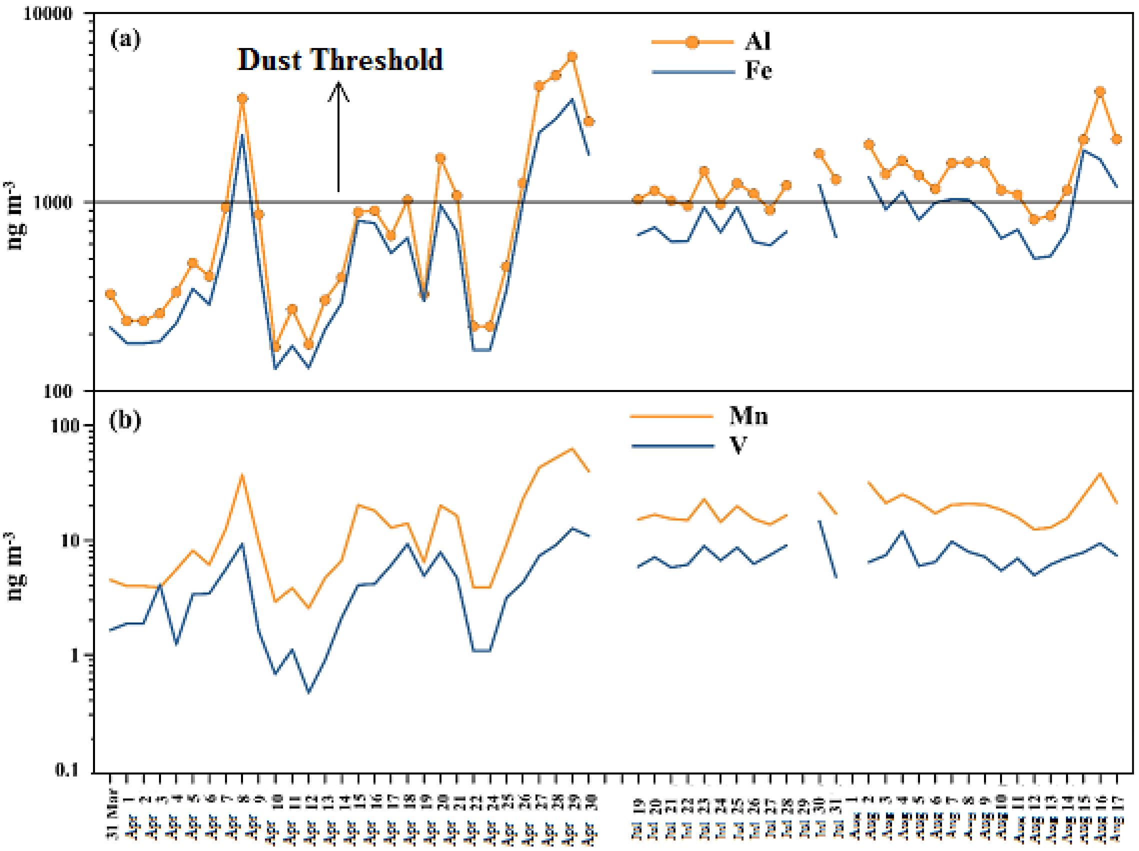
Trace metal composition and concentration of the Eastern Mediterranean atmospheric aerosols have been shown to be influenced by two main components (Kubilay and Saydam, 1995; Güllü et al., 1998; Kubilay et al., 2000), namely: (a) episodic mineral dust transport, (b) anthropogenic sources. Desert areas (Sahara and Middle Eastern deserts) surrounding the Mediterranean to the south and the east are the predominant sources of the mineral dust while industrialized and semi-industrialized regions bordering the Mediterranean in the north are the principal sources of anthropogenic aerosol. Daily variabilty of aerosol trace metals in Erdemli is presented in Figure 3.1.2. As can be seen from figures, aerosol composition and concentration showed great variability on a daily basis. Concentrations of aerosol trace metals of crustal origin such as Al, Fe, Mn differ significantly from day to day. These trace metals reached their highest concentrations during mineral dust episodes when air masses arriving at station from North Africa or Middle East regions. For instance, Al, Fe and Mn reached their highest concentrations on 29 April 2015 throughout the study period.

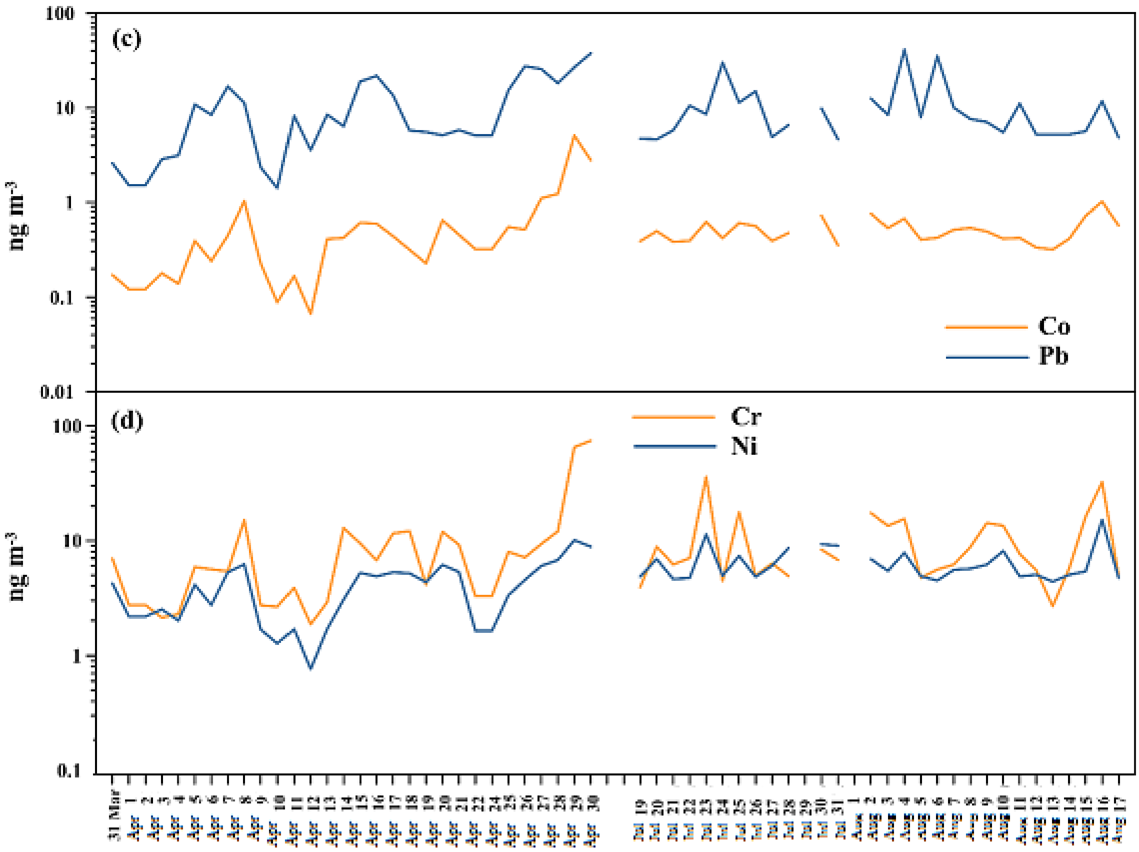
In Figure 3.1.3 are 3-day air mass back trajectory and OMI-Aerosol Index values belonging to 29 April. Aerosol index is a measure of how much light was scattered and back scattered due to the presence of uv-absorbing aerosols such as dust and soot. It is presented as the difference of between the observed and calculated values of absorbing and non absorbing (pure molecular atmospheric) spectral radiance ratios. Observed values include Mie scattering, Rayleigh scattering, and absorption, while only Rayleigh scattering was considered for a pure molecular atmosphere. For OMI, Aerosol Index is defined as:

$$AI = 100\ [\ \log_{10} (I_{360}/I_{331})_{measured} - \log_{10} (I_{360}/I_{331})_{calculated}]$$

Trajectories of air masses imply mineral dust transport from North Africa and Levantine basin was being influenced by an episodic dust event, while aerosol index value reached 2.5, confirming the dust episode. Similarly, P and Co elements illustrated their peak values in the aforementioned day.

Elements originating from human activities also demostrated significant daily variability. For instance, Pb indicated peak concentration on 4 August 2015 (42 ng m^{-3}) within the covered period, and 1000 m and 2000 m air mass back trajectories demonstrated transportation from northern direction i.e., air masses swept and brought anthropogenic aerosol from industrial regions of Anatolia before reaching at the station.




(c)
Co
Pb
(d)
Cr
Ni
ng m-3
100
10
1
0.1
0.01
0.1
31 Mar
1 Apr
30 Apr
Jul 19
Jul 31
Aug 1
Aug 17

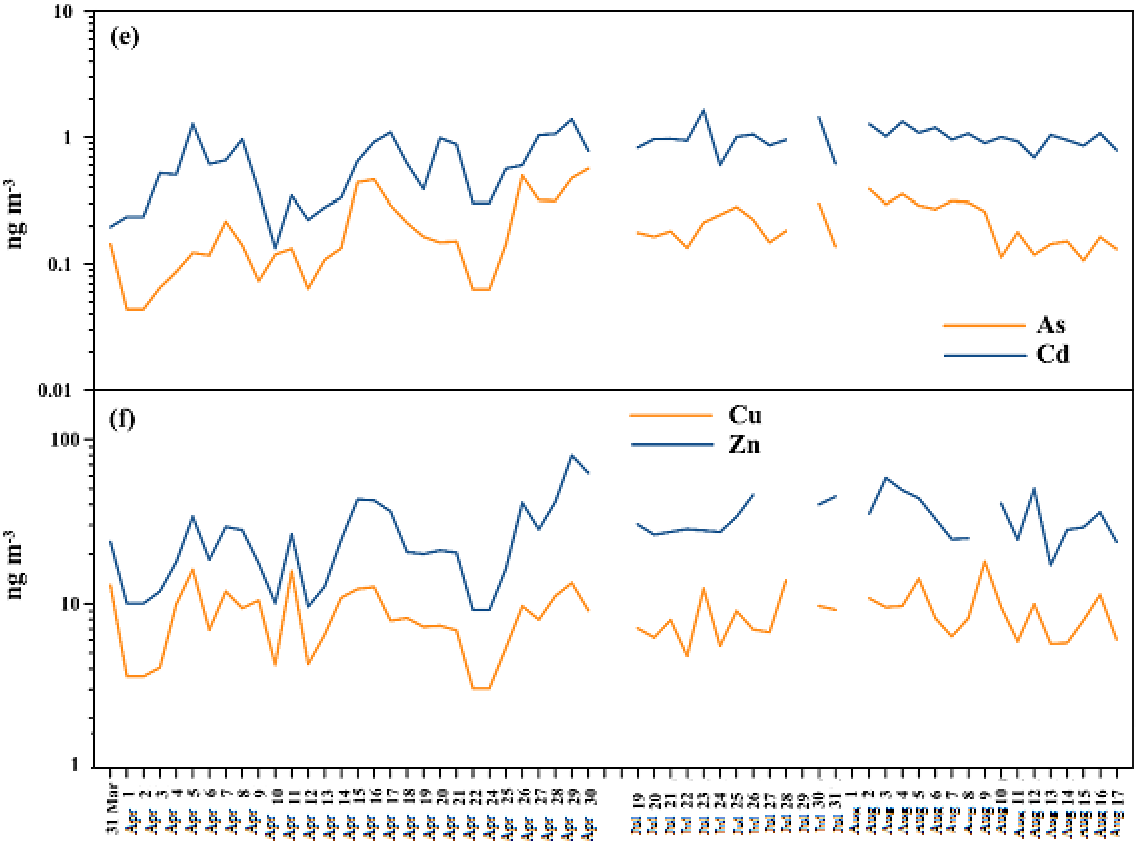


Figure 3.1.2 Daily variability of aerosol trace metals, **(a)** Al and Fe, **(b)** Mn and V, **(c)** Co and Pb, **(d)** Cr and Ni, **(e)** As and Cd, **(f)** Cu and Zn.

