

**COMPARISON OF THE RURAL ATMOSPHERE AEROSOL
COMPOSITIONS AT DIFFERENT PARTS OF TURKEY**

**A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY**

BY

GÜRAY DOĞAN

**IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF MASTER OF SCIENCE
IN
THE DEPARTMENT OF ENVIRONMENTAL ENGINEERING**

JANUARY 2005

Approval of the Graduate School of Natural and Applied Sciences

Prof. Dr. Canan Özgen
Director

I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Science.

Prof. Dr. Filiz B. Dilek
Head of Department

This is to certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

Prof. Dr. Gürdal Tuncel
Supervisor

Examining Committee Members

Prof. Dr. Celal F. Gökçay (METU, ENVE) _____

Prof. Dr. Gürdal Tuncel (METU, ENVE) _____

Asst. Prof. Dr. Ayşegül Aksoy (METU, ENVE) _____

Asst. Prof. Dr. İpek İmamoğlu (METU, ENVE) _____

Asst. Prof. Dr. Eftade O. Gaga (Anadolu Univ., CHEM) _____

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Name, Last name : Gray Dođan

Signature :

ABSTRACT

COMPARISON OF THE RURAL ATMOSPHERE AEROSOL COMPOSITIONS AT DIFFERENT PARTS OF TURKEY

Dođan, Gray

M.Sc., Department of Environmental Engineering

Supervisor: Prof. Dr. Grdal Tuncel

January 2005, 195 pages

Long term data generated at four rural stations are compared to determine similarities and differences in aerosol compositions and factors contributing to observed differences at different regions in Turkey. The stations used in this study are located at Mediterranean coast (20 km to the west of Antalya city), Black Sea coast (20 km to the east of Amasra town), Central Anatolia (Çubuk, Ankara) and Northeastern part of the Anatolian Plateau (at Mt. Uludađ). Data used in comparisons were generated in previous studies. However, some re-analysis of data were also performed; (1) to improve the similarities of the parameters compared and (2) to be able to apply recently-developed methodologies to data sets.

Data from Mediterranean and Black Sea stations were identical in terms of parameters measured and were suitable for extensive comparison.

However, fewer parameters were measured at Çubuk and Uludağ stations, which limited the comparisons involving these two stations. Comparison included levels of major ions and elements, short-term and seasonal variations in concentrations, background (baseline) concentrations of elements, flow climatology of regions, correlations between elements, potential source areas affecting regions, and source types affecting chemical composition of particles.

Comparison of levels of measured parameters in four regions showed that there are some differences in concentrations that arise from differences in the local characteristics of the sampling points. For example very high concentrations of elements such as Na and Cl in the Mediterranean region is attributed to closer proximity of the Antalya station to coast and not a general feature of the Mediterranean aerosol. There are also significant regional differences in the concentrations of measured elements and ions as well. Concentrations of anthropogenic elements are very similar at two coastal stations (Antalya and Amasra), but they are approximately a factor of two smaller at the two stations that are located on the Anatolian Plateau. This difference between coastal and high altitude plateau stations, which is common to all anthropogenic species, is attributed to different source regions and transport mechanisms influencing coastal regions and Anatolian Plateau.

Some statistically significant differences were also observed in the temporal variations of elements and ions measured in different stations. The elements with crustal origin showed similar seasonal pattern at all stations, with higher concentrations in summer and lower concentrations in winter. This difference between summer and winter is attributed to suppression of re-suspension of crustal aerosol from wet or ice-covered surface soil in winter. Concentrations of anthropogenic elements, on the other hand, did not show a statistically significant seasonal trend at

Amasra, Çubuk and Uludağ stations, but they have higher concentrations during summer months at the Antalya station. This difference between Mediterranean aerosol and aerosol at the Central and Northern Turkey is due to influence of more local sources on Çubuk, Amasra and Uludağ stations and domination of more distant source in determining aerosol composition at the Mediterranean region. A similar conclusion of strong influence of local sources on chemical composition of particles at the Central Anatolia was also suggested by the comparison of baseline concentrations in each station.

General features in flow climatology (residence times of upper atmospheric air masses) in each region are found to be similar with more frequent flow from W, WNW, NW and NNW wind sectors. Since these are the sectors that include high emitting countries in Eastern and Western Europe and Russia, transport from these sectors are expected to bring pollution from both distant European countries and more local Balkan countries and western parts of Turkey.

Flow climatology in stations showed small, but statistically significant, differences between summer and winter seasons. These variations suggested that the station at the Central Anatolia and Black Sea (Çubuk Amasra and Uludağ stations) are affected from sources located at the Western Europe in winter season and from sources located at the Eastern Europe in summer. Mediterranean aerosol, on the other hand, are affected from sources at the Western Europe and do not show any seasonal differences. This variation in flow climatology between summer and winter seasons (and lack of variation at the Mediterranean station) is supported by the seasonal variation (and lack of variation at the Mediterranean station) in $\text{SO}_4^{2-}/\text{NO}_3^-$ ratio measured at the stations.

Potential source contribution function (PSCF) values are calculated for selected elements and ions in each station. Statistical significance of

calculated PSCF values is tested using bootstrapping technique. Results showed that specific grids at Russia and at Balkan countries are common source regions affecting concentrations of anthropogenic elements at all four regions in Turkey. However, each station is also affected from specific source regions as well. Aerosol composition at the Anatolian Plateau are affected from sources closer to the sampling points whereas Mediterranean and Black Sea aerosol are affected from source regions that farther away from the receptors. It should be noted that the same conclusion is also reached in comparison of seasonal patterns and baseline concentrations at these stations.

Types of sources affecting aerosol composition at Black Sea, Mediterranean and Central Anatolia are also compared. Source types affecting atmospheric composition in these regions were calculated using positive matrix factorization (PMF). The results showed that aerosol at the Black Sea, Central Anatolia and Mediterranean atmosphere consists of 8, 6 and 7 components, respectively. Two of these components, namely a crustal component and a long-range transport component are common in all three stations. The chemical compositions of these common components are shown to the same within 95% statistical significance interval. Three factors, namely a fertilizer factor, which is highly enriched in NH_4^+ ion, a sea salt component and an arsenic factor are common in the Mediterranean and Black Sea aerosol but not observed at the Central Anatolia. Other factors found in the regions are specific for that region.

Keywords: Turkey, Black Sea, Mediterranean basin, Anatolian Plateau, Potential Source Contribution Function, Positive Matrix Factorization, Correlations between parameters, Rural Atmosphere Aerosols, SO_4^{2-} to NO_3^- ratio.

ÖZ

TÜRKİYE'NİN DEĞİŞİK BÖLGELERİNDEKİ KIRSAL ATMOSFER AEROSOL KOMPOZİSYONLARININ KARŞILAŞTIRILMASI

Dođan, Güray

M.Sc., Çevre Mühendisliđi Bölümü

Tez Yöneticisi: Prof. Dr. Gürdal Tuncel

Ocak 2005, 195 sayfa

Bu çalışmada, Türkiye'nin dört farklı bölgesinde, en az bir yıl süre ile çalıştırılan kırsal istasyonlarda üretilen veriler karşılaştırılarak aralarındaki benzerlik ve farklılıklar ortaya çıkartılmış ve bu dört bölgede ölçülmüş olan aerosol kompozisyonları arasındaki farklılıklara neden olan etmenler incelenmiştir. Çalışmada kullanılan veriler, Akdeniz bölgesinde, Antalya'nın yaklaşık olarak 20 km batısında (Antalya istasyonu), Karadeniz bölgesinde Amasra'nın 20 km doğusunda (Amasra istasyonu), İç Anadolu bölgesinde Ankara'nın 50 km kadar kuzey doğusunda (Çubuk istasyonu) ve Uludağ'da kurulan dört istasyonda üretilmiştir. Çalışmada yapılan karşılaştırmalarda kullanılan veriler, istasyonlarda daha önce yapılan çalışmalarda üretilmiş olup, bu çalışmada herhangi bir veri üretilmemiştir. Hem bütün istasyonlarda aynı istatistik modellerle elde edilen sonuçları karşılaştırabilmek, hem de yeni literatüre giren istatistik araçları veri setlerine uygulayabilmek için, bazı istatistik modeller bütün

İstasyonlardaki verilere bu çalışma çerçevesinde uygulanmıştır. Verilerin, bu şekilde tekrar analizi daha ziyade kaynak tür ve bölgelerinin belirlenmesi için yapılmıştır.

İstasyonlarda daha önce yapılan çalışmaların amaçları farklı olduğundan, her istasyonda aynı parametreler ölçülmemiştir. Antalya ve Amasra istasyonlarında toplanan örnekler INAA, AAS ve IC teknikleri kullanılarak çok sayıda (40 kadar) element ve iyon için analiz edilmiştir. Bu iki istasyonda kullanılan ölçüm ve analiz yöntemleri aynı olduğundan, ölçülen parametreler de aynıdır. Ancak, Çubuk ve Uludağ istasyonlarında, çok daha az sayıda parametre ölçüldüğünden bu istasyonların karşılaştırılması daha sınırlı olmuştur.

Çalışmanın amacı, bölgeler arasındaki farklılıklara neden olan etmenlerin ortaya çıkartılması olduğundan, verilerin karşılaştırılması sadece konsantrasyonların karşılaştırılmasıyla sınırlı kalmamış, konsantrasyonların yanında, element ve iyonların gösterdikleri kısa ve uzun dönemli (mevsimsel) değişimler, bölgesel fonu oluşturan konsantrasyonlar, element ve iyonlar arasındaki korelasyon ilişkileri, bölgelerdeki üst atmosfer hava akış klimatolojileri, bölgelerde ölçülen aerosol kompozisyonlarını etkileyen kaynak türleri ve bu kaynakların buldukları bölgeler de karşılaştırılmıştır.

İstasyonlarda ölçülen element ve iyonların konsantrasyonlarının karşılaştırılması, değişik bölgelerdeki aerosollerin kompozisyonları arasında istasyonların kuruldukları yerin özelliklerinden kaynaklanan farklılıklar olduğunu göstermiştir. Örneğin Antalya istasyonunda, diğer istasyonlara nazaran çok yüksek Na ve Cl düzeyleri ölçülmüştür. Bu Akdeniz bölgesindeki istasyonun denize çok yakın olmasından kaynaklanmaktadır ve bölgesel bir farklılık değildir. Ancak bunun gibi istasyon noktasının lokal özelliklerinden kaynaklanan farklılıkların yanında, bölgesel farklılıkların da olduğu görülmektedir. Antropojenik

kökenli element ve iyonların Antalya ve Amasra istasyonlarında ölçülen konsantrasyonları arasında istatistik olarak anlamlı bir fark görülmemiştir. Ancak bu iki istasyonda ölçülen konsantrasyon değerleri Orta Anadolu'daki Çubuk ve Uludağ istasyonlarında ölçülen değerlerden en az iki kat yüksektir. Sistematik olarak antropojenik kökenli bütün element ve iyonlarda gözlenen bu farklılık, bölgesel nitelikli olup, Anadolu Platosu'nun yüksek bölgelerinin kıyı kesimlerinden farklı kaynak bölgelerinden etkilendiğini ve/veya Orta Anadolu'ya kirletici taşınımına yol açan mekanizmaların, kıyı bölgelerinde çalışan mekanizmalardan farklı olduğunu göstermektedir.

Elementlerin mevsimsel değişimleri aerosol kompozisyonunu etkileyen kaynakların yakın veya uzak olması, emisyonlardaki mevsimsel değişimler, taşınım mekanizmalarındaki mevsimsel değişimler gibi konularda bilgi verdiği için önemlidir. Bu çalışmada da belirtilen konularda bölgeler arasında farklılıkların olup olmadığını anlayabilmek için elementlerin her istasyondaki mevsimsel değişimleri karşılaştırılmıştır. Yapılan karşılaştırmada, bazı element gruplarının farklı bölgelerde gösterdikleri mevsimsel değişikliklerin farklı olduğu görülmüştür. Toprak kökenli elementlerin (Al, Fe gibi) konsantrasyonlarının bütün istasyonlarda aynı mevsimsel değişikliği gösterdiği görülmektedir. Litofilik elementlerin hepsinin konsantrasyonları yaz mevsiminde yüksek, kış mevsiminde ise yaklaşık 3 kat düşüktür. Toprak elementlerinde gözlenen mevsimsel değişikliğin nedeni, toprak aerosollerinin emisyonlarındaki mevsimsel farklılıklardır. Kış mevsiminde toprak ıslak veya buzla kaplı olduğundan, yüzey toprağından aerosol oluşumu çok sınırlı olmaktadır. Yaz mevsiminde ise kuru olan yüzey toprağından daha fazla aerosol emisyonu olması doğaldır.