3.1.3 Correlation Coefficients Between Trace Metals

Correlation coefficients were divided in five categories (Koçak et al, 2004a)

a) r = 0, no correlation

b) r = 0-0.5, weak correlation

c) r = 0.5-0.7, moderate correlation

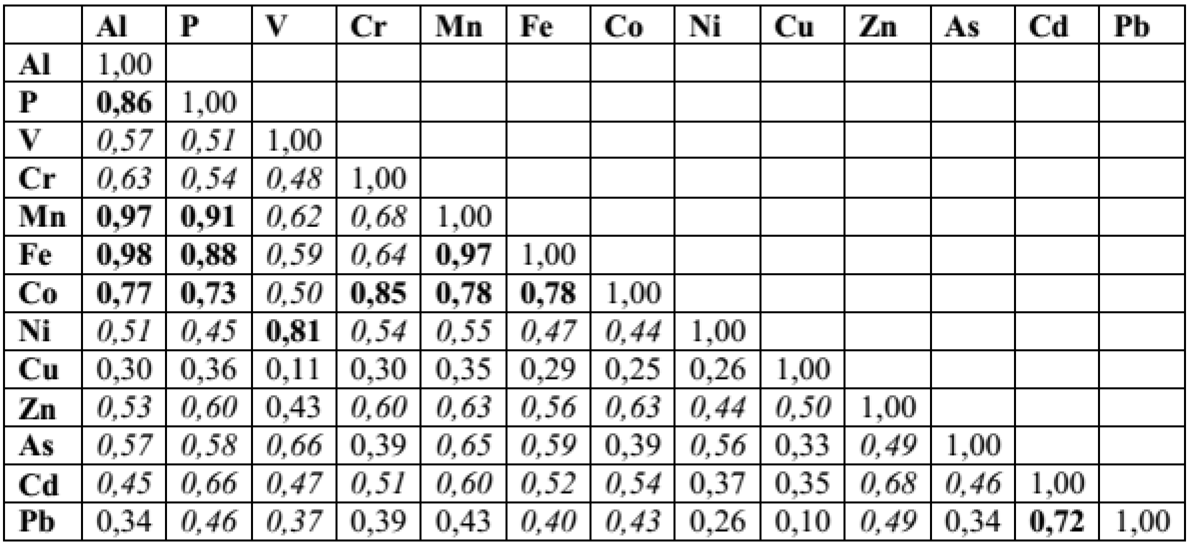
d) r = 0.7-1.0, strong correlation

e) r = 1.0, perfect correlation.

In Table 3.1.3 correlation coefficients between trace metals are given. Correlation coefficient between crustal elements Al, Fe and Mn was strikingly high ($r > 0,95$, $p < 0,05$), denoting nearly perfect correlation. In addition, both P (phosphorus) and Co (cobalt) exhibited strong correlations with these elements, which confirms that elements P and Co were also predominantly of crustal origin. Elements such as V, Cr, Ni, Zn and As were also found to be in moderate correlation with Al, implying that at least certain amount of these anthropogenic elements may originate from mineral dust.

There was another remarkable correlation between V and Ni ($r = 0.81$, $p < 0.05$). Previous studies carried out in the region (Koçak et al., 2009) demonstrated that enrichment of these two trace metals may result from oil combustion. Considering their strong correlation, it would not be wrong to assume that main source of both elements is residual oil combustion. Moreover, strong correlation between Cd and Pb ($r = 0.72$, $p < 0.05$) may also imply common main origin.

Rest of the trace metals showed certain levels of correlation from moderate to weak. Differing correlations between trace metals demonstrated that pollutant sources were varied, and they had different influence levels over aerosol trace metal compostion. Hence, although correlation coefficients are practical in application, they provide limited information, and are not sufficient alone for obtaining conclusive results regarding the origin of trace metals in the atmospheric aerosols.



	Al	**P**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**As**	**Cd**	**Pb**
Al	1,00												
P	**0,86**	1,00											
V	*0,57*	*0,51*	1,00										
Cr	*0,63*	*0,54*	*0,48*	1,00									
Mn	**0,97**	**0,91**	*0,62*	*0,68*	1,00								
Fe	**0,98**	**0,88**	*0,59*	*0,64*	**0,97**	1,00							
Co	**0,77**	**0,73**	*0,50*	**0,85**	**0,78**	**0,78**	1,00						
Ni	*0,51*	*0,45*	**0,81**	*0,54*	*0,55*	*0,47*	*0,44*	1,00					
Cu	0,30	0,36	0,11	0,30	0,35	0,29	0,25	0,26	1,00				
Zn	*0,53*	*0,60*	0,43	*0,60*	*0,63*	*0,56*	*0,63*	*0,44*	*0,50*	1,00			
As	*0,57*	*0,58*	*0,66*	0,39	*0,65*	*0,59*	0,39	*0,56*	0,33	*0,49*	1,00		
Cd	*0,45*	*0,66*	*0,47*	*0,51*	*0,60*	*0,52*	*0,54*	0,37	0,35	*0,68*	*0,46*	1,00	
Pb	0,34	*0,46*	*0,37*	0,39	0,43	*0,40*	*0,43*	0,26	0,10	*0,49*	0,34	**0,72**	1,00

Table 3.1.3 Correlation coefficients between trace metals.

3.1.4 Enrichment Factors

Enrichment factor is the ratio between relative abundance of an element in aerosol and relative abundance of the same element in the Earth's crust. For calculation of relative abundance of the element in question, a reference element is chosen. Crustal abundance of referance element must be ubiquitous, and relative contribution of anthropogenic sources to this element should be negligible in aerosol. Hence, typically elements such as Al, Si, K, Ca, Ti, and Fe are used since anthropogenic polluters have little or no influence on them. (Al is used as referance in this study). This way, calculating enrichment factors of trace elements in order to describe certain influences over the compostion of aerosols becomes possible, and commonly used (Chester et al., 1990). Figure 3.1.3 shows enrichment factors of elements with respect to the Earth's crust, and in Table 3.1.4 standart deviations for each element are given.

It can be seen that Fe and Mn enrichments remained in a limited extent with respect to Al (indicator of crustal origin). EF values of Fe and Mn are 1.06 and 1.58, respectively, meaning that % 94 of Fe and % 64 Mn found in the atmospheric aerosol originated from mineral dust. On the other hand, EF values of V and Co indicated moderate enrichment, (2.3 and 3.3). Contribution of the crust to the aerosol V concentration was thus found to be a significant % 44, while equally significant Co contribution was around % 30. Enrichment factors of Pb, Cr and Ni are found to be 6.6, 7.4 and 8.2, respectively. Crustal contribution to these elements remained around % 10 – 15. For the rest of the elements investigated, EF values were above 10, and crustal contributions to these elements ranged between % 3 and % 7.

Considering historical data of Erdemli station (Koçak, 2006), while no significant change was observed regarding elements of (predominantly) crustal origin, it is found out that there were dramatic differences for antropogenic trace metals. For instance, enrichment factor of Pb dropped to 6.6 from its historical value of 84.8, denoting steep decline in pollutant concentrations.

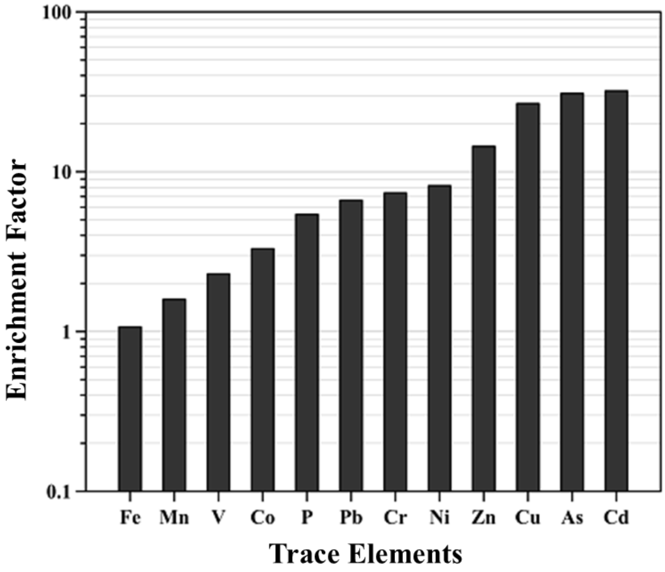


Figure 3.1.3 Enrichment factors of trace elements in aerosol.,

Trace Element	Standard Deviation
Fe	0.18
Mn	0.34
V	2.70
Co	2.20
P	3.08
Pb	14.99
Cr	6.65
Ni	9.29
Zn	13.12
Cu	29.52
As	21.40
Cd	30.61

Table 3.1.4 Standard deviations of enrichment factors.

3.1.5 Impact of Episodic Dust Events on the Aerosol Composition

In order to assess the extent of impact of mineral dust episodes, (a) concentration of Al > 1000 ng m^{-3} was applied as dust episode threshold, (b) 3 day air mass back trajectories, (c) OMI aerosol index and (d) SKIRON dust model was used in coordination (Koçak et al., 2012). While there were 9 dusty days in April 2015 with significantly high mineral dust concentration, 4 of them were associated with dust episodes. For July-August period, 5 out of 9 dusty days with high dust concentration were characterized by dust episodes. Before commencing to describe how dust episodes affect chemical composition of aerosols, two examples will be given for each period.

In April 8, 2015 concentration of Al increased 4 fold compared to the previous day, reaching value of 3538 ng m^{-3}. OMI-AI and SKIRON for day in question is given in Figure 3.1.4 (a). As can be deduced from the figure, mineral dust was predominantly originated from Sahara and affected all Levantine Basin. The most intense and long dust episode of April was observed between April 26 and 30 with the average Al concentration of 3728 ng m^{-3} while the highest Al concentration was identified on April 29, with a value of 5903 ng m^{-3} (Figure 3.1.4 (b)). Results obtained from both OMI-AI data and SKIRON model indicated that the main source of mineral dust was Saharan desert.

Another dust episode was observed from August 2 to 5, 2015 during which daily average Al concentration was found to be 1600 ng m^{-3}. As the average dust concentration suggests, it was a relatively weak dust episode and the graphics shown in Figure 3.1.4 (c) indicated a predominantly Middle Eastern origin. The last example (Figure 3.1.4 (d)) the dust episode observed between August 15 and 17, with an average Al concentration of 2713 ng m^{-3}. Considering SKIRON and OMI-AI data, it can be suggested that the main source of the mineral dust within this period was Sahara desert.

Previous research carried out in the region have demonstrated that mineral dust events may modify the trace metal composition dramatically (Kubilay and Saydam, 1995; Kubilay et al., 2000). In Table 3.1.5 geometric means of trace metals in aerosol are given separately for dust and non-dust days. For the dust episodes, the threshold value of Al as 1000 ng m^{-3} was chosen. The days that exhibit 1000 ng m^{-3} or higher Al concentrations were denoted as “dust days” while the rest was labeled as non-dust days. As Table 3.1.5 suggests, crustal elements (Al, Fe, Mn) comprehensibly exhibited 3 times higher concentrations in dust days with regard to non-dust days. On the other hand anthropogenic elements similarly showed higher enrichment during the dust days compared to the non-dust days. In dust days concentrations of V, Cr, Co, Ni, As, Cd and Pb were at least 1.5 times higher than those of non-dust days, while Zn and Cu concentrations were about 1.2 times higher. This greater enrichment of anthropogenic elements can be attributed to several reasons:

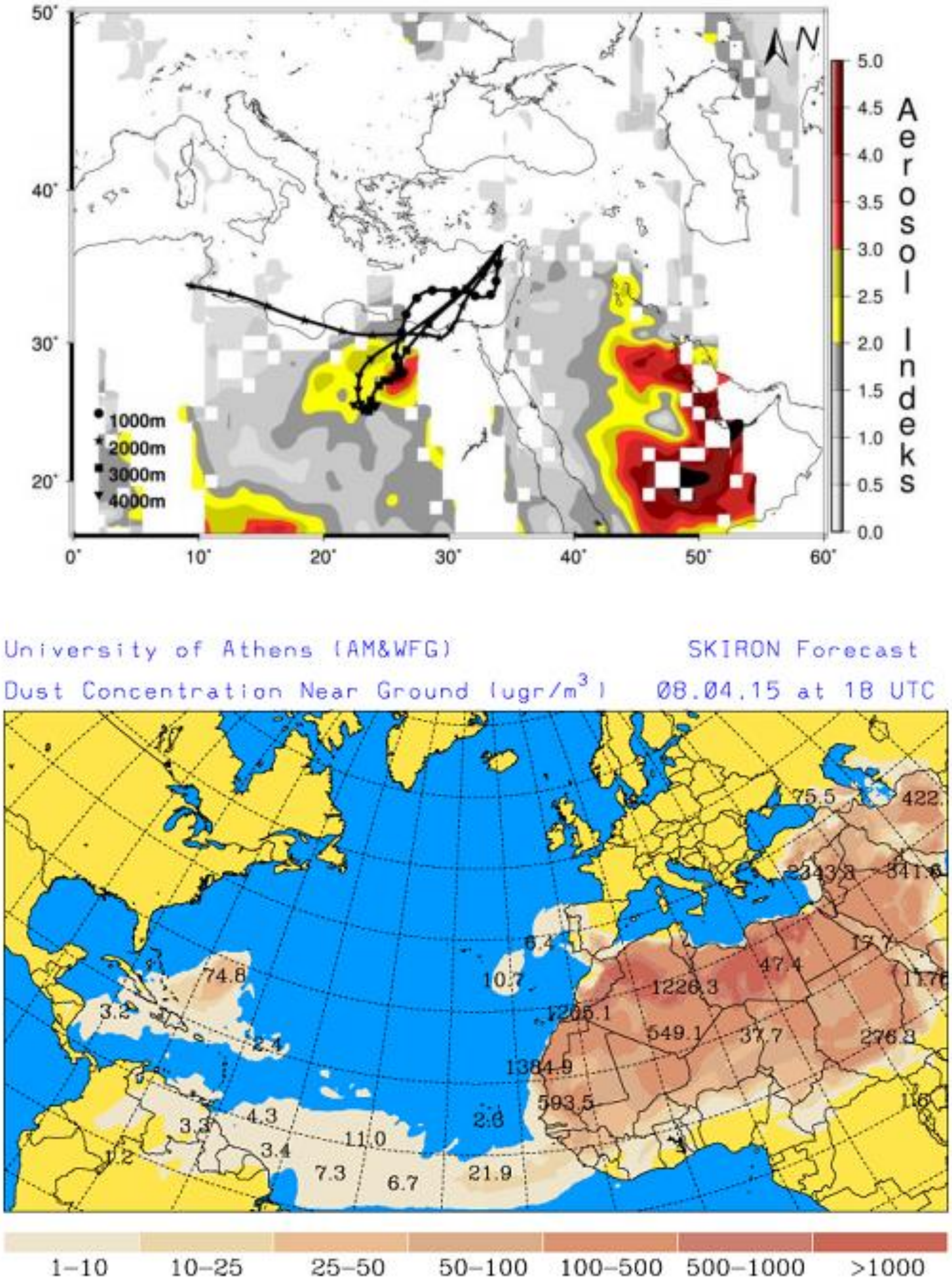
(i) In the course of long range transport, particles of mineral dust provide surface for anthropogenic particles, and are modified by them (Mamane and Gottlied, 1989, 1992).

(ii) Even when the main source of aerosol is Saharan mineral dust, industrial, semi-industrial and urban aerosol emitted in the southern coast of Mediterranean might still modify the mineral dust composition in a similar fashion.

(iii) Depending on the pattern of trajectory, air masses carrying mineral dust might sweep across industrialized Europe, Balkans and Marmara region, which deepens the aformentioned affect, in turn, increasing the enrichment of anthropogenic elements (Güllü et al., 1998; Choi et al., 2001; Guo et al., 2004; Koçak et al., 2012).

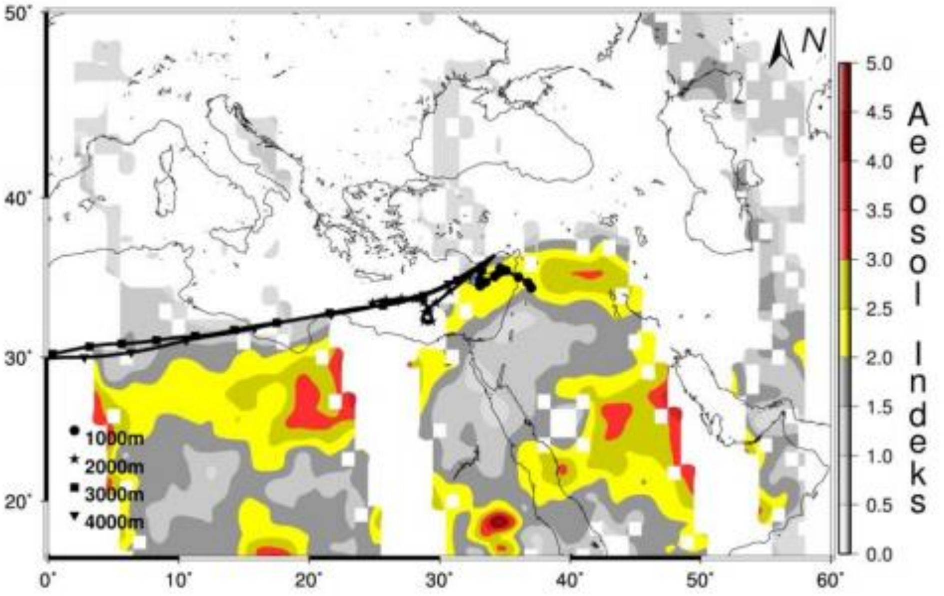
Table 3.1.5 Geometric means of aerosol trace metals in dust days and non-dust days.

	Dust Days		Non-dust Days		Dust/Non-dust	
	Crustal	**Pollutant**	**Crustal**	**Pollutant**	**Crustal**	**Pollutant**
Al	2175		626		3.5	
P	2.13		1.1		1.9	
V	8.39	3.0	3.6	2.0	2.4	1.5
Cr	139	11.5	5.5	4.8	2.5	2.4
Mn	27.5		9.8		2.8	
Fe	1364		428		3.2	
Co	0.81	0.48	0.33	0.23	2.5	2.1
Ni	6.7	5.2	3.8	3.4	1.8	1.5
Cu	9.14	8.4	7.5	7.3	1.2	1.2
Zn	32.9	28.4	23.4	22.1	1.4	1.3
As	0.97	0.92	0.61	0.59	1.6	1.5
Cd	0.26	0.24	0.15	0.14	1.8	1.7
Pb	11.9	8.7	6.7	5.8	1.8	1.5



(a)

Figure 3.1.4 3-day air mass back trajectories with OMI Aerosol Index results (above) and SKIRON rendering (below) for **(a)** April 8 2015, **(b)** April 29 2015, **(c)** August 5 2015 **(d)** August 17 2015.



(b)

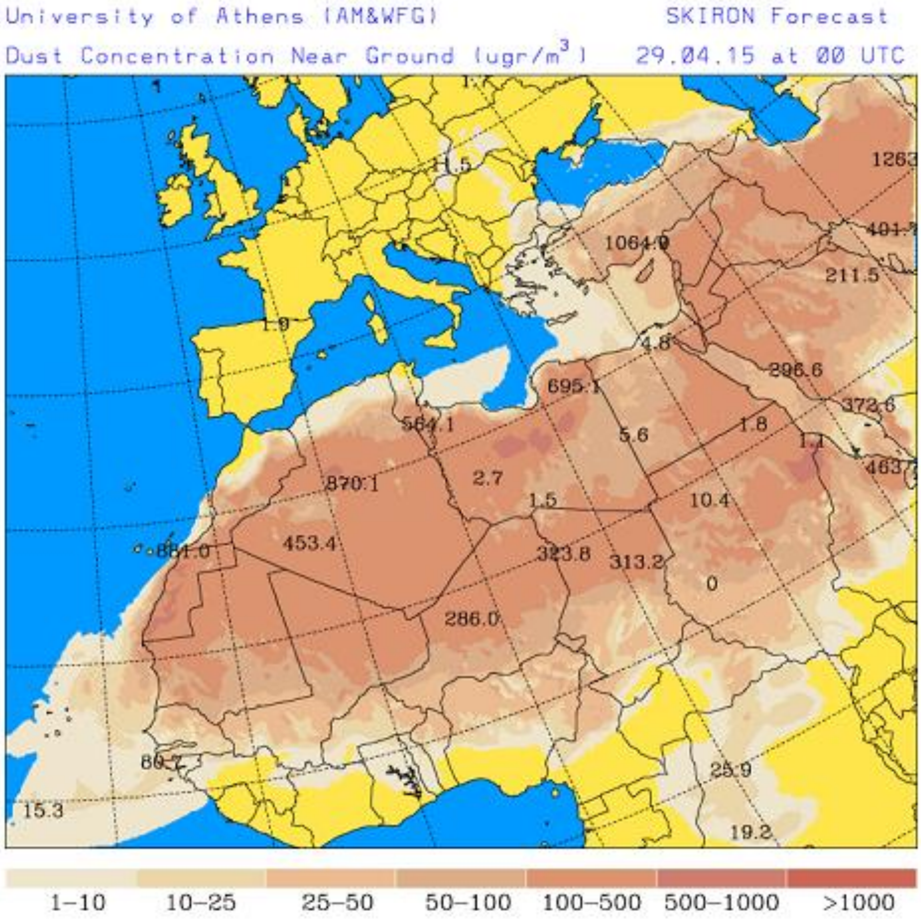
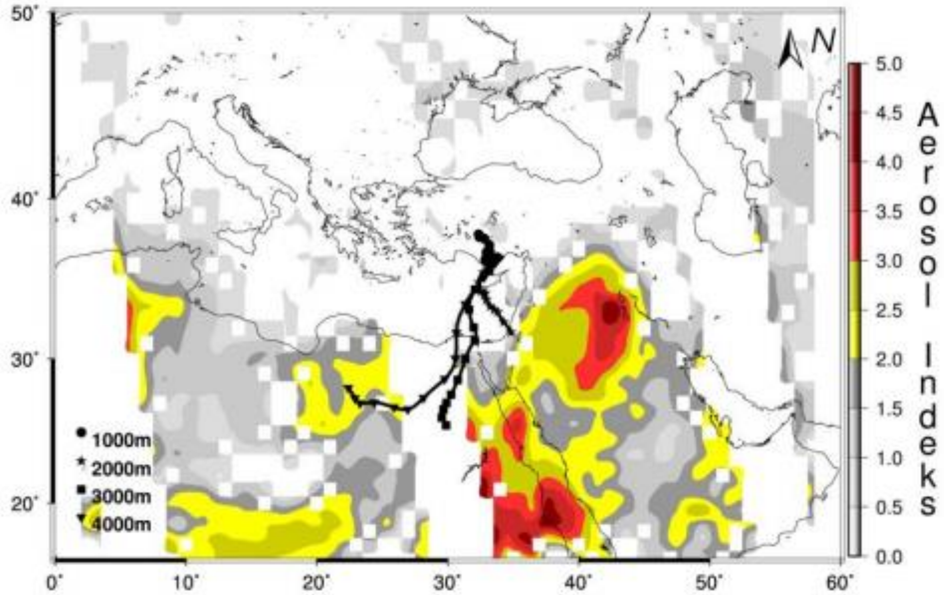