Antropojenik kökenli elementlerin konsantrasyonları, Amasra, Çubuk ve Uludağ istasyonlarında, yaz ve kış aylarında bir farklılık

göstermemektedir. Buna karşılık aynı elementlerin Antalya istasyonunda ölçülen konsantrasyonlarının yaz aylarında, kış mevsimine nazaran, %95 istatistik güvenilirlik sınırı içerisinde daha yüksek olduğu görülmektedir. Akdeniz bölgesi aerosollerinde görülen mevsimsel değişimlerin diğer üç bölgedekinden farklı olması, Karadeniz ve İç Anadolu bölgelerindeki aerosollerin daha yakınlardaki kaynaklardan etkilenidiğini göstermektedir. Gerek bölgesel düzeyler ve gerekse kaynak bölgelerinin belirlenmesine yönelik çalışmalar, varılan bu sonucu teyid etmektedir.

Deniz kökenli aerosollerin konsantrasyonlarındaki mevsimsel değişimler de, antropojenik elementlerde olduğu gibi, Akdeniz istasyonu ile diğer üç istasyon arasında farklılıklar göstermesine rağmen, gözlenen farklılıklarının bölgesel olmadığı, Antalya istasyonunun, diğer üç istasyona nazaran denize çok yakın olmasından kaynaklandığı sonucuna varılmıştır.

Akdeniz, Karadeniz ve İç Anadolu bölgelerinin üst atmosfer taşınım klimatolojileri (900, 850 ve 700 mb seviyelerinde hava kütlelerinin her rüzgar sektöründen taşınma frekansı) karşılaştırıldığında, B, BKB, KB ve KKB sektörlerinin toplam hava kütlesi taşınımına en çok katkıda bulunduğu (diğer bir deyişle, hava kütleleri zamanlarının en büyük bölümünü bu sektörlerden geçirek istasyon noktalarına geldiği) görülmüştür. Batı Avrupa, Doğu Avrupa ve Rusya'daki büyük emisyon kaynaklarının bu sektörlerde olduğu göz önüne alınırsa, söz konusu sektörlerden gelen hava kütlelerinin kirleticileri de getireceği ve bütün bölgelerin Avrupa ve Rusya'daki emisyonların etkisi altında olduğu, bu bölgelerdeki emisyonlarda olacak değişimlerin Türkiye'de de görüleceği söylenebilir.

Üst atmosfer akış klimatolojisinin yaz ve kış mevsimlerinde, küçük ancak istatistik olarak anlamlı farklılıklar gösterdiği görülmüştür. Gözlenen farklılıklar kirletici taşınımı açısından değerlendirildiğinde, Karadeniz ve İç

Anadolu bölgelerinin (Çubuk, Amasra ve Uludağ istasyonları) kış mevsiminde daha çok Batı Avrupa'nın etkisi altında olduğu, yaz mevsimindeyse bu bölgelere kirleticilerin daha ziyade Doğu Avrupa'dan geldiği söylenebilir. Akdeniz istasyonunda ise yaz ve kış mevsimlerindeki üst atmosfer akış klimatolojileri arasında istatistik olarak anlamlı bir farklılık görülmemiştir. Bölgedeki aerosollerin her iki mevsimde de daha çok Batı Avrupa'daki kaynakların etkisi altında olması beklenmektedir. Karadeniz ve İç Anadolu bölgelerinin kış mevsiminde Batı Avrupa'daki, yaz mevsiminde de Doğu Avrupa'daki kaynaklardan etkileniyor olması, istasyonlarda ölçülen SO_4^{2-}/NO_3^- oranlarındaki mevsimsel değişiklikler kullanılarak teyid edilmiştir.

Bölgelerdeki antropojenik kökenli elementlerin kaynak bölgeleri, Potansiyel Kaynak Katkı Fonksiyonu (PKKF) tekniği kullanılarak belirlenmiştir. Hesaplanan PKKF değerlerinin istatistiksel olarak anlamlı olup olmadığı "bootstrap" tekniği ile değerlendirilmiştir. Yapılan hesaplar, çalışmanın yürütüldüğü 3 bölgenin hepsinin, Balkanlar ve Rusya'daki bazı bölgelerdeki kaynaklardan etkilendiğini, ancak bu ortak kaynak bölgelerinin yanında, sadece belirli bölgeleri etkileyen kaynak bölgelerin de olduğu görülmüştür. PKKF hesaplarından çıkartılan diğer bir genel sonuç ise Anadolu Platosu'nun, Karadeniz ve Akdeniz bölgelerine nazaran daha yakınlardaki kaynaklardan etkilendiği olmuştur.

Akdeniz, Karadeniz ve İç Anadolu bölgelerindeki aerosollerin kompozisyonlarını belirleyen kaynak bölgelerinin yanında, bu üç bölgedeki aerosolleri oluşturan bileşenler de karşılaştırılmıştır. Böyle bir karşılaştırılmanın yapılabilmesi için, önce her bölgedeki aerosolleri oluşturan bileşenlerin bulunması gereklidir. Her bölgedeki aerosol kütlesini oluşturan bileşenler Positive Matriks Faktörizasyonu (PMF) yöntemiyle bulunmuştur. Bu teknik daha önceki çalışmaların yapıldığı zamanlarda henüz mevcut olmadığından, PMF hesapları bu çalışma

çerçevesinde yapılmıştır. PMF çalışması sonunda, Akdeniz bölgesindeki aerosol kütlesinin 7, Karadeniz aerosollerinin 8, İç Anadolu bölgesindeki aerosollerin de 6 bileşenden oluştuğu görülmüştür. Bu bileşenler arasında, birisi toprak parçacıklarını, diğeri de uzun mesafeli taşınım ile bölgeye ulaşan parçacıkları temsil eden iki faktör her üç bölgede de görülmüştür. Bu iki bileşenin her üç bölgedeki kimyasal kompozisyonlarının %95 istatistik güvenilirlik sınırı içersinde aynı olduğu da gösterilmiştir. Ayrıca, gübre kullanımından kaynaklanan ve çok yüksek düzeylerde NH_4^+ iyonu içeren bir faktör ile deniz tuzu aerosollerini temsil eden bir faktörün yanısıra arsenik faktörü de Akdeniz ve Karadeniz aerosollerini için ortak olduğu, ancak bu bileşenlerin İç Anadolu bölgesindeki aerosollerde mevcut olmadığı ortaya çıkmıştır. Her bölgedeki aerosollerin diğeri bileşenlerini temsil eden diğeri faktörler, o bölgeye özeldir. Bu sonuçlar Akdeniz, Karadeniz ve İç Anadolu bölgelerinin bazı ortak kaynak bölgelerinden etkilendiğini ve bunun sonucu olarak da her bölgede ortak olarak görülen aerosol bileşenlerinin olduğunu, bölgelerdeki aerosol kütlesinin bu ortak özelliklerinin yanında kendilerine özgü kaynak bölgelerinden de etkilendiğini ve kendilerine özgü bileşenlerinin de olduğu ortaya çıkarmaktadır.

Anahtar Kelimeler: Türkiye, Karadeniz, Akdeniz havzası, Anadolu Platosu, Potansiyel Kaynak Katkı Fonksiyonu, Kırsal Atmosfer Aerosollerini, SO_4^{2-} 'ün NO_3^- 'e oranı.

To my family...

ACKNOWLEDGEMENTS

I like to express my sincere appreciation to my supervisor Prof. Dr. Gürdal Tuncel for his guidance, advice, criticism and encouragement throughout the research.

I wish to express my appreciation to Assoc. Prof. Dr. Gülen Güllü, Dr. Duran Karakaş, Dr. Serpil Karakaş and Mrs. Canan Yeşilyurt for the generation of the data sets used in this study.

I extend my sincere thank to Derya Deniz Genç, Fatma Öztürk, Haydar Tokgöz, İlker Yıldırım, Ayhan Yavuzoğlu, Tuğba Özal, Baran Sarı, Ahmet Türküm, Ceren İpekgil, Deniz Küstü, Mihriban Yılmaz, Ebru Tuna, Evrim Çelik, Ulaş Canatalı and Ayşegül Otuzoğlu for their encouragement and friendship during my hard working days.

I would like to thank all the members of Department of Environmental Engineering of Middle East Technical University and Department of Environmental Engineering of Akdeniz University for their support during this study.

Finally, I would like to express my deepest appreciation to my family for their endless support, understanding and patience not only during this study but also throughout my life.

TABLE OF CONTENTS

PLAGIARISM.....	iii
ABSTRACT.....	iv
ÖZ.....	viii
ACKNOWLEDGMENTS.....	xv
TABLE OF CONTENTS.....	xvi
LIST OF TABLES.....	xviii
LIST OF FIGURES.....	xix
CHAPTER	
1. INTRODUCTION.....	1
1.1. Characteristics of Atmospheric Particulate Matter...	1
1.2. Sources of Atmospheric Particulate Matter.....	5
1.2.1. Natural Particles.....	5
1.2.2. Anthropogenic Particles.....	7
1.3. Long Range Transport.....	9
1.4. International Actions to Control Long Range Transport of Air Pollutants.....	11
1.5. Aim of the Study.....	18
2. MATERIALS AND METHODS.....	24
2.1. Sampling Site Descriptions.....	24
2.1.1. Mediterranean Station.....	26
2.1.2. Black Sea Station.....	27
2.1.3. Marmara Station.....	27
2.1.4. Central Anatolia Station.....	28
2.1.5. Comparison of Station Characteristics.....	29

2.2. Sample Collection and Analysis of the Samples.....	32
2.3. Positive Matrix Factorization.....	34
2.4. Trajectory Statistics.....	38
2.4.1. Flow Climatology.....	40
2.4.2. Potential Source Contribution Function Analysis.....	41
3. RESULTS AND DISCUSSION.....	44
3.1. General Characteristics of Data Sets.....	44
3.1.1. Comparison of Geometric Mean Concentrations.....	46
3.1.2. Comparison of Seasonal Variations of Elements.....	50
3.2. Comparison of Background Concentrations.....	58
3.3. Comparison of Correlation between Parameters.....	66
3.4. Comparison of Flow Climatology of Stations.....	80
3.5. Comparison of Geological Locations of Potential Source Regions for Major Pollutants.....	95
3.6. Source Apportionment and Quantification.....	111
3.6.1. Treatment of Values and Extraction of Factors.....	112
3.6.2. Antalya PMF Results.....	115
3.6.3. Amasra PMF Results.....	141
3.6.4. Comparison of PMF Results.....	174
4. CONCLUSION.....	180
4.1. Recommendations for Future Research.....	184
REFERENCES.....	185

LIST OF TABLES

TABLES

Table 1.1. Marker elements and their possible sources.....	9
Table 2.1. Analytical techniques of measured species for each station.....	35
Table 3.1. Geometric mean concentrations of sampling sites Antalya, Amasra, Çubuk and Uludağ.....	45
Table 3.2. The results of student t-test of elements which have statistically significance between the average concentrations of the elements within 95% confidence level.....	46
Table 3.3. Calculated regional background concentrations of each element and ion.....	61
Table 3.4. Contribution of episodes on average concentrations of element groups.....	64
Table 3.5. Correlations between measured parameters in Antalya station.....	69
Table 3.6. Correlations between measured parameters in Amasra station.....	71
Table 3.7. Correlations between measured parameters in Çubuk station.....	73
Table 3.8. Correlations between measured parameters in Uludağ station.....	73