Figure 3.1.4 (*continued*) **(b)** April 29 2015.



(c)

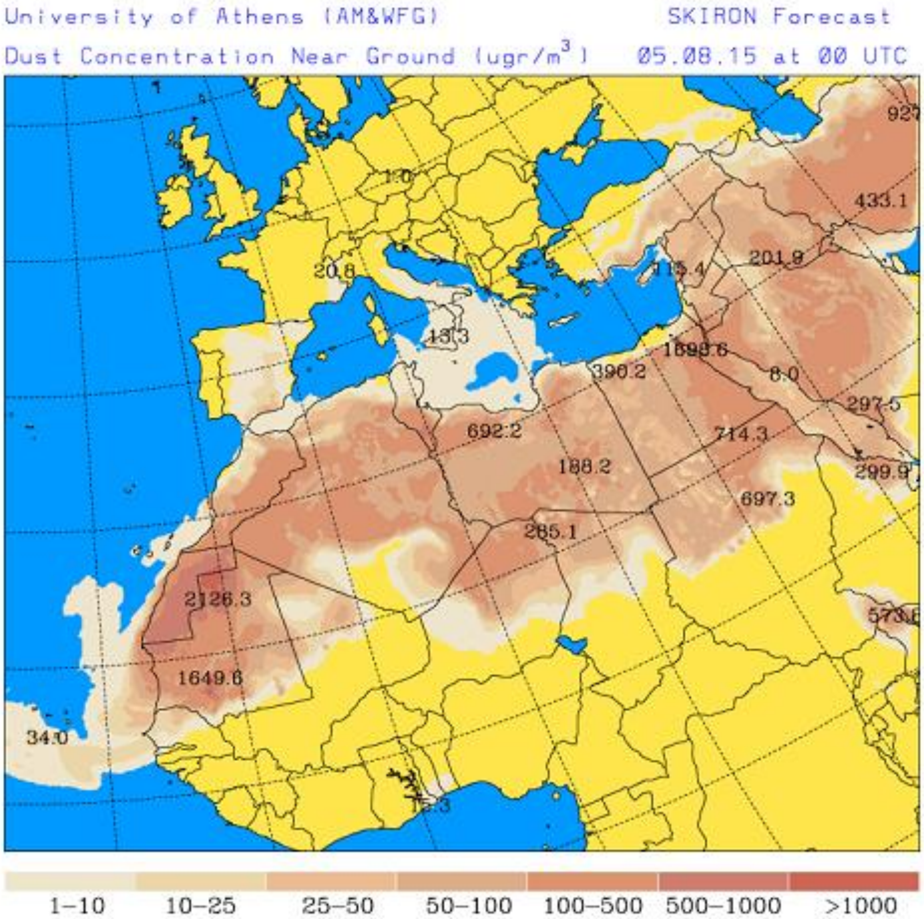
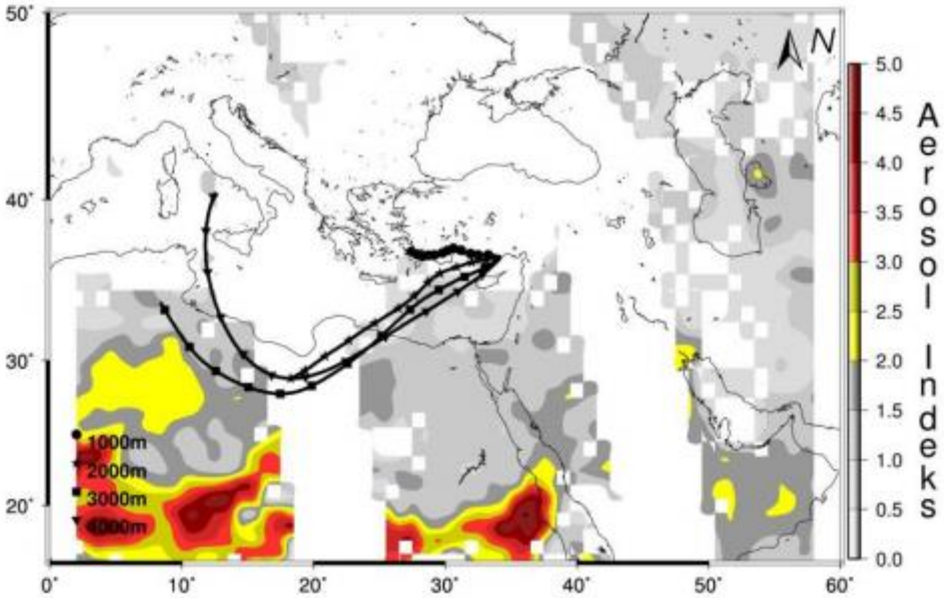


Figure 3.1.4 *(continued)* **(c)** August 5 2015.



(d)

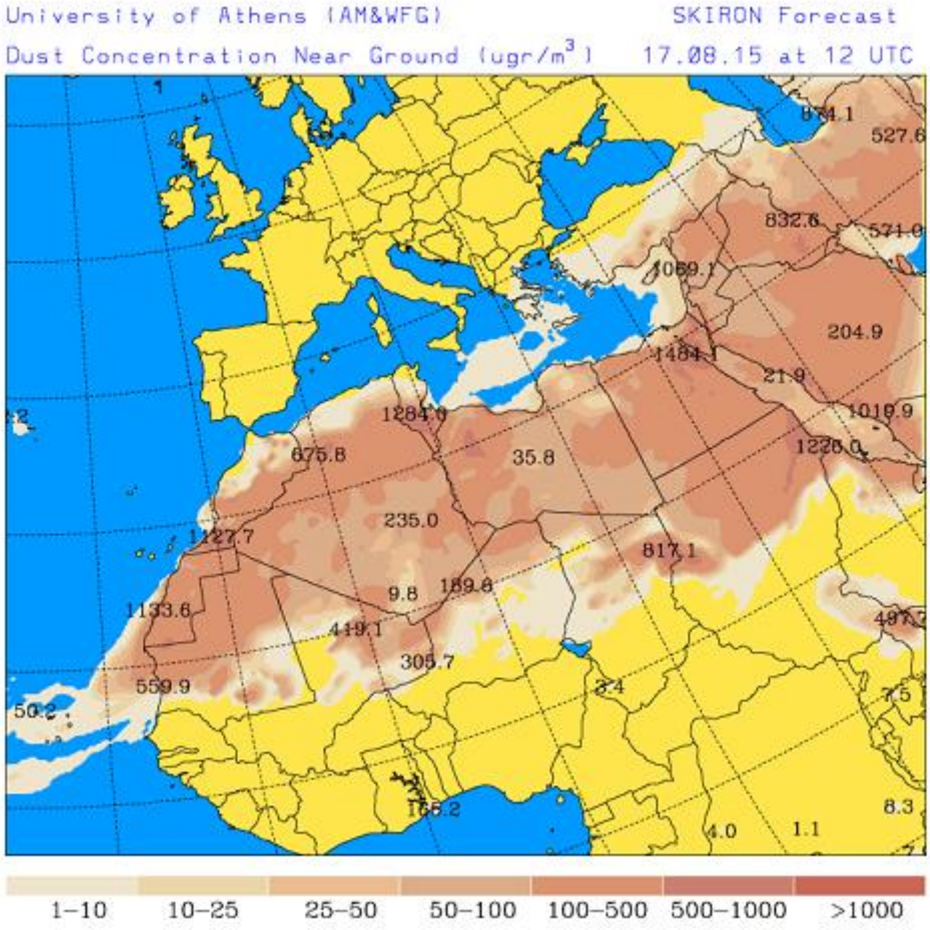


Figure 3.1.4 (*continued*) **(d)** August 17 2015.

3.1.6 Phosphorus, Phosphate, Polyphosphates and Al

In Table 3.1.6 a statistical summary of total P, phosphate and polyphosphate species (trimetaphosphate, tripolyphosphate) is given. While there are numerous studies about soluble phosphate in the aerosols, there is only a limited number of studies concerned with total P (Bergametti et al., 1992; Migon and Sandroni, 1999; Herut et al., 1999; Migon et al., 2001; Markaki et al., 2003), and even fewer regarding polyphosphates.

Bergametti et al. (1992) measured total P in aerosol samples obtained from the Western Mediterranean, and demonstrated that total P concentration could reach up to 100 ng m^{-3} while the geometric mean was reported to be 15.5 ng m^{-3}, showing that geometric mean of total P in Erdemli aerosols was about three times higher. This significant difference between the geometric means of aerosol populations can be plausibly attributed to the proximity of the Eastern Mediterranean to arid areas compared to the Western, and in turn, higher exposure to the mineral dust, which is a primary P source. On the other hand, geometric mean observed of Erdemli aerosols was % 20 lower than those in Migon et al. (2001). However, it should be noted that the sampling station Cap Ferrat is an urban site in the close vicinity of the city of Nice, and the observed total P concentration is under the influence of human activity.

Table 3.1.6 Statistical summary of P-species found in the aerosols (ng m^{-3})

This Study	**Total P**	**Phosphate**	**Trimetaphosphate**	**Tripolyphosphate**
Arithmetic Mean	50.6	10.9	0.7	4.0
SD	30.2	8.8	0.0	0.1
Min	13.1	0.2	3.7	14.1
Max	174.6	48.6	0.8	2.9
Geometric Mean	43.8	7.4	0.7	4.0
Bergametti et al. (1992)				
Geometric Mean	15.5			
Migon et al. (2001)				
Geometric Mean	51.0			

Figure 3.1.5 shows the daily variability of phosphate, trimetaphosphate (TMP) and tripolyphosphate (TPP) during the periods of April, July – August 2015. In resemblance to other species found in the atmospheric particles, polyphosphate species

displayed signficant daily variability. Even though such variability of total P was reported in previous studies in the Mediterranean (Bergametti et al., 1992; Herut et al., 1999; Migon et al., 2001; Markaki et al., 2003), no conclusive report included polyphosphates.