LIST OF FIGURES

FIGURES

Figure 1.1. Ideal scheme of aerosol size distribution based on mechanisms of aerosol formation and extraction from the atmosphere.....	3
Figure 2.1. Sampling stations.....	25
Figure 3.1. Monthly geometric mean concentrations of the K and Ca for each station and Al and Fe for Antalya and Amasra stations.....	52
Figure 3.2. Monthly geometric mean concentrations of Mg for each station and Na and Cl for Antalya, Amasra and Uludağ stations.....	53
Figure 3.3. Monthly geometric mean concentrations of anthropogenic elements and ions for each station.....	55
Figure 3.4. Calculated regional background concentrations of elements in each station.....	62
Figure 3.5. Contribution of episodes on average concentrations of elements and ions in each station.....	67
Figure 3.6. Flow climatologies of Antalya, Amasra and Çubuk stations as trajectory roses.....	82
Figure 3.7. Countries in each wind sector.....	84
Figure 3.8. Seasonal variations in flow climatologies of Antalya, Amasra and Çubuk stations as trajectory roses.....	87

Figure 3.9. Seasonal contributions of Eastern and Western European countries to the seasonal variation of flow climatology in Çubuk.....	88
Figure 3.10. Variation of SO_4^{2-} concentrations in atmospheric aerosol in the Western European and former USSR countries, between 1978 and 2000.....	90
Figure 3.11. Variation of aerosol NO_3^- concentrations in Western Europe and former USSR countries, between 1978 and 2000.....	92
Figure 3.12. SO_4^{2-} to NO_3^- ratio at EMEP network and Turkish stations.....	93
Figure 3.13. Monthly variation of SO_4^{2-} to NO_3^- ratio at Mediterranean, Black Sea and Central Anatolia.....	94
Figure 3.14. Effect of bootstrap to the potential SO_4^{2-} regions of Antalya region; without bootstrapped; with bootstrapped.....	97
Figure 3.15. Comparison of the PSCF calculations performed defining highest 20% and 40% of measured concentrations as polluted.....	99
Figure 3.16. The vertical profile of the trajectories that corresponds to the highest 20 % concentration of SO_4^{2-} in Antalya.	100
Figure 3.17. Calculation of PSCF for highest 40% of SO_4^{2-} concentrations at Antalya using only trajectory segments below 1000 m, same with bootstrapping and using all trajectory segments and applying bootstrapping wit 3000 iteration.....	101
Figure 3.18. Distribution of SO_4^{2-} PSCF values in the Mediterranean, Black Sea and Central Anatolia.....	104
Figure 3.19. Distribution of NO_3^- PSCF values in the Mediterranean, Black Sea and Central Anatolia.....	106

Figure 3.20. Distribution of NH_4^+ PSCF values in the Mediterranean, Black Sea and Central Anatolia.....	108
Figure 3.21. Distribution of Pb PSCF values in the Mediterranean, Black Sea and Central Anatolia.....	110
Figure 3.22. Explained Variation, Flooding, Calculated Enrichment Factor with reference element Al and Sc and Monthly Variation in Factor Scores of Antalya Factor 1.....	116
Figure 3.23. Top and side view of backtrajectories corresponding to highest 20% of the factor scores of Factor 1 of Antalya.....	118
Figure 3.24. Explained Variation, Flooding, Calculated Enrichment Factor with reference element Al and Sc and Monthly Variation in Factor Scores of Antalya Factor 2.....	120
Figure 3.25. Correlation of ratios between lithophilic elements Al ratio in Factor 2 and in Mason.....	121
Figure 3.26. Top and side view of backtrajectories corresponding to highest 20% of the factor scores of Factor 2 of Antalya.....	122
Figure 3.27. Explained Variation, Flooding, Calculated Enrichment Factor with reference element Al and Sc and Monthly Variation in Factor Scores of Antalya Factor 3.....	124
Figure 3.28. Explained Variation, Flooding, Calculated Enrichment Factor with reference element Al and Sc and Monthly Variation in Factor Scores of Antalya Factor 4.....	125
Figure 3.29. Top and side view of backtrajectories corresponding to highest 20% of the factor scores of Factor 4 of Antalya.....	127
Figure 3.30. Calculated PSCF values for highest 40% factor scores of Factor 4 of Antalya.....	128

Figure 3.31. Explained Variation, Flooding, Calculated Enrichment Factor with reference element Al and Sc and Monthly Variation in Factor Scores of Antalya Factor 5.....	129
Figure 3.32. Top and side view of backtrajectories corresponding to highest 20% of the factor scores of Factor 5 of Antalya.....	131
Figure 3.33. Calculated PSCF values for highest 40% factor scores of Factor 5 of Antalya.....	132
Figure 3.34. Explained Variation, Flooding, Calculated Enrichment Factor with reference element Al and Sc and Monthly Variation in Factor Scores of Antalya Factor 6.....	133
Figure 3.35. Explained Variation, Flooding, Calculated Enrichment Factor with reference element Al and Sc and Monthly Variation in Factor Scores of Antalya Factor 7.....	135
Figure 3.36. Top and side view of backtrajectories corresponding to highest 20% of the factor scores of Factor 7 of Antalya.....	136
Figure 3.37. Contribution of each of the factor component to the aerosol mass in Eastern Mediterranean region.....	138
Figure 3.38. Contribution of each of the factor component to the aerosol mass in Eastern Mediterranean region, excluding sea salt.....	139
Figure 3.39. Correlation of calculated X/Al ratios for Factor 3 and Factor 6 in the Antalya region with the X/Al ratio for Mason.....	140
Figure 3.40. The top profiles of backtrajectories of the highest 20% contributing days for Factor 3 and Factor 6.....	142
Figure 3.41. The vertical profiles of backtrajectories of the highest 20% contributing days for Factor 3 and Factor 6.....	143

Figure 3.42. Explained Variation, Flooding, Calculated Enrichment Factor with reference element Al and Monthly Variation in Factor Scores of Amasra Factor 1.....	144
Figure 3.43. Top and side view of backtrajectories corresponding to highest 20% of the factor scores of Factor 1 of Amasra.....	146
Figure 3.44. The comparison of X/Al ratios of lithophilic elements in Factor 1 with the same ratio in the Mason.....	147
Figure 3.45. Explained Variation, Flooding, Calculated Enrichment Factor with reference element Al and Monthly Variation in Factor Scores of Amasra Factor 2.....	148
Figure 3.46. Top and side view of backtrajectories corresponding to highest 20% of the factor scores of Factor 2 of Amasra.....	149
Figure 3.47. Calculated PSCF values for highest 40% factor scores of Factor 2 of Amasra.....	151
Figure 3.48. Explained Variation, Flooding , Calculated Enrichment Factor with reference element Al and Monthly Variation in Factor Scores of Amasra Factor 3.....	152
Figure 3.49. Top and side view of backtrajectories corresponding to highest 20% of the factor scores of Factor 3 of Amasra.....	153
Figure 3.50. Explained Variation, Flooding, Calculated Enrichment Factor with reference element Al and Sc and Monthly Variation in Factor Scores of Amasra Factor 4.....	155
Figure 3.51. Top and side view of backtrajectories corresponding to highest 20% of the factor scores of Factor 4 of Amasra.....	156
Figure 3.52. Calculated PSCF values for highest 40% factor scores of Factor 4 of Amasra.....	157

Figure 3.53. Explained Variation, Flooding , Calculated Enrichment Factor with reference element Al and Monthly Variation in Factor Scores of Amasra Factor 5.....	158
Figure 3.54. Top and side view of backtrajectories corresponding to highest 20% of the factor scores of Factor 5 of Amasra.....	160
Figure 3.55. Calculated PSCF values for highest 40% factor scores of Factor 5 of Amasra.....	161
Figure 3.56. Explained Variation, Flooding, Calculated Enrichment Factor with reference element Al and Monthly Variation in Factor Scores of Amasra Factor 6.....	162
Figure 3.57. Top and side view of backtrajectories corresponding to highest 20% of the factor scores of Factor 6 of Amasra.....	163
Figure 3.58. Calculated PSCF values for highest 40% factor scores of Factor 6 of Amasra.....	165
Figure 3.59. Explained Variation, Flooding , Calculated Enrichment Factor with reference element Al and Monthly Variation in Factor Scores of Amasra Factor 7.....	166
Figure 3.60. Top and side view of backtrajectories corresponding to highest 20% of the factor scores of Factor 7 of Amasra.....	167
Figure 3.61. Calculated PSCF values for highest 40% factor scores of Factor 7 of Amasra.....	168
Figure 3.62. Explained Variation, Flooding, Calculated Enrichment Factor with reference element Al and Sc and Monthly Variation in Factor Scores of Amasra Factor 8.....	169
Figure 3.63. Top and side view of backtrajectories corresponding to highest 20% of the factor scores of Factor 8 of Amasra.....	171

Figure 3.64. Calculated PSCF values for highest 40% factor scores of Factor 8 of Amasra.....	172
Figure 3.65. Contribution of factors to total mass and percent contribution of components to the total mass obtained in Amasra.....	173
Figure 3.66. Correlation of crustal components in Factor 3 of Antalya station and Factor 1 of Amasra station.....	175
Figure 3.67. Top and vertical profiles of highest 20 % contributing days to the crustal factors of Antalya and Amasra stations.....	175
Figure 3.68. Comparison of compositions of elements and ions in the SO_4^{2-} components of the Antalya and Amasra aerosols.....	177
Figure 3.69. Comparison of compositions of elements and ions in the fertilizer components of the Antalya and Amasra aerosols.....	178

CHAPTER 1

INTRODUCTION

1.1. Characteristics of Atmospheric Particulate Matter

Transport of particles and gases via the atmosphere is the most important mechanism for dispersion of pollutants in the regional and global scales. Estimates of the atmospheric fluxes of metals and nutrients to the oceans suggest that the atmosphere can be a major source for the input of pollutants to the deep parts of the ocean and formation of deep water sediments (Duce et al., 1991; Prospero et al., 1996; Herut et al., 1999). Naturally, relative contribution of atmosphere to coastal waters is not as large.

Atmospheric particles, also named as aerosol, consists of a wide variety of components including, nutrients, sulfates, nitrates, biological particles, marine particles, meteoritic debris, crustal material and particles that originate from various anthropogenic activities.

Before 1970's air pollution exclusively referred to high levels of pollutants, particularly SO₂ and particulate matter, in settlement areas. However, after 70's interest has shifted to regional and global air pollution problems. Today, all countries on the world are concerned for the increasing atmospheric levels of greenhouse gases that threaten to

change the climate, chemicals that reduce the ozone layer and pollutants that cause acid rain.

The role of aerosol particles in atmospheric processes is extremely important in climate research, rain formation, weather forecasting, biogeochemical cycling as well as remote sensing of the reflectance and texture of ground and other surfaces. Atmospheric aerosols affect the atmosphere in two ways: (1) direct effect – where aerosols reflect and absorb solar radiation; (2) indirect effect – where aerosols affect clouds by (a) increasing droplet concentration and optical depth and (b) by reducing drop size making the clouds more stable with lower potential to produce rain. The last effect extends the lifetime of the clouds and modifies ground wetness and surface albedo. For this reason, systematic studies are undertaken now in order to retrieve global as well as regional distributions of aerosols (Israelevich et al., 2001).

Aerosols occur both in troposphere and stratosphere, but there are considerable differences in the size ranges, chemical nature and sources of tropospheric and stratospheric particles. Particles may be classified as primary and secondary depending on their formation mechanism. Primary particles are directly emitted into the atmosphere, or are formed in the air after by rapid condensation of the emitted gas molecules. Secondary particles, on the other hand, are formed in the air after chemical transformation of the gaseous precursors. These chemical reactions may involve only gaseous reactants (homogenous processes) or may include reactions with solid and/or liquid phase (heterogeneous processes).