Total P reached its highest values during the dust episodes. Moreover, the correlation coefficient between total P and crustal elements Al, Fe and Mn was found to be above 0.85 ($p < 0.05$). On the other hand, there was a moderate correlation between total P and anthropogenic polluters As and Cd ($r > 0.5$, $p < 0.05$). In the light of this observation, it is plausible to assume that a great majority of total P was of crustal origin, yet, human activity was a significant contributor. Bergametti et al., (1992) found out that P/Al ratio was 0.06 for the (northerly) air masses loaded with pollutants, and 0.03 for mineral dust episodes. In this study, P/Al average of whole dataset was calculated to be 0.05; of dust episodes 0.031; and of non-dust days 0.06. Observed P/Al ratio was in accordance with those reported by Bergametti et al. (1992).

In general TMP and TPP values was found to be higher during summer. In the region known for its exclusively dry summers, lack of precipitation allows deposition of atmospheric particles, and resuspension of local soil might be the reason of observed high concentrations of P. In addition to that, vicinity of the region is frequently struck by forest fire in the summer season. In such cases, biomass burning may also become a contributor of P.

Table 3.1.7 shows contributions of phosphate, TMP, TPP to the overall P concentration. Contributions were calculated in nmol m^{-3} of equivalent phosphorus. The highest contributor was phosphate, with % 7.3, and the second was TPP with % 2.1, while contribution of TMP was only % 0.4. In the light of these findings, it can be concluded that nearly % 10 of total phosphorus in the atmospheric aerosols was water soluble, while the rest is found in water insoluble forms.

Table 3.1.7 Percent contribution of P species to total phosphorus.

P species	Relative contribution to total P (%)
Phosphate	7.3
Trimetaphosphate	0.4
Tripolyphosphate	2.1

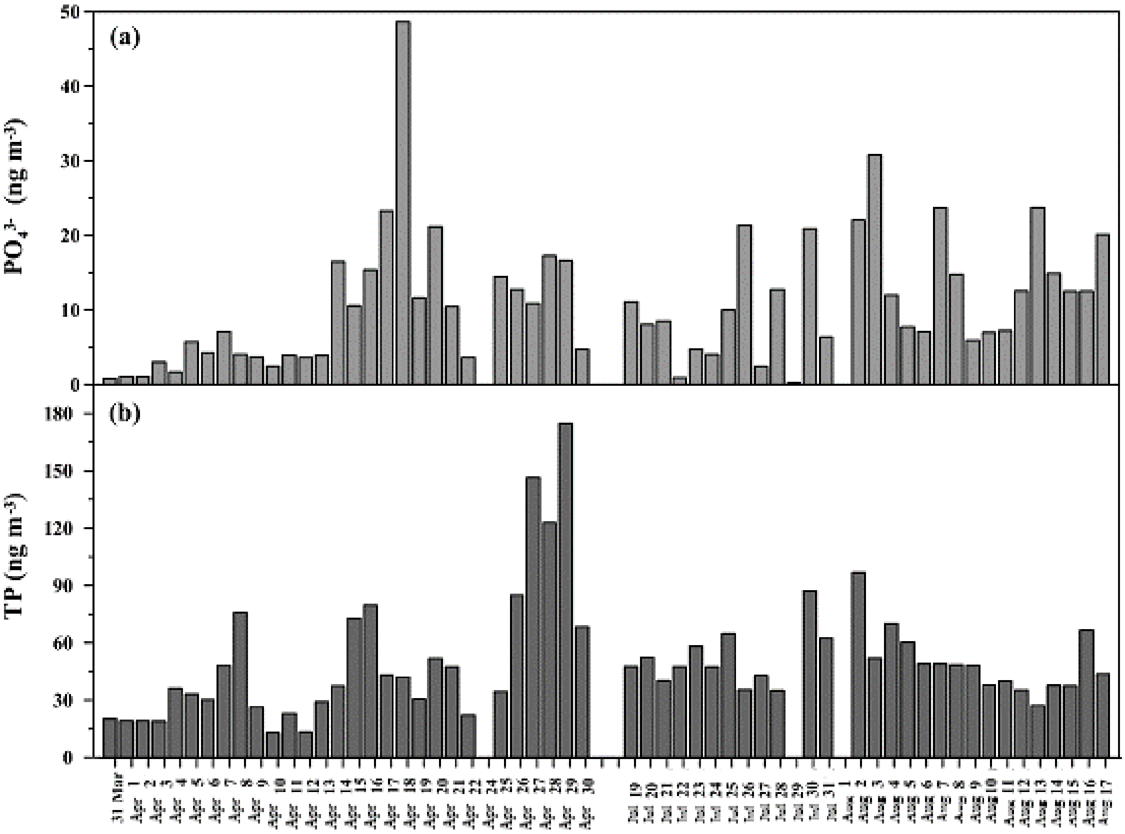


Figure 3.1.5 Daily variability of **(a)** PO_4^{3-}, **(b)** total P, **(c)** trimetaphosphate, **(d)** tripolyphosphate.

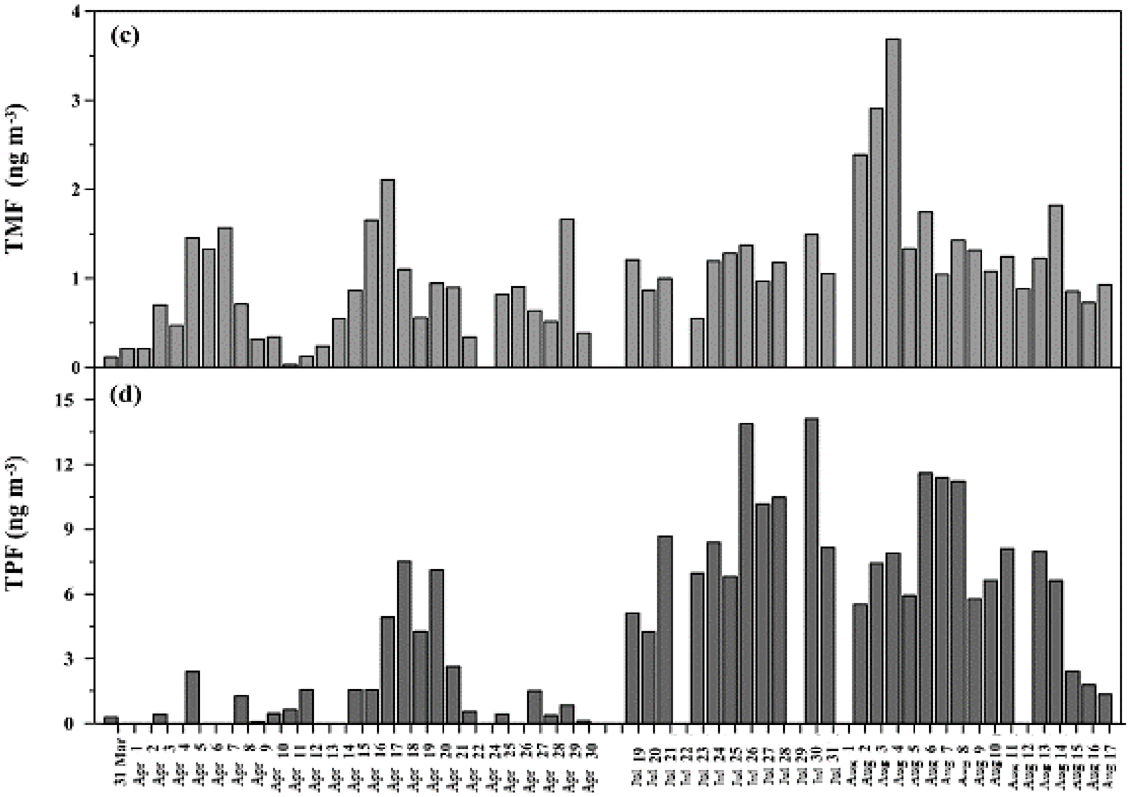


Figure 3.1.5 *(Continued)*

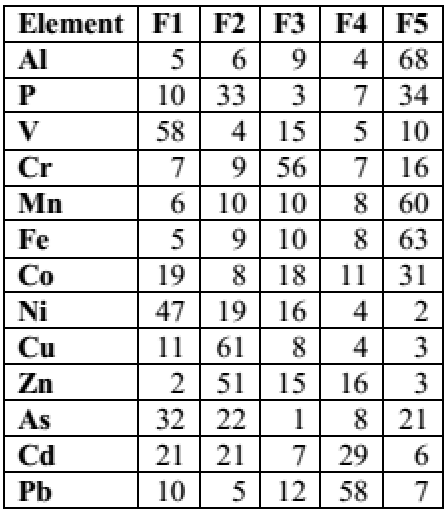
3.1.7 Determination of Origins of Phosphorus by Positive Matrix Factorization

In order to determine and separate the different origins of phosphorus species, an analysis of positive matrix factorization (PMF) was employed. Dataset of matrix were comprised of total P and trace metals representing both mineral dust and different pollutant sources. PMF analysis indicated 5 main groupings; results of the test can be seen at Table 3.1.8. In table every factor is expressed with percent contributions from each element.

Factor 1 accounts for a great fraction of V (% 58) and Ni (% 47), and thus can be attributed to heavy oil combustion (Ha-Na Jang et al., 2006). This grouping can also account for % 10 of total P. Factor 2 dramatically represented % 61 and % 51 of Cu and Zn. Cu and Zn are predominantly anthropogenic elements which are extensively used in agriculture as fungicide and pesticide (Koçak, 2006). Along with Cu and Zn, Factor 2 also accounted % 33 of total P, establishing a possible connection with agricultural activities. Factor 3 represented a remarkable % 56 of Cr and % 3 of total phosphorus. Because of the high Cr loading , Factor 3 can be attributed to the ophiolithic rock formation which are relatively abundant in the region (Kubilay and

Saydam, 1995). Factor 4, which explained % 58 of Pb and % 29 of Cd, also accounted for % 7 of P. Pb and Cd originate mainly from human activities, and Factor 4 might be understood as the battery industry. The last group (Factor 5) accounted for the % 68, % 63, % 60 and % 34 of Al, Fe, Mn and P, respectively, and thus can be attributed to the mineral dust. It can be concluded that at least % 34 of total P had crustal origin.

Table 3.1.8 Percentages of factor loadings obtained by positive matrix factorization.



Element	F1	F2	F3	F4	F5
Al	5	6	9	4	68
P	10	33	3	7	34
V	58	4	15	5	10
Cr	7	9	56	7	16
Mn	6	10	10	8	60
Fe	5	9	10	8	63
Co	19	8	18	11	31
Ni	47	19	16	4	2
Cu	11	61	8	4	3
Zn	2	51	15	16	3
As	32	22	1	8	21
Cd	21	21	7	29	6
Pb	10	5	12	58	7

3.1.8 Trace Metal Concentrations in Rainwater

Volume weighted means of trace metal concentrations determined in rainwater samples are given in Table 3.1.9, in addition to that, concentrations observed in particle phase are also present in the table. Al-Momani et al. conducted a comprehensive research regarding rainwater in region (1998), and for any comparisons, this research will be used, along with the study carried out by Özsoy and Saydam (2000, 2001) which presents the rainwater samples from 1996-1997. in Erdemli. Such a comparison may provide insight about the general trend of pollutants since it provides information about the concentrations of trace elements measured in the rainwater samples collected between 1992 and 1994.