Idealized mass distributions of particle sizes found in the atmosphere are given in Figure 1.1. The smallest diameter range is called as the nucleation range (or Aitken range), which consists of particles with diameters less than 0.08 μm . The main sources of particles in this size range are combustion sources or secondary particle formation from

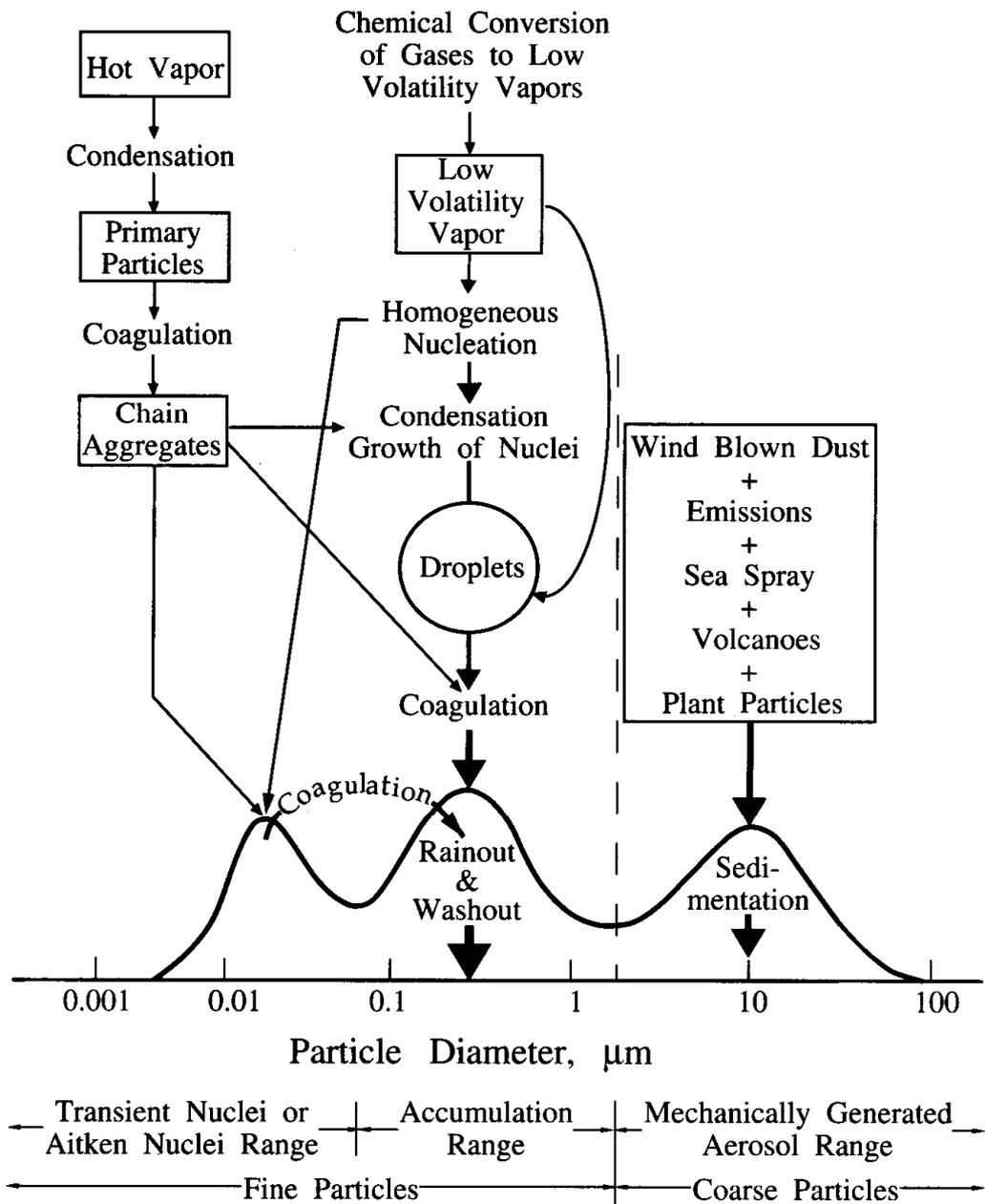


Figure 1.1. Ideal scheme of aerosol size distribution based on mechanisms of aerosol formation and extraction from the atmosphere (Seinfeld and Pandis, 1998)

gaseous precursors. The lifetimes of particles in nucleation range are generally short (up to one hour in polluted atmosphere), because aitken

particles rapidly coagulate with larger particles or onto each other. Aitken particles are very important in atmospheric processes, because they serve as nuclei for the formation of cloud and fog droplets (Watson and Chow, 1994).

The size range that extends from 0.08 μm to 2.5 μm is called accumulation range. Particles in this range are formed by coagulation of smaller particles emitted from combustion sources, by condensation of volatile species and by grinding of larger soil particles.

Particles with diameters $>2.5\mu\text{m}$ are called coarse particles. Coarse particles are by mechanical processes and have natural sources. Crustal material from wind-blown dust, pollen, spores, bubble bursting over the ocean, and biogenic emissions are the most common natural sources of coarse particles in the atmosphere. Among these, wind blown crustal dust is particularly important, ubiquitous component of atmospheric aerosol. Arid and semi-arid areas around the world are the major continuous sources of the crustal particles. Natural sources do not always produce coarse particles. Sources such as volcanoes, biogenic processes and forest fires emit fine particles to the atmosphere as well. (Cunningham and Zoller, 1981).

The residence time of the particles in the atmosphere is a strong function of their sizes. Owing to the effect of gravity, coarse particles are rapidly removed from the atmosphere by sedimentation within few hours. Particles in the Aitken size range ($<0.08 \mu\text{m}$) are also removed from atmosphere rapidly, because they quickly coagulate (within minutes) to form coarser particles. Consequently, particles in the accumulation mode have the longest residence time in the atmosphere.

Since accumulation mode particles are generally made up of soluble material they make up efficient cloud condensation nuclei and are mainly

removed from atmosphere by precipitation process (mainly in-cloud scavenging). For this reason, the residence time of these particles is similar to that of water, which is approximately 10 days (Posfia and Molnar, 2000). However, a significant fraction of carbonaceous particles, which are also in the accumulation size range, are hydrophobic. For these particles a period is also necessary for surface oxidation before they can be wetted and removed from the atmosphere. This results in a longer residence time for soot carbon and organic particles, which can be as long as 46 days compared to soluble fraction (Gaffney et al., 2002).

1.2. Sources of Atmospheric Particulate Matter

Atmospheric particulate matter can have either natural or anthropogenic sources. The major particulate material (PM) components include sulfate, nitrate, ammonium, sodium, chloride, carbon (organic and elemental), mineral dust and water. The predominance of these chemical components in PM and their size distribution are closely linked to their origin and formation mechanisms.

1.2.1. Natural Particles

Mineral particles, which originate from the soil accounts for a large fraction of the natural primary aerosol in the atmosphere. Chemical composition and mineralogy of these particles may show regional variations, due to different geology in different parts of the earth. Natural mineral dust contributions to ambient PM may result from the re-suspension of local soil by wind action or from the long range transport from arid regions.

Volcanic emission is also an important source of mineral material in the Atmosphere, particularly in remote oceanic regions where soil is source is not available. However, their contribution to aerosol mass is rather limited

over continents, where soil particles dominate atmospheric concentrations of lithophilic particles.

Droplets generated by bursting bubbles on the sea surface dry and form marine aerosol, which is an ubiquitous component in aerosol mass at the coastal areas or at inland locations that are not too far from the coast. Sea spray is mainly generated by bubble bursting processes on the ocean surface, which increases exponentially by the surface wind speed (Martensson et al., 2003). Bubble bursting process, by mechanism, generates both fine (film-drops) and coarse (jet-drops) particles (Martensson et al., 2003; Warneck, 1987). Although large sea salt particles dominate the marine mass in the atmosphere, large particles sediment out quickly and fine sea salt particles remain in the aged aerosol mass. The composition of marine particles in the atmosphere is similar to the composition of bulk sea water, which means that these particles contain high concentrations of species such as Na, Cl, Mg, K, Ca, Br and SO_4^{2-} .

Biogenic sources are also important sources of particles in the atmosphere. Some of the particles with biogenic sources are secondary in nature. These are formed by reactions of biogenically produced gases in the atmosphere. For example, a certain fraction of sulfate particles in the atmosphere is produced by atmospheric reactions of dimethylsulfide which, is produced by biogenic activity in the ocean (Andreae and Raemdonck, 1983). Primary particles with biogenic sources, on the other hand, consist of vegetal debris, pollen, spores, and minor amounts of micro-organisms.

Sulfate, nitrate and organic aerosol make up a secondary fraction of naturally produced particles. Natural sources of sulfate are the oxidation of SO_2 emitted from volcanoes and dimethylsulfide (DMS) produced by biogenic processes in the marine environment. Nitrate is the final product

formed by the oxidation of the nitrogen oxides. The main natural sources of NO_x are the soil transpiration (Roelle et al., 2001) and lightning (Price et al., 1997).

Natural organic aerosol is observed in high concentrations only in forested areas, particularly in the rain forests at the equatorial region, where substantial amounts of organic vapors such as isoprene and monoprene are emitted during plant transpiration (Yu et al., 1999; Harrison et al., 2001). Oxidation of these organic vapors gives rise to low vapor pressure gases which form new particles by nucleation (Christoffersen et al., 1998; Koch et al., 2000).

1.2.2. Anthropogenic Particles

The main sources of anthropogenic aerosol are in urban and industrial areas. In urban airshed, primary particles consists of mineral particles eroded from the pavement by road traffic (road dust), remains from the abrasion of breaks and tyres, fly ash particles produced during combustion process, unburned fuel particles, particles emitted from vehicle exhaust and particles emitted from a variety of industrial activities.. Particles mechanically generated by road traffic and unburned fuel particles consist of coarse aerosol ($d > 2.5 \mu\text{m}$) and all other particles are in the form of fine aerosol ($d < 2.5 \mu\text{m}$).

Combustion of fossil fuels, industrial activities, construction activities, mining, manufacture of cement, ceramics and bricks, and smelters are typical sources of primary particles in urban and industrial areas., Coal combustion, by far, is the most important source of anthropogenic particles, nor only in urban and industrial areas, but also in the regional scale. Coal combustion mostly occurs in power plants (coal burning for residential heating is minor compared to quantities of coal burned in thermal power plans). Since most of the power plants are equipped with

stacks that are as high as 600 m, combustion products are emitted to approximately 1 km altitude in the atmosphere (600 m physical stack height, plus plume rise). Combustion gases and particles emitted to such high altitudes have better chance to diffuse into free troposphere and transported in regional scales. Primary particles associated with smelter emissions are mostly consists of fine aerosol. Chemical composition of particles emitted from smelters varies depending on the type of ore processed, but Ni, V, Mn and Cu are frequently emitted (Pacyna, 1998). Particles emitted from construction activities and from and industrial processes such as, mining and cement, ceramics and brick production are mostly in coarse fraction and have composition, which is similar to composition of crustal material (Pacyna et al., 1998).

Anthropogenic secondary aerosol mainly consists of sulfate, nitrate and organic particles. A large proportion of SO₂ emissions are caused by coal combustion in power plants and other industrial activities. The SO₂ oxidation gives rise to the formation of sulfuric acid which could be neutralized by ammonia (NH₃), calcium carbonate (CaCO₃) or sodium chloride (NaCl), forming (NH₄)₂SO₄, NH₄HSO₄ and CaSO₄ particles

Nitrogen oxides are mainly emitted by industrial processes and motor vehicles in urban environments. However, emissions are generally dominated by vehicular activities. Oxidation of NO_x leads to the formation of nitric acid (HNO₃-gas), which may be neutralized by the same bases and transformed into NH₄NO₃, Ca(NO₃)₂ or NaNO₃.

Primary particles emitted from anthropogenic sources are enriched in chalcophilic elements, such as, As, Se, Sb, In, Zn, Cd, Cr, Pb, etc. and pose a significant health effects for the population. Enrichments of these elements are different in different source types. This provided a unique opportunity to use trace elements as natural tracers of sources in source

apportionment studies (Hopke, 2003; Ölmez et al., 1997). Elements that are used as tracers of different sources are given in Table 1.1.