Table 3.1.9 Volume weighted mean concentrations of water soluble trace metals in rainwater.

Trace Metal (µg L^{-1})	Al-Momani et al. (1998)	This study
Cd	4.3	0.1
Cu	3.1	2.5
Pb	6.4	0.6
Al	73.0	30.0
Ni	11.0	0.8
Cr	3.7	0.7
Zn	124	32.0

When the findings of this study was compared with the historical dataset, it is seen that nearly all anthropogenic elements except Cu has decreased significantly. Similar decline was observed for aerosols in the Eastern Mediterranean (Koçak et al., 2004b). While the decline in the concentration of Pb was observed to be 10 fold, it was 40 times for Cd. Cr and Zn concentrations decreased 5 times, while decrease in Ni concentration was found to be 10 times. As mentioned earlier (see Section 3.1.1) decrease in Pb concentration was also observed in aerosol, which is in accordance with the trend in the rainwater.

Following the filtration process of rainwater samples with serially connected polycarbonate filters with pore sizes 2 μm and 0.4 μm, the filters then was dried, and analyzed for their trace metal content in order to determine trace metal abundance in particulate matter in two different size (for details, see Section 2.3.1). Results are presented in Table 3.1.10. As can be seen in the table, two different particle size were equally affected from pollutants of anthropogenic origin. However, this odd trend, which anthropogenic elements Cd, As, Zn, Cu unexpectedly follows, requires further research to be enlightened. Applications of SEM and TEM would further expand our knowledge on the subject matter.

When results by Al-Momani et al. (1998) were compared with those by Özsoy and Saydam (2000, 2001) it is found out that the latter reports 3 times higher concentrations of particulate Al in the eastern part of the Northern Levantine Basin. The concentrations reported by Al-Momani et al. (1998) and the current study may differ 5 to 10 times in some elements, while a comparison of Al and Fe concentrations with the historical Erdemli data (Özsoy and Saydam, 2000, 2001) demonstrated threefold difference (Table 3.1.11). However, it should be noted that the period of sampling in the study is heavily inluenced by episodic mineral dust events, which may, in turn, increase the overall concentration of crustal elements. Lack of long term time series data on the subject matter obstructs comprehensive understanding of the nature of observed phenomena.

Table 3.1.10 Distribution of trace metals according to particle size in rainwater particulate matter samples.

TM (μg L^{-1})	Coarse (d > 2 μm)	Fine (d:2-0.4 μm)	Coarse/Fine
Al	2685	2602	1.0
V	13.4	5.7	2.3
Cr	39.4	26.9	1.5

Mn	24.5	22.5	1.1
Fe	2424	2116	1.1
Co	1.4	1.0	1.4
Ni	15.3	10.6	1.4
Cu	13.0	7.0	1.8
Zn	142	98.9	1.4
As	0.9	0.6	1.6
Cd	0.4	0.2	1.9
Pb	18.9	31.6	0.6

Table 3.1.11 Particulate phase trace metal concentrations in rainwater in past studies.

Trace Metal (µg L^{-1})	Al-Momani et al. (1998)	Özsoy and Saydam (2000, 2001)
Cd	0.2	
Cu	2.0	
Pb	4.0	
Al	540	1519
Fe	-	1456
Ni	13.0	
Cr	6.0	
Zn	11.0	

3.1.9 Speciation of Trace Metals

Table 3.1.12 shows arithmetic means of trace metal concentrations obtained from the speciation carried out in (a) rainwater, (b) aerosol samples. It can be seen that majority of Al was in anionic form in rainwater, while V was equally distributed among both forms (anionic and cationic). Co, Zn and As were distributed between two forms with a tendency toward cationic form. The soluble fractions of the rest of the elements were dominated by cationic form.

As for aerosol samples, a dramatic difference for As was observed between two modes of samples. For instance, aerosol anionic/cationic ratio of As was almost 100 times higher than that was observed for rainwater. More than half of soluble Fe (% 55), which plays a major role as an essential micronutrient in marine ecosystems, was found to be in anionic form, which may be an implication of complex formation with organic ligands.

Table 3.1.12 Separation of anionic and cationic forms of water soluble trace metals in (a) rainwater (b) aerosol samples.

	(a) Rainwater		
TM (µg L^{-1})	**Anionic**	**Cationic**	**Anionic/Cationic**
Al	59.4	9.7	6.1
V	0.13	0.15	0.9
Mn	0.2	1.2	0.2
Co	0.01	0.02	0.6
Ni	0.5	1.9	0.3
Cu	0.7	6.1	0.1
Zn	56.7	85.4	0.7
As	7.3	10.8	0.7
Cd	0.04	0.16	0.3
Pb	0.6	2.5	0.2
	(b) Aerosol		
TM (µg L^{-1})	**Anionic**	**Cationic**	**Anionic/Cationic**
Al	95.0	56.0	1.7
V	0.3	0.7	0.4
Cr	0.3	0.1	3.7
Mn	0.8	3.8	0.2
Fe	8.0	6.4	1.2
Co	0.01	0.04	0.4
Ni	0.4	1.0	0.4
Cu	0.4	0.5	0.7
Zn	19.0	13.7	1.4
As	3.5	0.1	61.3
Cd	0.01	0.04	0.4
Pb	0.12	0.30	0.4

3.2 Addition of Atmospheric Dust to the Coastal and Open Seawater Samples

Experimental setup describing the addition of atmospheric dust particles to open and coastal surface waters and the amounts of dust is given in Table 3.3.1. For the experiment 20 L Nalgen bioassay bottles were used, and the bioassay laboratory was redesigned in terms of light setting and temperature. The dimensions of the containers in which the experiment was carried out play a significant role. For the best results, at least % 70 – 75 of the initial amount of water must remain in the bottles (Assoc. Prof. Dr. Nebil Yücel, personal communication). For instance, as the liquid amount decreases, precipitating phytoplankton causes unrealistic increase in abundance. On the other hand, since volume/surface ratio increases in the bigger bottles, choosing bigger bottles are considered to be more successful at eliminating biases caused by adsorption of phytoplankton to the surface of the experimental containers. It should be emphasised that, the dust addition assay should be repeated as a mesocosm experiment (for example, with 9 10000 L experimental container) in order minimize or completely rule out this effect.

Before the experiment, the reaction between experimental containers and the seawater was monitored for 15 days. Interestingly it has been observed that the nutrient concentration in the seawater increased continuously during the process. It is known that the containers excrete Biphenol-A to the water and their surface are active against ionic species contained in seawater. The surface of the containers were probably enriched with ionic species during the production process. Therefore, before proceeding with the bioassay, the containers should be treated to eliminate these unwanted effects. In order to prevent the nutrient release, the containers were treated and stirred with seawater for 4 months. Afterwards, they were cleaned with HCl and Milli-Q water.

As indicated in the Table 3.3.1, for each group two control and two parallels were used (4 control and 24 experimental bottles in total). Estimated nutrient amounts provided for each experimental setup were also included in the table. The nutrient amounts found in the samples taken from the open and coastal areas for experiment were presented in Table 3.3.2. While ammonium and silicate amounts were observed to be comparable in two stations, it is found out that phosphate and nitrate amounts were twice lower in the open station compared to the coastal station.

Table 3.2.1 Experimental setup of dust addition experiments, dust type, and estimated phosphate (nM) amount provided with dust.

Incubation Bottle	Label	Dust Added)	Added P-PO_4^{3-} (nM)
Coastal Station			
1	Control1		
2	Control2		
3	DB1	1 mg	0.6
4	DB1	1 mg	0.6
5	DB3	3 mg	1.8
6	DB3	3 mg	1.8
7	DB5	5 mg	3.0
8	DB5	5 mg	3.0
9	BB1	1 mg	1.2
10	BB1	1 mg	1.2
11	BB3	3 mg	3.6
12	BB3	3 mg	3.6

13	BB5	5 mg	6.0
14	BB5	5 mg	6.0
Open Station			
15	Control1		
16	Control2		
17	DB1	1 mg	0.6
18	DB1	1 mg	0.6
19	DB3	3 mg	1.8
20	DB3	3 mg	1.8
21	DB5	5 mg	3.0
22	DB5	5 mg	3.0
23	BB1	1 mg	1.2
24	BB1	1 mg	1.2
25	BB3	3 mg	3.6
26	BB3	3 mg	3.6
27	BB5	5 mg	6.0
28	BB5	5 mg	6.0

Table 3.2.2 Initial nutrient (phosphate, nitrate, silicate and ammonium) concentrations (μM) found in the open and coastal water samples used in the bioassay.

Nutrient	Coastal	Open
Phosphate	0.04	0.02
Nitrate	0.20	0.08
Silicate	0.73	0.71
Ammonium	0.36	0.35

When the information given in the two tables are compared, it can be seen that atmospheric particles provide a significant amount of N and P to the surface waters in both stations. In the dust addition experiment conducted by Herut et al. (2005) the amount of phosphate added into each experimental setup varied between 1 and 16 nM (in which experiment 2 control and 5 experimental setup was employed). In the experiment, two different dust samples were used, namely DB and BB, which provided 0.6 – 3.0 and 1.2 – 6.0 nM phosphate to the experimental setups, respectively. Figure 3.3.1 and 3.3.2 showed Chl-a concentration versus time in the coastal water samples throughout the experiment. DB (Dark Brown) and BB (Bright Brown) represent anthropogenic+mineral dust and mineral dust dominated aerosol populations, respectively. Both DB and BB populations were observed to have impact on primary production. Relative Chl-a concentrations increased at least 3-fold with respect to control group at the end of the fifth day (T5). Another remarkable result is that, primary production rate increased with the increasing dust amount. Therefore, the amount of nutrient provided for primary producers increased with increasing dust concentration. Research regarding nutrient solubility showed that nitrate solubility is comparable between pure water and seawater, whereas the solubility of phosphate may decrease to half in seawater compared to the pure water (Koçak, 2015). In the light of these findings, it should be noted that the amount of available phosphate might be overestimated up to % 50. Despite this fact, in both dust addition setup, rate of primary production increased with the increasing dust concentration. The effects of two dust treatments to the coastal water samples were observed to be different in terms of primary production rates. BB dust increased phytoplankton production at a higher rate than DB did. Even though N contents of two dust populations were documented to be different, both treatments provided excessive amount of N to the experimental setups. For instance, the molar N/P ratio of DB was around 700 while it was 200 for BB. On the other hand, BB provided 2 times more P than DB (0.6 nM/mg for DB and 1.2 nM/mg for BB). Hence the difference in production rates between two dust treatments might be attributed to the partial contribution of phosphorus.

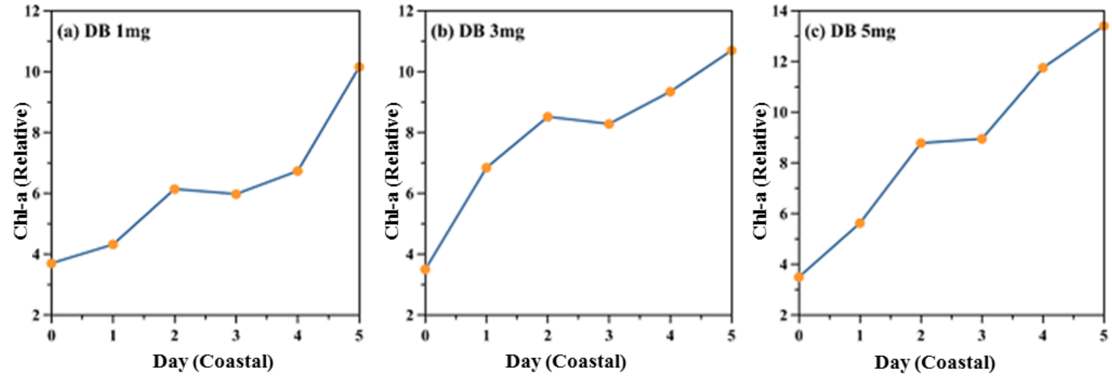


Figure 3.2.1 Daily change in chl-a in coastal water samples after DB dust has been added **(a)** DB 1 mg/L, **(b)** DB 3 mg/L **(c)** DB 5 mg/L.

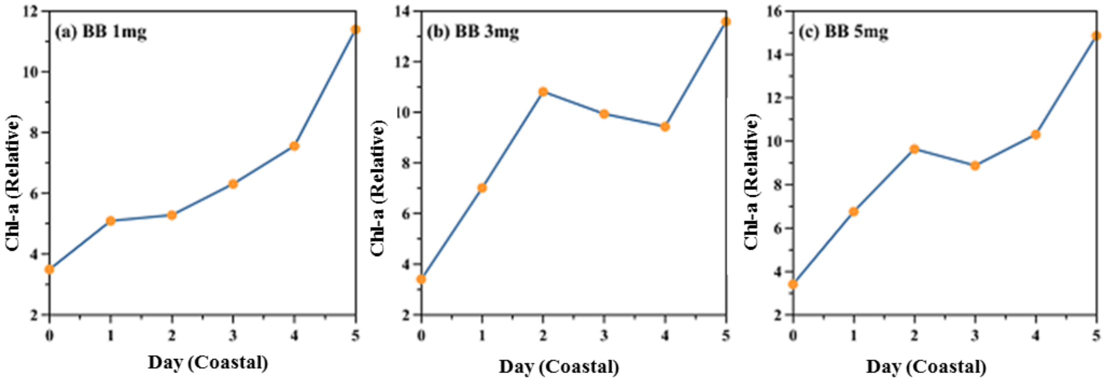


Figure 3.2.2 Daily change in chl-a in coastal water samples after BB dust has been added **(a)** DB 1 mg/L, **(b)** DB 3 mg/L **(c)** DB 5 mg/L.

Prochlorococcus, synechococcus and picoeukaryote abundances for coastal station samples (for both DB and BB treatment) are given in Figure 3.3.3, 4, 5, 6, 7, 8. In both experimental setups, prochlorococcus abundance increased until day 2, which was followed by a steep decline. Synechococcii was observed to display a more complex pattern. In DB 1 mg setup, day 3 and 4 showed an increase reaching up to 70 million cells/L. Increase in DB 3 and 5 mg was less significant. However, in all BB treatments, a time dependent decrease was recorded. Picoeukaryotes in general was observed to decrease in day 2 and 3 and attained their initial abundances in day 4 and 5.

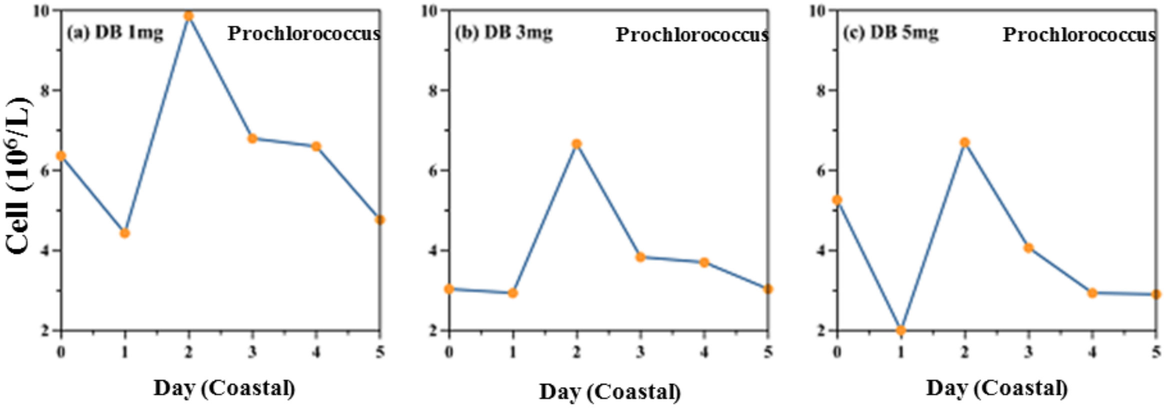


Figure 3.2.3 Daily change in prochlorococcus in coastal water samples after DB dust has been added **(a)** DB 1 mg/L, **(b)** DB 3 mg/L **(c)** DB 5 mg/L.

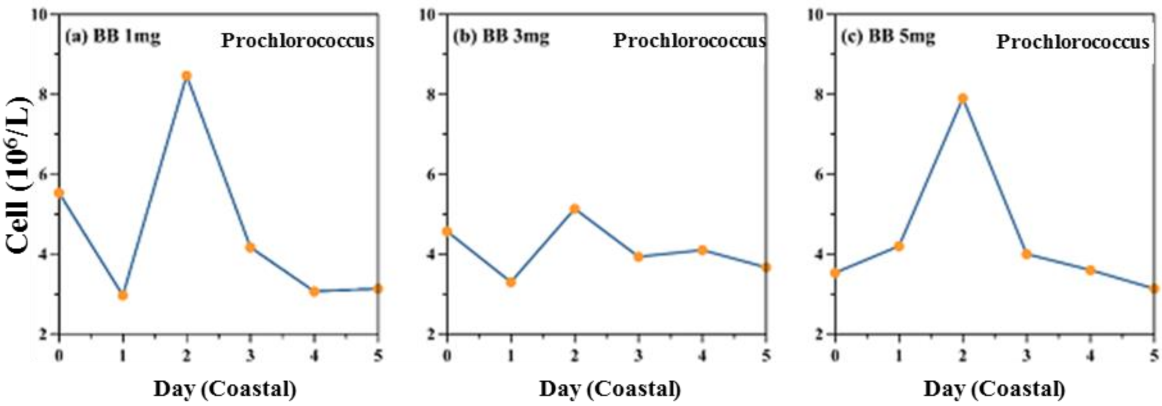


Figure 3.2.4 Daily change in prochlorococcus in coastal water samples after BB dust has been added **(a)** DB 1 mg/L, **(b)** DB 3 mg/L **(c)** DB 5 mg/L.

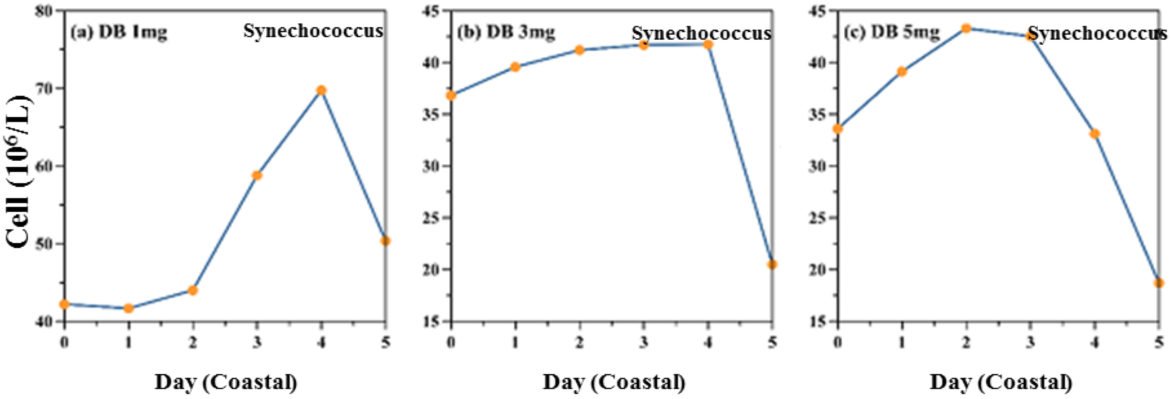


Figure 3.2.5 Daily change in synechococcus in coastal water samples after DB dust has been added **(a)** DB 1 mg/L, **(b)** DB 3 mg/L **(c)** DB 5 mg/L.

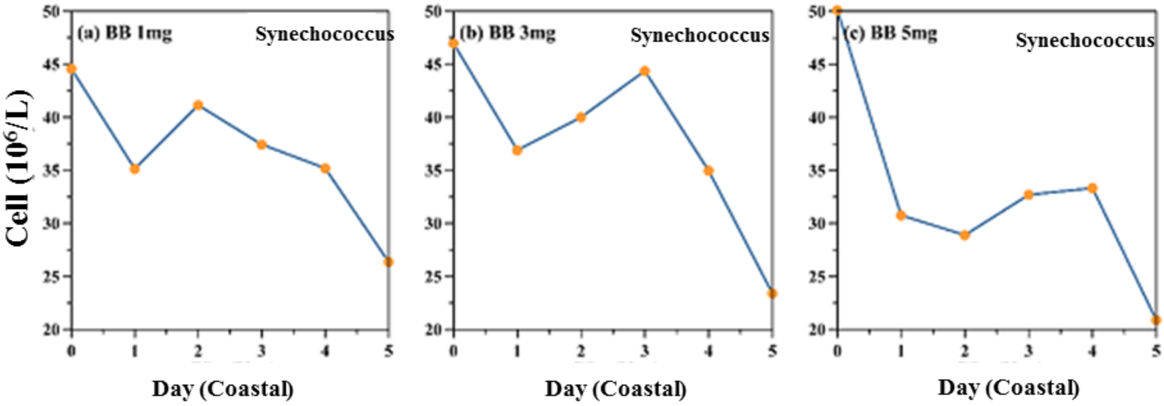


Figure 3.2.6 Daily change in synechococcus in coastal water samples after BB dust has been added **(a)** DB 1 mg/L, **(b)** DB 3 mg/L **(c)** DB 5 mg/L.

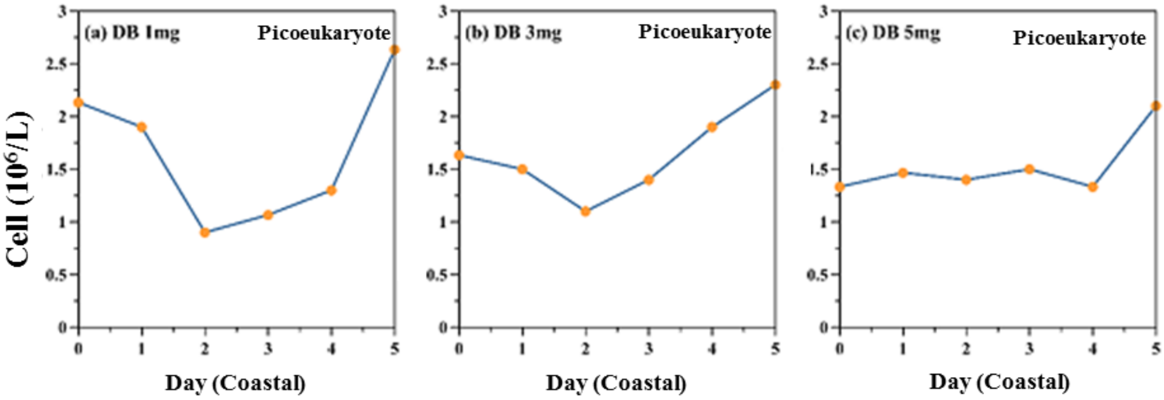


Figure 3.2.7 Daily change in picoeukaryote in coastal water samples after DB dust has been added **(a)** DB 1 mg/L, **(b)** DB 3 mg/L **(c)** DB 5 mg/L.