Table 1.1 Marker elements and their possible sources
(from Ölmez, et al. 1997)

Source	Elements
Crustal Material	Al, Sc, Mn, Fe, REE*, Th, U
Marine Aerosols	Na, Cl
Coal Combustion	As, Se, Hg, Be, Co, Mo, Sb
Oil Combustion	V, La, La/Sm
Refineries	REE
Motor Vehicles	Br, Zn, Sb
Wood Burning	K
Incinerators	Na, K, Cl, In, Hg
Chlor-alkali Plants	Cl, Hg
Precious and Other Metal Works	Co, Zn, Au
Aluminum Plant	Al, Mg
Industrial Urban Areas	V, Zn, As, Se, Br, Sb
Iron/ Steel Works	Fe, Zn, Se, Mo, Sb
Regional Transport	Fine mass, As, Se, Hg
Zn, Cd, Pb Smelters	In, Zn, Cd, Pb, Sb
Ni, Cu Smelters	Ni, Cu, Hg, As, As/Se

*REE: Rare Earth Elements, i.e., La, Ce, Sm, etc.

1.3. Long Range Transport

Tropospheric chemistry and transport govern the distribution of trace species and alter the chemical state in which trace constituents move through the atmosphere. The resulting changes in global atmospheric

chemical composition can affect the climate. It has been long known, for example, that increases in carbon dioxide (CO₂) in the atmosphere from burning fossil fuels can contribute to a global warming through "greenhouse effect". However, now it is realized that other trace gases and species that can also contribute to the greenhouse effect are originating from man's activities and now appear to be accumulating in the troposphere. This fact should not be ignored when the solar radiation balance for the region is calculated. An understanding of the behavior of these events will lead to the construction of a more accurate solar radiation balance models (Sokolik et al., 2001). One of the most important findings in recent years, in relation to atmospheric processes, is the contribution of atmospheric aerosol on global warming. For long time climate change was attributed to greenhouse gases and none of the climate change models included an aerosol module. Although, negative feedback of atmospheric particles on global warming was known, it was assumed to be insignificant compared to climate forcing by greenhouse gases. However, recent studies had clearly demonstrated that, the negative feedback of atmospheric particles on climate change is much larger than anticipated and model results would not be realistic unless aerosols are taken into account in calculations (Kuhlbusch et al., 1998; Thunell, 1998; Arimoto, 2001; Slater et al., 2002; Feczko et al., 2002; Treffeisen et al., 2005). For this reason, aerosol studies have focused on the chemical and physical properties of aerosols that relate to radiation and to hygroscopic behavior (Prospero, 1999). It is now very apparent that there are no boundaries within the earth's atmosphere. Gases and particles produced on one continent can easily be transported around the globe, often in a matter of days or weeks.

There are various international monitoring networks to investigate long-range transport of pollutants. In Europe, long range transport of pollutants are being studied through the European Monitoring and

Evaluation Program (EMEP) (EMEP-WHO, 1997; Eliassen and Saltbones, 1983; Tarasson and Tsyro, 1998; Pacyna et al., 1991) and also through several national and international efforts supported by the European Union (Berdowski et al., 1998; EPA, 1996a,b; Quality of Urban Air Review Group, 1996).

The interest had shifted strongly to long range transport of particles in the atmosphere, not only because their impact on climate had been revealed, but also because of the serious public health risks, associated with particles, particularly fine particles, for susceptible members of the population and their potential risks to sensitive ecosystems (EPA, 1996a; EMEP-WHO, 1997; WHO, 1996)

The transport mechanism for atmospheric fine-particles is similar to that of gaseous pollutants. Large particles, on the other hand, do not stay in the atmosphere very long, due to their high sedimentation rate. Consequently, aged aerosol masses consist of fine particles.

1.4. International Actions to Control Long Range Transport of Air Pollutants

United Nations Conference on the Human Environment in Stockholm, held in 1972 is the first meeting where the focus was the long range transport of pollutants. The conference signaled the increasing acid rain problems in Europe and the need for international action. Early studies on wet deposition of sulfur compounds in Western Europe demonstrated that the countries with largest sulfur dioxide emissions are not necessarily the countries, which received the highest acid deposition (Elsom, 1987; Yörük, 2004).

The basics of the Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP) was established in 1978. Thirty four Economic Commission for Europe (ECE)

countries and the European Community participated to the program. In time, EMEP evolved as the main program for the scientific studies on long-range transport of air pollutants over Europe. The program is an instrument for international cost-sharing of a monitoring programme which forms the backbone for review and assessment of relevant air pollution in Europe in the light of agreements on emission reduction. EMEP has three main components: collection of emission data for SO₂, NO_x, VOCs and other air pollutants; measurement of air and precipitation quality; and modeling of atmospheric dispersion. At present, there are approximately 100 monitoring stations in 24 ECE countries, which participate in the programme.

The basic principles of the protocol for Reduction of Sulphur Emissions or their Transboundary Fluxes by at least 30 percent (so called the first sulfur protocol) was discussed in Convention on Long-range Transboundary Air Pollution meeting held at Helsinki in 1985. The first Sulfur protocol entered into force in 1987. Twenty-one ECE countries were parties to the protocol, which aims to reduce atmospheric concentrations of SO₄²⁻, which is the most important acid forming specie, throughout the Europe. Substantial cuts in sulphur emissions have been achieved in Europe, since the protocol became effective. Twenty one parties to the 1985 Sulphur Protocol reduced their sulphur emissions by more than 50% by 1993. Thus, based on the latest available data, all parties to the protocol have reached the reduction target. Eleven parties have gone further and reduced their emissions by more than 60% Given It can be concluded that all parties to that protocol have reached the target of reducing emissions by at least 30%. The reductions in SO₂ emissions clearly reflected to the atmospheric SO₄²⁻ concentrations. In last years more than 70% decrease in SO₄²⁻ concentrations are reported throughout the Western Europe.

The Protocol concerning the Control of Emissions of Nitrogen Oxides or their Transboundary Fluxes was adopted in Sofia (Bulgaria), in 1988. This protocol mandated, as a first step, to freeze emissions of nitrogen oxides at their 1987 emission levels (except for the United States where 1978 was chosen as the reference year). Nineteen of the 25 parties to the 1988 NO_x protocol have reached the target and stabilized their emissions at 1987 (or in the case of the United States 1978) levels or reduced emissions below 1987 emission levels.

The Protocol (to the Convention on Long-range Transboundary Air Pollution) on the Control of Emissions of Volatile Organic Compounds (VOCs, i.e. hydrocarbons) or Their Transboundary Fluxes, the second major air pollutant responsible for the formation of ground level ozone, was adopted in Geneva in November 1991. The protocol has entered into force at 29 September 1997. The VOC protocol specifies three options for emission reduction targets that have to be chosen upon ratification:

(i) 30% reduction in emissions of volatile organic compounds (VOCs) by 1999 using a year between 1984 and 1990 as a reference. This option was adopted by Austria, Belgium, Estonia, Finland, France, Germany, Netherlands, Portugal, Spain, Sweden and the United Kingdom with 1988 as base year, by Denmark with 1985 as the reference year, by Liechtenstein, Switzerland and the United States with 1984 as the reference year, and by Czech Republic, Italy, Luxembourg, Monaco and Slovakia with 1990 as the reference year);

(ii) The same reduction as in option (i) within a Tropospheric Ozone Management Area (TOMA) specified in annex I to the protocol and ensuring that by 1999 total national emissions should not exceed 1988 levels. (Annex I specifies TOMAs in Norway (base year 1989) and Canada (base year 1988));

(iii) Stabilization at 1988 levels by 1999. However this option could only be adopted by countries where 1988 emissions did not exceed certain specified levels. This option had been chosen by Bulgaria, Greece, and Hungary.

The 1994 Oslo Protocol on Further Reduction of Sulphur Emissions (second sulfur protocol) had entered into force at August 5, 1998. An effects-based approach, the critical load concept, best available technology, energy savings, the application of economic instruments and other considerations was applied in the preparation of the protocol. This has led to a differentiation of emission reduction obligations of parties to the protocol. The effects-based approach, which aims at gradually attaining critical loads, sets long-term targets for reductions in sulphur emissions.

The Protocol on Heavy Metals was adopted at June 24, 1998 in Aarhus (Denmark). It targets three particularly harmful metals: cadmium, lead and mercury. According to one of the basic obligations, parties will have to reduce their emissions for these three metals below their levels in 1990 (or an alternative year between 1985 and 1995). The protocol aims to cut emissions from industrial sources (iron and steel industry, non-ferrous metal industry), combustion processes (power generation, road transport) and waste incineration. The protocol laid down stringent limit values for emissions from stationary sources and suggests to apply the best available control techniques (BAT) such as, special filters or scrubbers for combustion sources or mercury-free processes, at these sources,. The protocol demanded parties to phase out leaded gasoline. It also introduced measures to lower heavy metal emissions from other products, such as mercury from battery production, and proposed introduction of management measures for other processes involving Hg, such as production of electrical components (thermostats, switches),

measuring devices (thermometers, manometers, barometers), fluorescent lamps, dental amalgam, pesticides and paint.

The Protocol on Persistent Organic Pollutants (POPs) was accepted at June 24, 1998 in Aarhus (Denmark). The protocol focuses on a list of 16 POPs that have been selected depending on their health effects. The substances comprise eleven pesticides, two industrial chemicals and three by-products. The ultimate objective was to eliminate any discharges, emissions and losses of POPs to atmosphere. The Protocol banned the production and use of aldrin, chlordane, chlordecone, dieldrin, endrin, hexabromobiphenyl, mirex and toxaphene. Others, including DDT, heptachlor, hexachlorobenzene, PCBs were scheduled for gradual phase out. Finally, it severely restricted the use of DDT, HCH (including lindane) and PCBs. The Protocol included provisions for dealing with the wastes of products that were or will be banned. It also obliged parties to reduce their dioxin, furan, PAHs and HCB emissions below 1990 levels (or below an alternative year between 1985 and 1995). Limit values were also established for emissions of POPs from incineration of municipal, hazardous and medical wastes.

The Protocol to Abate Acidification, Eutrophication and Ground-level Ozone formation was adopted in Gothenburg (Sweden) at November 30, 1999. The Protocol set emission ceilings for the year 2010 for SO₂, NO_x, VOCs and NH₃. These ceilings were negotiated on the basis of scientific assessments of pollution effects and abatement options. Parties whose emissions have a more severe environmental or health impact and whose emissions are relatively cheap to reduce will have to make the biggest cuts. Once the protocol is fully implemented, sulphur emissions in Europe will be cut by at least 63%, NO_x emissions by 41%, VOC emissions by 40% and NH₃ emissions by 17% relative to 1990 emission levels. The protocol also set stringent limit values for emission sources

such as, combustion plants, electricity production, dry cleaning, motor vehicles and lorries, and demanded best available techniques to be used to keep emissions down. Guidance documents were also adopted along with the protocol. These documents provide a wide range of abatement techniques and economic instruments for the reduction of emissions in the relevant sectors, including transport.

Critical load studies have demonstrated that 93×10^6 ha land area in Europe exceeds critical acid loads (indicating that this much area had lost acid buffering capacity and acidified). It had been estimated that once the protocol is implemented, the area where critical acid loads will be exceeded will decrease to 15×10^6 ha. Similarly, the land area with excessive levels of eutrophication will decrease from 165×10^6 ha in 1990 to 108×10^6 ha. The number of days with ozone levels exceeding standards will be halved. It is also estimated that life-years lost due to chronic effects of ozone exposure will be about 2,300,000 years lower in 2010 than in 1990, and there will be approximately 47,500 fewer premature deaths resulting from ozone and particulate matter in the air. Similarly, exposure of vegetation to excessive ozone levels will be 44% lower in 2010 than in 1990.

All the protocols discussed so far are annexes to the framework convention, which is Convention on Long-range Transboundary Air Pollution, which is binding for all countries in Europe. In addition to these continent-wide actions, there are also regional agreements to improve environmental conditions at certain parts of the continent. The regions covered by these agreements include the Mediterranean basin, Black Sea region, Baltic Sea region and the North Sea region. Naturally, the ones that are important for Turkey are the conventions involving the Mediterranean Sea and the Black Sea.

The first international action for Mediterranean Region was adopted at an international meeting, convened by UNEP at Barcelona in 1975, which is known as Barcelona Convention. The convention was ratified by 16 bordering countries. The Mediterranean Action Plan, which is an annex to the Barcelona Convention, was adopted in the same year. The action plan had three components:

1. The management component, which included planning of the development and management of the resources in the Mediterranean Basin.
2. The assessment component, which included coordinated program for research, monitoring and exchange of information and assessment of the states of pollution and of protection measures. The monitoring and research in this component is being carried out under MED POL program. The program is being coordinated by the MED UNIT at Athens Greece.
3. The legal component, which included the enforcement measures for the framework convention and related protocols with their technical annexes.

As pointed out before, the MED POL is the program under which monitoring and research activities are being carried out. The MED POL consists of national monitoring programs carried out by parties, which are the countries bordering the Mediterranean Sea. Data from national monitoring programs are collected at the MED UNIT, where the data is collectively evaluated to assess the status of pollution in the Mediterranean region.

Until 1988, the MED POL program included exclusively the monitoring of the Mediterranean Sea itself and did not have an atmospheric component. In May 1988, with the realization of importance of

atmospheric pollution transport on marine ecosystems especially for the semi closed seas, airborne studies were included, as a separate component, within MED POL program, with the coordination of World Meteorological Organization (WHO).

The first international coordinated action plan for the protection of Black Sea is the “Convention for the Protection of the Black Sea Against Pollution” which was signed in Bucharest in 1992 by the ministers of the six Black Sea countries. The Bucharest convention included a basic framework agreement and three specific protocols on:

1. The control of land based sources of pollution,
2. The control of dumping of waste,
3. Joint action in case of an accident (such as oil spills)

This convention establishes rules, but it does not set the goals, priorities and timetables needed to bring about environmental actions. For this reason, all six ministers of the environment signed a Ministerial Declaration on the Protection of the Black Sea Environment in Odessa in April 1993 (Güllü, 1996).

1.5. Aim of the Study

There had been fair amount of studies on rural air quality in Turkey in last 15 years. Most of this work was done by our group. Studies have started by the first station that is established on the at the Menemen area on the Aegean coast in July 1991. The station was operated by our group for one year. Only precipitation samples were collected at the station, but the data provided the first information on the composition of rain water in Turkey (Al Momani et al., 1995). The second station was established on the Mediterranean coast of Turkey, at approximately 20 km to the west of the town of Antalya in December 1991 (the Antalya station in this study).

The station was operated, again by our group, between 1992 and 2000. Daily aerosol and precipitation samples were collected, without any interruption for 8 years. All of the collected samples were not analyzed. Aerosol samples collected in 1992 and 1993 were analyzed using a combination of analytical techniques and a very large data set consisting of concentrations of approximately 40 elements and ions in more than 600 samples were generated and evaluated by Güllü (1996). Precipitation samples were also analyzed for trace elements and major ions (Al-Momani, 1995). The data set generated was the most comprehensive one in the whole Mediterranean region and provided fairly detailed information on the composition of the Eastern Mediterranean aerosol. Remaining samples were stored for future analysis. Several additional works were also performed at the station. Kuloğlu (1997) measured size distribution of particles and elements associated with them, Uzun and Tuncel (2000) measured biogenic component in aerosol. In the process he analyzed trace elements and major ions in samples collected 1998. Erduran and Tuncel (2001) measured gas phase pollutants, such as HNO_3 , NO_2 , O_3 , NH_3 . Çetin (2002) measured solubility of elements in size separated samples collected at the station. Currently 1700 samples, which were not analyzed before are being analyzed.

A third station was established, again on the Mediterranean coast, at approximately 400 km to the east of the Antalya station, at Erdemli, İçel in 1992. The station was operated by The METU, Marine Science Institute, for two years. In Erdemli station daily aerosol samples were collected and analyzed for approximately 10 trace elements. Data were evaluated with special emphasis to dust transport from North Africa (Kubilay, 1996). A fourth station was established at Mt. Uludağ in 1993 (Uludağ station in this study). The station was the only high altitude station in Turkey and operated jointly by the METU, Chemistry Department and Uludağ University, Chemistry Department for about one year. The station was

somewhat different from other stations existing at that time. Only gas phase pollutants (SO_2 , NO , NO_2 and O_3) and PM mass were measured hourly, using automated measuring devices (Tuncel et al., 1994). However, aerosol samples collected on the glass fiber strips of the automated PM measuring device (a β -gauge) were dissolved and analyzed to determine the ionic composition of atmospheric particles (Karakaş, 1995).

A fifth station was established on the Black Sea coast, 20 km to the east of the town of Amasra, in 1995 (Black Sea station in this study). The station was operated by our group for 5 years. Daily aerosol and precipitation samples were collected, continuously for 5 years. Collected aerosol samples were analyzed by a combination of instrumental neutron activation analysis (INAA) atomic absorption spectrometry (AAS), ion chromatography (IC) and colorimetry for approximately 40 elements and ions (Karakaş 1999). Collected rain samples were also analyzed for 20 elements and ions (Al-Agha and Tuncel, 2003).

The sixth rural station was established at the central Anatolia, 50 km from Ankara and 12 km from Çubuk town, in 1993 (Çubuk station in this study). The Çubuk station is the only EMEP station we have in Turkey. The site selection, sampling and analytical procedures were based on the EMEP protocols, which were applied in all 100 EMEP station around Europe. The station is operated by the Ministry of Health, Refik Saydam Hygiene center since 1993. Daily aerosol and precipitation samples are being collected and gas phase parameters (SO_2 , NO_2 , HNO_3 and NH_3) are being measured at the station. Parameters measured in Çubuk station are identical with the parameters measured in all EMEP stations and are not exactly similar to the parameters measured in other stations in Turkey. Refik Saydam Hygiene Center is responsible in generating the data and delivering them to the NILU, Norway, which is the chemical

coordination center for EMEP. At NILU, data is entered to the data base, along with data from other 100 EMEP stations and used for (1) continent-wide assessment on the variation in concentrations of measured parameters and (2) calibration of EMEP models. Detailed evaluation of data is not performed in EMEP. Huge amounts of data are generated in the Çubuk station since 1993. These data could be evaluated with sophisticated statistical tools to provide valuable information on the characteristics of atmosphere at the Central Anatolia. However, such detailed analysis is beyond the scope of studies in the EMEP program and left for the national centers. However, since the Refik Saydam Hygiene Center does not have the necessary expertise for sophisticated data evaluation, a protocol was signed between the METU and the Center, so that data evaluation could be done by our group. Based on this protocol, both aerosol (Yörük, 2004) and precipitation (Tuncer et al., 2001) data from Çubuk station between 1993 and 2000 were evaluated in our group.

The introduction provided clearly demonstrates that there had been extensive data generation and evaluation for rural atmosphere in different parts of Turkey in last 15 years. Most of this work, particularly data evaluation, is performed in the METU, Department of Environmental Engineering. Such extensive data evaluation revealed valuable and extensive information on the composition of particles (and precipitation) in different parts of Turkey. Assessments also demonstrated some differences between the compositions of particles in different parts of the country. These differences could be different source regions affecting regions, different transport mechanisms to the regions or different topographical features of the regions. The reasons behind observed differences were not known.

There were two main objectives of this study:

1. Systematic comparison of data generated in different stations to demonstrate the differences between aerosol compositions measured at different parts of the country and to assess the reasons causing these differences. Here the term “differences” does not only mean the differences in the levels of parameters measured, but it also includes differences in temporal variability of measured parameters, differences in correlations between parameters, differences in source types affecting regions and source regions where these sources are located. Consequently the study included extensive comparison of aerosol data generated in previous studies at different regions of the country. As pointed before, in addition to levels of measured parameters, short and long-term variability of elements in different stations, correlations between elements in different stations, background levels of parameters in different stations, source types affecting different stations and source regions affecting different stations were compared to understand the mechanisms resulting in observed differences between stations. Data from Antalya, Amasra, Çubuk and Uludağ stations were included in the comparison as we had access to these data sets.

2. Reanalysis of data. Evaluation of data generated at Antalya, Amasra, Uludağ and Çubuk stations have started in 1994 at Antalya and ended in 2004 for Çubuk station. In this 13 year period new statistical tools that can be used data evaluation were developed and some of older statistical tools were improved. For example, in most of the previous studies factor analysis was the main statistical tool to determine types of sources affecting the receptor, but a new tool of the same purpose, namely positive matrix factorization (PMF), which has some significant advantages over FA, recently appeared and found very wide use in the literature. Similarly, potential source contribution function (PSCF)

approach was the main statistical tool to determine potential emission source areas affecting receptors in the previous studies performed in our group. Again, recently using statistical bootstrapping technique it became possible to test the statistical significance of PSCF values calculated for the grids in the study area. Also, in some of the previous studies in our group, trajectories extending 3 days backwards in time were used. However, in more recent studies 5.5 days long trajectories were used. Based on these arguments we reanalyzed some of the data generated in previous studies (a) to compare similar computational outputs in all stations and (2) to be able to use more developed statistical tools. Reanalysis were generally confined to sophisticated statistical treatment to apportion source types and regions.

CHAPTER 2

MATERIALS AND METHODS

2.1. Sampling Site Descriptions

Site selection is an important step in establishing reference stations where sampling is performed to study long-range transport. The sampling site should not be under the influence of any local point or area sources to be able to detect low levels of pollutants that are being advected from upper atmosphere. Site selection criteria are fairly well established and include factors such as minimum distance from settlement areas, from industrial point sources, from major and secondary roads. However, there are additional requirements, which were dictated by the logistics of sampling. Some of the criteria that are being used in international networks, such as EMEP, MED POL, GAW etc include:

1. Data generated should be representative for the whole region,
2. The generated data should give information about fluxes of pollutants to each region,
3. Major pollution sources like power plants, cities with a population higher than 10 000 must be at least 10 km away,

4. The sampling site should be at least 1 km from major roads and small towns with a population > 1 000,
5. There must be no obstacles, such as buildings, walls etc in the immediate vicinity of the station.
6. Station must be located at a site where power is available,
7. Station must be on the grounds of a government property so that it can be protected against potential vandalism,
8. There must be capable people to change samples,

Figure 2.1 shows the locations of the sampling stations that were used in this study. Aerosol data in these stations were generated by Güllü (1996) at the Mediterranean station, by Karakaş (1999) at the Black Sea station, by the Ministry of Health through EMEP program at the Çubuk station, and Karakaş (1995) at the Uludağ station.



Figure 2.1. Sampling stations

Since data is generated during previous studies, only a brief description of experimental techniques will be discussed in this thesis, detailed description of methods used for sampling and analysis of aerosols (Güllü, 1996; Karakaş, 1999; Yörük, 2004; Karakaş, 1995) are given elsewhere.

2.1.1. Mediterranean Station

The Mediterranean station is located at the coast approximately 20 km to the east of Antalya (31.0°E, 36.8°N). The station is located on a rock structure at a height of 20 meters above the sea level. One difficulty to establish a reference station on the Mediterranean coast was the extensive domestic and foreign tourism in the region. A rest area owned by the Ministry of Forestry was selected as the site where the station is established. The area was under the protection throughout the year and power is available. The nearest population center was the city of Antalya, which was approximately 20 km away.

The platform and the field laboratory are two components of the station. The platform was built on the rock structure near the sea approximately 20 km above the sea level. It consists of 4m x 4m concrete base and surrounded by a 2 m high fence. The wiring of the fence was covered by polyethylene to avoid contamination of collected samples by metal particles that can result from corrosion of fence material. Equipments including a wet only precipitation sampler, a wet and dry deposition sampler, a Hi-Vol sampler and a Hi-Vol impactor were anchored to the concrete base of the platform.

The field laboratory was a container with dimensions of 3m x 2m x 2m. The power was distributed from the container to equipments on the platform. The field laboratory included a storage area, a refrigerator to

store samples until they were shipped to the central laboratory in Ankara and a sample change area.

The sampling at the station was started in December 1991 and continued until 2000. In this study, results of 1992 and 1993 aerosol samples will be discussed. During this period, a total of 600 daily aerosol samples were collected.

2.1.2. Black Sea Station

The station on the Black Sea coast is implemented at a storage area, which belongs to the Ministry of Forestry. The storage area is located 20 km to the east of the town of Amasra. The distance between the station to the Black Sea coast is approximately 3 km (32.3°E, 41.5°N). The altitude of the station is approximately 150 m. The station was located in the platform whose ground was filled with large sand stones.