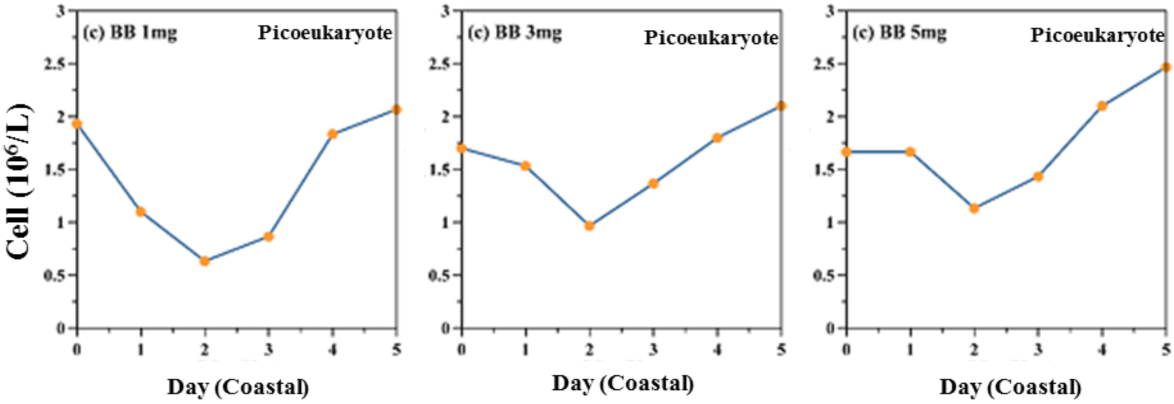


Figure 3.2.8 Daily change in picoeukaryote in coastal water samples after DB dust has been added **(a)** DB 1 mg/L, **(b)** DB 3 mg/L **(c)** DB 5 mg/L.

Figure 3.3.9 and 3.3.10 show chl-a versus time for DB and BB in open station. It can be seen that both DB of mixed origin and BB of predominantly crustal origin had their impacts on primary production. At the day 5, chl-a concentration increased 2-fold for DB, and 3-fold for BB, with respect to controls. In DB, primary production rate increased with the increasing concentration. On the other hand, for BB, highest rate of production was observed in 1 mg setup. In DB experiment, prochlorococcii displayed similar trends as in the coastal station samples, and abundance of prochlorococcii increased in day 2.

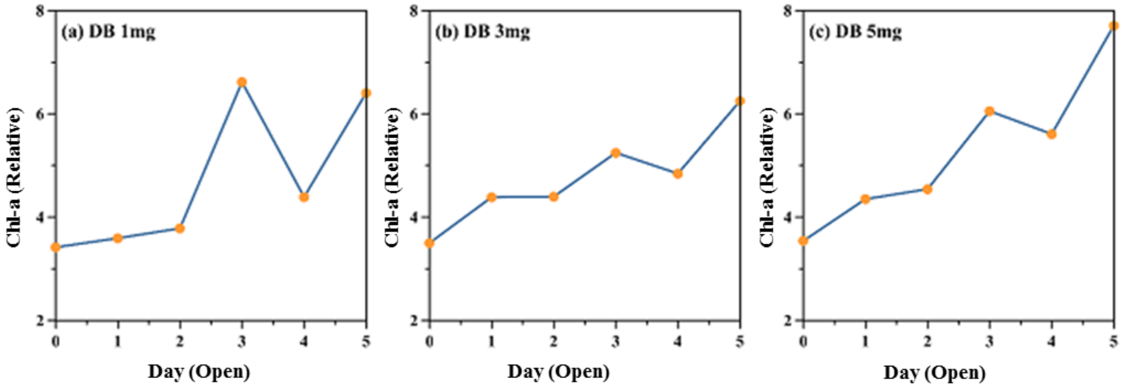


Figure 3.2.9 Daily change in chl-a in open water samples after DB dust has been added **(a)** DB 1 mg/L, **(b)** DB 3 mg/L **(c)** DB 5 mg/L.

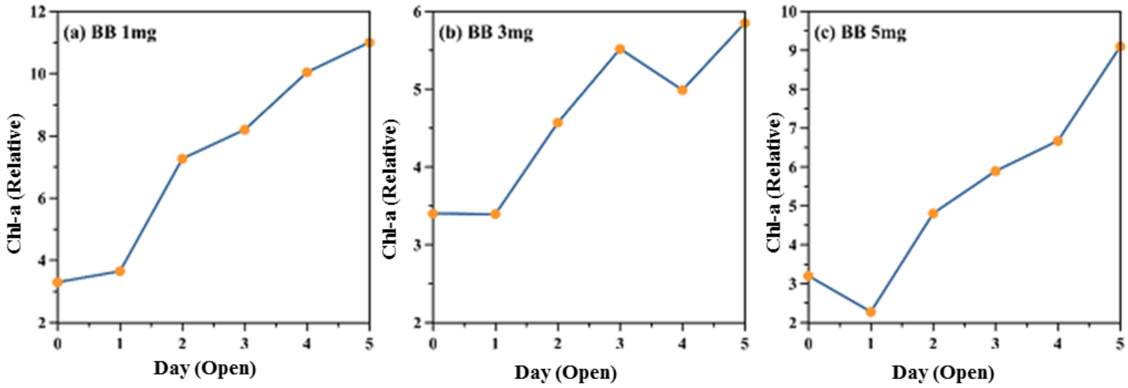


Figure 3.2.10 Daily change in chl-a in open water samples after BB dust has been added **(a)** DB 1 mg/L, **(b)** DB 3 mg/L **(c)** DB 5 mg/L.

HPLC pigment analysis was found to be in accordance with the results. For instance, pigments beta-carotene, zeaxanthin (an indicator for synechococcii) and divinyl Chl-a (an indicator for prochlorococcii) dropped from 10 ng/L to below detection limit (~1 ng/L) while Chl-a rised from 20 ng/L (at day 2) to 60 ng/L (at day 5). Chl-2 and Chl-3 increased as much as % 40 from day 2 to day 5. Another remarkable resul is that anionic and cationic Cu concentration displayed an increasing trend throughout the experiment, cationic Cu rising from initial 0.012 nM to 4 nM day 5. Paytan et al. (2009) claimed that Cu might have toxic effect on synechococcii. In every experimental setup both synechococcii and prochlorococcii populations increased until day 2, which was followed by significant decreases while Cu concentrations exhibited an opposite pattern. Within the light of these findings, it can be said that Cu might have a toxic effect on these taxa.

4 CONCLUSION

The sampling carried out which reflect different seasonal features demonstrates dramatic daily variability in the trace metal concentrations. Especially episodic dust events change the composition and concentration of trace metals found in the atmospheric particles.

It has been observed that concentrations of crustal elements (Al, Fe, Mn) were nearly three times higher during the episodic dust event than those in the non-dust days. On the other hand, anthropogenic originated elements exhibit a similar enrichment trend during dust events compared to the non-dust days. Concentrations of V, Cr, Co, Ni, As, Cd and Pb, were observed to be 1.5 times in dust days, while for Zn and Cu relative enrichment in dust events is about 1.2. These enrichment trend in athropogenic elements can be attributed to: (i) Modification of mineral dust by anthropogenic aerosols during the long range transport. In other words, mineral dust might provide a surface to adhere to the anthropogenic aerosols, which explains the enrichment, (ii) The aeorosols of anthropogenic origin directly emitted from the regions in the southern coast of the Mediterranean. (iii) The path of mineral dust. Depending on the trajectory of the air mass, the aerosols are affected by pollutants in varying degrees. The route mineral dust follows before reaching the Erdemli station defines and modifies its chemical composition to a great extent.

Comparing the current Pb concentrations to historic values of Erdemli showed a sharp decrease, along with other pollutants.

Positive matrix factorization analysis carried out with P and the other trace metals found in the aerosol samples indicated that nearly % 34 percent of total P originates from the Earth’s crust, while % 33 of total phosphorus can be attributed to agricultural activities.

Investigations regarding the water-soluble fraction of trace elements revealed that the majority of dissolved Al is anionic. Concentrations of anionic and cationic V were found to be comparable in rainwater. The speciation study also showed that Co, Zn and As were moderately cationic while the rest of the elements were dominated by cationic species in rainwater. The study regarding water soluble forms found in the aerosol revealed a dramatic difference for As: The anionic/cationic ratio observed in aerosol is almost 100 times higher than of rainwater. The % 55 of water-soluble fraction of Fe, which plays a major role in marine production, was found to be anionic.

As the first speciation study carried out in the region with ion exchanging methods, the research needs to be supplemented with comprehensive and more elaborate structure determination methods. In order to investigate any differentiation between the aerosol and dry depositional modes, the same method needs to be applied to the dry deposition samples.

The annual fluxes of phosphate, trimetaphosphate and tripolyphosphate were found to be 0.65, 0.06 and 0.09 mmol m^{-2} y^{-1}, respectively. It was observed that % 85 of all soluble phosphate flux originated from dry deposition (aerosol). It can be concluded that phosphorus provided by the atmospheric input alone can sustain new production at a rate of 3.1 mg C m^{-2} d^{-1}. Aeoliean phosphorus can account for % 0.8 - 1.7 of total primary production. When only new production is considered, it can be seen that atmospheric P input can account for the % 5 – 11 of new production.

On the other hand, atmospheric nutrient input becomes more important for the surface waters in terms of new production, during the summer season with the stratification of water column. For instance, in time of stratification (June – October period), atmospheric input of P can support up to % 38 of new production.

Dust addition experiment showed that, in coastal surface waters, addition of both mineral dust (BB) and anthropogenic+mineral dust (DB) caused an increase in marine primary production, (up to 4-fold chl-a increase). It was observed that BB increased primary production at a greater rate than DB did. Even though the two aerosol types differ in their nitrogen content, it was understood that both aerosol populations provide extensive amount of nitrate to the water samples regarding their N/P ratios. N/P ratios of DB and BB were found to be 700 and 200, respectively, extceedingly higher than the normal Redfield ratio of 16, ensuring neither of the experimental setups were N-limited. It should be also noted that BB contains twice higher P than equivalent amount of DB (0.6 nM/mg for DB and 1.2 nM/mg for BB); the difference in production rates can be attributed to the strictly but not exclusively P-limited conditions. In the course of the experiment, phosphate concentration decreased, which is in accordance with the findings. For instannce, BB 5 mg treatment dropped from the initial ~9 nM to the 0.3 nM at 5th day.

In the dust addition experiment, dissolved Cu concentrations increased throughout the experiment. In all the experimental setups, both prochlorococcii and synechococcii abundances faced a steep decrease after the first two days of the experiment. In the given conditions, it can be hyphothesized that Cu might have toxic effects on these bacterial communities. Further studies such as marine in situ research, mesocosm dust addition experiments will be needed to achieve a better understanding of our environment.

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