The Black Sea station also consists of a platform and a field laboratory. The platform contains Hi-Vol aerosol sampler and a wet and dry deposition collector. The field laboratory is a container with dimensions of 3 m x 2 m x 2 m and it contains automated; sulfur dioxide, nitrogen oxides, ozone, PM-10 mass analyzers and a recording rain gauge. The power was distributed from the container to equipments on the platform.

Daily aerosols samples were collected in between April 1995 and July 1997. During this time period 354 daily aerosol samples were collected.

2.1.3. Marmara Station

Marmara Station is located in Sarıalan region of the Uludağ Mountain, which has a 1685 m altitude and located at approximately 20 km south of the city of Bursa. The station was operated by cooperation of the Chemistry Department of METU and Uludağ university. Samples

collected at the Uludag station were analyzed in the METU, Department of chemistry.

The Sarialan where the station is located is shown to be both below above the boundary, depending on the variations in the boundary layer height. When the station is above the boundary layer, collected samples represent relatively clean free tropospheric air, when it is below the boundary layer, measured values represent aged polluted air masses from the Bursa region. This station is approximately 7 km away from the ski resort area and approximately 30 km from the Marmara Sea.

The monitoring station is equipped with automatic analyzers for the gas phase pollutants including dioxide, nitrogen oxides, ozone and TSP, and meteorological sensors for wind speed and direction, temperature and humidity. The station was fully operational, continuously for two years in 1993 and 1994. After 1994, the station was operated from time to time, due to difficulty in getting access to the station under severe winter conditions. One hundred and eighty-four daily aerosol samples collected between September 1993 and March 1994 were used in this study.

2.1.4. Central Anatolia Station

Central Anatolia Station is located at Çubuk, which is approximately 50 km away from the city of Ankara (33.10°E, 40.10°N).

Çubuk station is the only operational EMEP station in Turkey. The station is operated by the Ministry of Health and collected data is delivered to the EMEP secretariat, where it is entered to the EMEP data base. In EMEP data is used for continent wide comparisons and model calibration. More detailed evaluation of the data generated at the Çubuk station is being done at our group through a protocol between the University and the Ministry of Health.

Since it is an EMEP station, site selection, sampling and measurement procedures used are identical with protocols applied in all EMEP stations in Europe. For example, the following site selection criteria were used: Sampling site must be at least 50 km away from the large pollution sources (towns, power plants, major motorways), 100 m away from the small scale domestic heating with coal, fuel oil or wood, 100 m away from minor roads, 500 m away from the main roads, 2 km away from the application of manure, stabling of animals, and 500 m away from the grazing by domestic animals on fertilized pasture with taking into consideration of the meteorological and topographic conditions, and quantity of emissions from the sources. Sampling site must also be representative of a larger area and the size of this area depends on the spatial resolution in the concentration and deposition fields and the variability of the air and precipitation quality.

Sampling station consists of a rectangular cabin (field station) with a surface area of 12 m², which hosts automated measurement devices and a platform onto which a high volume sampler, a precipitation meter meteorological mast and a stack filter unit are installed.

The station became operational in 1992 and air and precipitation samples are being collected since 1993. In this study, aerosol samples collected between February 1993 and September 1998 were used. During this time period 1806 daily aerosol samples were collected. Aerosol samples were analyzed in the laboratories of Ministry of Health, Refik Saydam Hygiene Center.

2.1.5. Comparison of Station Characteristics

Since the objective of the study is to compare aerosol composition at different parts of the country, the data generated at each station should be regionally representative. Each of the station used in this study was

established with the aim of generating regionally representative data. The most crucial requirement for the data generated at a station to be regionally representative is that the station should not be under the influence of any local source. Although this essential point was kept in mind during site selection for all the stations used in this study, complete adherence to this rule was not possible in some of them due to logistic requirements and some received unexpected local pollution. It should be noted that, limited impact of local sources does not mean that the stations are not appropriate for regional comparisons, but these impacts must be kept in mind when data are regionally compared.

The most likely station that can be affected from a local impact is the Antalya station, as it is only about 20 km away from City of Antalya, which is a large settlement area with substantial emissions. Surface wind patterns at Antalya station is extensively investigated by Güllü (1996), Author have shown that surface winds blow from the direction of the city in only 20% of the time and strong impact of the city on data generated at the station is not likely. This was supported by SO₂ measurements performed at the station for two years. The SO₂ mixing ratio measured on hourly basis were less than 1 ppbv (<2.4 µg m⁻³) which is a clear indication that there is no strong influence of local combustion sources on the data generated at the Antalya station. Furthermore, data generated in that station is not higher than data generated at other remote stations at the Mediterranean region.

Uludağ station is located at the Sarıalan region. There are three strong pollution sources in the region. One of them is the town of Bursa which is 24 km from the station. The other one is the Orhaneli thermal power plant which is approximately 30 km away and the last one is hotels at the resort area which approximately 20 km away from the station. Continuous, hourly measurements of gaseous pollutants, SO₂, NO₂, NO,

O₃ at the station for approximately 2 years have shown that the station receive plume from Bursa between 3 pm and 4 pm in some of the days. But since the plume is transported approximately 25 km before it reaches to station, concentrations measured when the plume arrives is only slightly higher than concentrations measured when there is no urban plume at the station. No effect of power plant and hotels were identified in the data set (Tuncel et al., 1994).

Çubuk station is located 50 km from Ankara which is fairly long distance to have a significant impact on observed concentrations of measured parameters. Another possible pollution source is the Çubuk village which is 12 km from the station. Previous analysis of aerosol data did not show any observable impact of urban plume at the station. However, statistical analysis revealed a factor with high SO₂ loadings, which is identified as local pollution (Yörük 2004). The contribution of this factor to particle load was very small indicating that it cannot alter chemical composition of aerosol significantly (Yörük, 2004).

Station on the Black Sea coast is the one which is closest to be regionally representative. The nearest emission sources are the town of Amasra which is >20 km away from the station and Bartın which is 30 km from the station. Neither Amasra, nor Bartın are as large settlement areas as Bursa, Ankara and Antalya. Previous analysis of data set generated in this station did not show any indication of local pollution.

One limitation of the data set, for the objective of this study, is the different time periods in which the samples are collected in different stations. Samples are collected between 1992 and 1993 at Antalya station, 1993 – 2000 at Çubuk station, 1993 – 1994 at Uludag station and 1995 – 1997 at Amasra station.

As pointed out in Chapter 1, concentrations of some of the pollutants showed dramatic decreases (up to 70%) at the Western Europe after 1987 when first S protocol became effective. Which means that comparison data collected at different times in such sharp transition period may not result in realistic assessment of source regions. However, there are two points that should be discussed before making such a statement. (1) The decreases observed are only for some of the pollutants, like SO_4^{2-} and Pb. For example decrease observed in NO_3^- and NH_4^+ concentrations are not as fast as the decrease observed in SO_4^{2-} concentration, (2) the decrease in SO_4^{2-} and Pb concentrations is observed in only certain parts of Europe, namely in the western Europe. The change in SO_4^{2-} concentration was observed much later in the Eastern Europe and Balkan countries and the observed decrease is much smaller.

Long-term SO_4^{2-} and NO_3^- measurements at Çubuk (Yörük, 2004) and Antalya (Öztürk unpublished data) showed that there is no detectable change in SO_4^{2-} concentrations within Turkey. It should also be noted that most extensive comparison on this study is performed between Antalya and Amasra stations due to measurement of large number of parameters in these two stations. Sampling in these stations are only 3 years apart. Based on these discussions it was concluded that contributions of differences in source regions, transport patterns or in other regional differences between stations should be significantly larger than the differences arising due to different sampling years in stations

2.2. Sample Collection and Analysis of the Samples

In Antalya and Amasra stations samples were collected with Andersen PM-10 Hi-Vol samplers. In Çubuk station samples were collected with Digitel, model DHA-80 Hi-Vol sampler, where as in Uludağ station, MPSI 100 type TSP analyzer was used for sample collection.

Aerosol samples of Antalya, Amasra and Çubuk stations were collected on Whatman-41 cellulose filters for 24 hour periods. Since samplers at Çubuk and Uludag stations were not equipped with PM-10 pre-impactor, collected samples were total particulate matter (TSP). Previous studies on particle size distributions indicated that difference between PM-10 and TSP is less than 10% for crustal elements, and even smaller for anthropogenic elements (Kuloğlu, 1997). Because of this, aerosol samples collected at Çubuk and Uludağ were included to comparisons in this study. Glass fiber filters were used in both Uludag and Çubuk stations for collection.

Although the sampling techniques used in all four stations were not dramatically different, Analytical methods and consequently measured parameters substantially different in each station. Collected samples at Antalya and Amasra stations were analyzed by a combination of Instrumental Neutron Activation Analysis (INAA), Atomic Absorption Spectrometry (AAS) and Ion Chromatography (IC). Data in these two stations consists of concentrations of SO_4^{2-} , NO_3^- , NH_4^+ and Cl^- ions and approximately 35 elements (Güllü, 1996; Karakaş, 1999). The data generated in these two stations are PM-10 as the Hi-Vol samplers used at Amasra and Antalya stations are equipped with a pre-impactor that removes particles with diameter $> 10 \mu\text{m}$. However, samples collected at Uludağ station were analyzed only with ion chromatography for SO_4^{2-} , NO_3^- , NH_4^+ and Cl^- and by AAS for Na, Mg, K and Ca. Samples collected at Çubuk station is measured for parameters that are included in EMEP measurement protocol (HNO_3 , SO_2 , NO_2 , NH_3 , SO_4^{2-} , NO_3^- , NH_4^+). In addition to these parameters that were measured in all samples, Na, K, Mg, Ca, Pb, V and Cd are measured in limited number of samples. As can be seen from this discussion, data generated in all stations are not identical. There are parameters that are measured in all stations, but

there are much fewer parameters at Çubuk and Uludağ stations. This naturally affected comparisons between stations.

Summary of analytical techniques for elements and ions analyzed at each station are given in Table 2.1.

2.3. Positive Matrix Factorization (PMF)

Receptor modeling is powerful alternative to source oriented dispersion models in source apportionment studies. The techniques bases on application of statistical tools to generated data to identify and quantify sources affecting a receptor point. The statistical tool used, which is generally a multivariate techniques, determines the type of receptor modeling approach used. In air pollution studies, among all multivariate statistical approaches, Principle Component Analysis (PCA) (Thurston and Spengler, 1985; Mishra et al., 2004; Wang et al., 2000; Ho et al., 2002), Factor Analysis (FA) (Hopke, 1985), Chemical Mass Balance (CMB) (Freidlander, 1973; Gordon, 1980; Hellén et al., 2003; Khalil and Rasmussen, 2003) and Positive Matrix Factorization (PMF) (Paatreo, 1997; Huang et al., 2001; Qin et al., 2002; Paatero and Tapper, 1994; Juntto and Paatero; 1994; Anttila et al., 1995; Prendes et al., 1999) have been most commonly applied to arrays of pollution variables, to aerosols elemental composition data or to spatial pollution distributions in order to derive information about pollution sources influencing the data.

In this study, positive matrix factorization (PMF) (Qin et al., 2002; Paatero and Tapper, 1994; Juntto and Paatero, 1994; Anttila et al., 1995; Paatero, 1997) was used for re-analysis of data and results obtained at each station are compared.

Positive matrix factorization was developed recently as an alternative to more conventional receptor modeling approaches, such as factor analysis and principle component analysis.

Table 2.1. Analytical techniques of measured species for each station

Analyses Techniques	Antalya Station	Amasra Station	Uludağ Station	Çubuk Station
GFAAS (Perkin Elmer 1100B Spectrophotometer coupled with HGA 700)	Pb, Ni, V, Cr	Pb, Ni, Cr, Cd, V		Pb, Cd, V, K, Ca, Mg
FAAS (Perkin Elmer 1100B Spectrophotometer)	Al, Zn, Fe, Mg	Al, Zn, Fe, Ca, Mg,	Mg	
FAES (Perkin Elmer 1100B Spectrophotometer)	K, Na, Ca	K, Na	K, Na, Ca	
Colorimetric (Nessler's Method)	NH ₄ ⁺	NH ₄ ⁺	NH ₄ ⁺	NH ₄ ⁺ , NH ₃
INAA	Na, Mg, Al, Cl, K, Sc, Ti, V, Cr, Mn, Fe, Co, Zn, As, Se, Br, Rb, Sr, Mo, Cd, In, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Dy, Yb, Lu, Hf, Hg, Th	Na, Mg, Al, Cl, K, Sc, Ti, V, Cr, Mn, Fe, Co, Zn, As, Se, Br, Rb, Sr, Mo, Cd, In, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Dy, Yb, Lu, Hf, Hg, Th,		
IC	Cl ⁻ , NO ₃ ⁻ , SO ₄ ²⁻	Cl ⁻ , NO ₃ ⁻ , SO ₄ ²⁻	Cl ⁻ , NO ₃ ⁻ , SO ₄ ²⁻	SO ₄ ²⁻ , NO ₃ ⁻ , HNO ₃ , NO ₂

Advantages of PMF compared to FA are: (1) It utilizes information more efficiently by using error estimates of the measured parameters. (2) It separates sources with better resolution than FA. (3) Its positive loadings

and scores are much more useful for CMB models (Huang, 1999). (4) Quantitatively, the factor mass profiles produced by the PMF model can apportion them among the factors in a more reasonable manner. (5) PMF can feed subjective information into factor analysis by using enforced rotation techniques (Qin et al., 2002) and (6) handling of missing and below detection limit values are much better than handling of these values in FA

PMF uses a weighted least-squares fit with the known error estimates of the elements of the data matrix used to derive the weights. It produces quantitative non-negative solutions which can be written as:

$$X = GF + E \quad (2.1)$$

or by using the element-wise notation, bilinear factor analytic model is written as:

$$x_{ij} = \sum_{h=1}^p g_{ih} f_{hj} + e_{ij} \quad (2.2)$$

where X is known $i \times j$ matrix of the j measured chemical species with species in i samples. G is an $i \times h$ matrix of source contributions of the samples (time variations). The F is an $h \times j$ matrix of the source compositions (source profiles). E is the residuals matrix, i.e., the difference between the measurement X and the model as a function of the factors G and F. PMF provides a solution that minimizes an object function, Q(E), based upon uncertainties for each observation (Paatero, 1997; Polissar et al., 1998). This function is defined as

$$Q(E) = \sum_i^n \sum_j^m \left(\frac{e_{ij}}{h_{ij} s_{ij}} \right)^2 \quad (2.3)$$

where s_{ij} is an uncertainty estimate in the j^{th} element measured in the i^{th} sample and $h_{ij}^2=1$ if $|e_{ij} / s_{ij}| \leq \alpha$; otherwise, $h_{ij}^2 = |e_{ij} / s_{ij}| / \alpha$.

The robust mode can be selected to handle outlier values in the data. For this purpose, the value of outlier threshold distance, α , can be taken as 2.0, 4.0, or 8.0.

Based on the standard deviation values of each data point PMF computes individual error estimates for each observed data point. This feature of PMF makes the missing and below-detection-limit data to be handled by adjusting the corresponding error estimates. The error estimates used in this study are calculated by the program itself considering the detection limit value of the element and summing up with a certain ratio of concentration value. The ratio of the concentration can be any number in between 0.01 and 0.1. For this study, the ratio for the concentration value is taken as 0.05, after testing for various values between the indicated limits.

If the standard deviations for the data array are theoretically known, then it is possible to judge the quality of fit based on the Q value. The value of Q should be approximately equal to the number of points in the data matrix minus the total number of elements in the factor matrices (Paatero, 2000). In the presence of outliers, it may be difficult to know if the observed value of Q is normal or too large. It may be more helpful to investigate the distribution of scaled residuals, (e_{ij} / s_{ij}) (Paatero, 2002). Ideally, the scaled residuals should appear random to the eye. There should be a random pattern of positive and negative values between -2.0 and 2.0 (Paatero, 2000).

2.4. Trajectory Statistics

Multivariate statistical models can provide information on the sources of particles collected at the station. This sort of information is sufficient in urban areas, because once the types of sources affecting composition of collected aerosol samples are identified, their locations are generally known. However, situation is different in receptor modeling applications to rural or remote data. The question that is addressed in application of receptor modeling to rural data is not only identification of source types affecting aerosol composition, but also their locations as well. Emission sources affecting samples collected at a rural station are distributed in a circle with approximately 5000 km radius (study area). For example, if you identify a power plant source affecting your site, there are several hundred power plants in Europe that can be the identified source. Consequently, in rural studies one must not only identify types of sources, but must also find where those sources are located.

Concentration data obtained by measurements must be combined with geographical information to determine sources regions. Necessary geographical data is provided by backtrajectory modeling. Backtrajectory is the time integration of an air parcel's position while it is transported by the wind. Trajectory models, which describe the paths of the air parcels followed in the atmosphere, before they are intercepted at the station, are useful tools for the determination of source-receptor relationships of air pollutants in the regional scale. Various trajectory computation methods have been developed based on different assumptions.

In most of the trajectory models, observed or analyzed winds are used to compute horizontal advection component. The vertical components of the trajectories, on the other hand, are computed based on one of the following assumptions:

1. Isobaric: trajectory is assumed to follow a constant pressure surface,
2. Isentropic: trajectory is assumed to follow a constant temperature potential,
3. Kinematic: trajectory is assumed to move with the vertical velocity wind fields generated by diagnostic or prognostic model.

The isobaric trajectory modes were used extensively in the past. However, it has been found that the significant vertical motions were ignored in isobaric assumption (Harris and Kahl, 1994). Currently, isentropic trajectory models are widely used in trajectory calculations. Isentropic models are advantageous due to not requiring vertical motion data. The vertical motions occur implicitly as air parcel move along sloping isentropic surfaces (Fuelberg et al., 1996).

Back trajectories, as the name implies, they give information about the history of an air parcel in the previous days before reaching to a receptor location, provide necessary geographic information which can be coupled to concentrations of parameters measured at the station.

Backtrajectories in this study were calculated using European Centre for Medium Range Weather Forecast (ECMWF) three dimensional isentropic model. One backtrajectory was calculated for each sample in all stations (more than 2000 trajectories totally). Trajectories used in this study were 5.5 days long (gives the path of the air mass within 5.5 days before the sample collected). Trajectories, which are 5.5 days long, were available for Antalya (Öztürk unpublished data) and Çubuk (Yörük, 2004) stations. However, Amasra and Uludağ trajectories were calculated in this study, because trajectories calculated for these stations in previous studies were only 3.5 days long.

Calculated trajectories can be handled in different ways. If there are few samples collected at the station individual trajectories, corresponding to high concentrations of measured parameters, can be visually inspected to understand which sources can be responsible for observed high concentrations. This approach does not have any statistical significance, and also visual inspection is not a practical approach when there are hundreds of samples, as in this study.

When there are many samples and many trajectories corresponding to those samples, handling of trajectories using statistical tools becomes a more practical approach to establish source receptor relationship. Techniques that use statistics to evaluate trajectory data are collectively called trajectory statistics.

In this study two different trajectory statistics methods are used to compare the source regions affecting chemical compositions of particles at four stations. These are flow climatology (FC) and potential source contribution function (PSCF) approaches.

2.4.1. Flow climatology

Flow climatology is the earliest statistical method for the identification of the sources of air pollutants. It is often used to determine the pollution input from distant sources to a selected region and also allows understanding of airflow patterns.

The approach involves computing several years of trajectories ending at a selected receptor site and their classification according to their transport speed and direction.

In the flow climatology performed in this study, each trajectory was separated into 1-hr long segments and coordinates of the end points of these segments. Number of segments in each of the 16 wind sectors,

which gives the residence time of air masses in each wind sector, and which is a measure of the air mass transport frequency is computed for each station. The countries, which fall into the sectors associated with high pollutant concentrations at the receptor site, are pronounced as the source regions of air pollutants.

2.4.2. Potential Source Contribution Function Analysis

Potential Source Contribution Function (PSCF) was developed by Ashbaugh (1983) to identify the source areas of pollutants individually. PSCF is receptor-oriented method that uses chemical measurements of pollutants at the receptor site and meteorological information. Therefore, it combines flow frequency with the measured elemental composition of the region. The concept of PSCF was introduced to identify geographical regions that may have a higher probability of being source areas of potentially harmful substances like sulfate in the study area.

It is assumed that a species emitted within a grid cell is swept into the air parcel and transported to the receptor site without loss through diffusion, chemical transformation or atmospheric scavenging (Cheng et al., 1993; Lupu and Maenhaut, 2002).

The value of PSCF for a grid cell (i,j), is calculated by counting the 1 hr trajectory segment endpoints that fall into that grid cell. Assuming N as the total number of trajectory segment endpoints for the study period, T, if the number of endpoints that fall in the ij-th cell is n_{ij} , then the probability of an event at the receptor site is related to that cell, A_{ij} , over entire study period T is given by,

$$P[A_{ij}] = \frac{n_{ij}}{N} \quad (2.4)$$

If there is m_{ij} counts among n_{ij} , for which the measured pollutant concentration exceeds a selected criterion value, then the probability of event B_{ij} that is related to the high concentration at the receptor site is given by,

$$P[B_{ij}] = \frac{m_{ij}}{N} \quad (2.5)$$

Then PSCF of the single grid ij -th cell is calculated as follows,

$$PSCF = \frac{P[B_{ij}]}{P[A_{ij}]} = \frac{m_{ij}}{n_{ij}} \quad (2.6)$$

PSCF value can be interpreted as the conditional probability, which gives the geographical distributions of the possible source regions. The cells with higher PSCF value are the potential source areas of pollutants. It is important to notify that grid cell size must be sufficiently large for the assimilation of reasonable trajectory segment endpoints. It should not be ignored that there is still an uncertainty involved in the calculation of the back trajectory.

In this study the study area is between 20°W and 60°E longitude in east – west direction (starts from west of the UK at west and extends to east of the Caspian Sea at east) and between 75°N and 15°N latitudes in north – south direction (Starts from the middle of the Siberia at north extends almost to the equator at south). The study area is divided into 1° x 1° grids (total of 4800 grids)

The value of PSCF ranges between 0 and 1. Any grid cell having PSCF of 0 is unlikely to be the source region, while the opposite is true for PSCF of 1. For large values of n_{ij} , the results are statistically stable. Therefore it is necessary to reduce the effect of small values of n_{ij} by developing a weight function.

In order to identify the high PSCF values that have arisen purely by chance, it is necessary to test values against the null hypothesis that there is no association between concentrations and trajectories (Vasconcelos et al., 1996).

The statistical significance of the spatial distribution of the PSCF values is examined by making the use of non-parametric bootstrap method (Wehrens et al., 2000). The method assumes that the concentration values are independent and identically distributed (Lupu and Maenhaut, 2002). A trajectory is randomly picked with replacement from the ensemble of trajectories. The chosen trajectory is checked to determine if it is associated with a sample whose concentration for the species of interest is above the criterion level. If it is, then both the contaminated and total point counters (m_{ij} and n_{ij}) for the grid cells in which this trajectory's end point fall are incremented. If the sample value is below the criterion level, only the total point counters (n_{ij}) for the trajectory's grid cells are incremented (Hopke et al., 1995). Then the PSCF values calculated for each of the grid cells are sorted. Let the number of iterations as B and the significance level as β . If

$$P_{ij} \geq P_{\left((B+1) \binom{1-\beta/2}{2} \right)_{ij}}^* \quad (2.7)$$

the null hypothesis is rejected at $(1 - \beta)100\%$ confidence level. Then, for the further analysis only PSCF values satisfying the above relation are retained (Lupu and Maenhaut, 2002).

CHAPTER 3

RESULTS AND DISCUSSION

3.1. General Characteristics of Data Sets

The distribution properties of aerosol composition over a long period of time are dependent on the fluctuations of meteorological and source emission variables. Even though the emissions from the sources are approximately constant, successive mixing and dilution of pollutants as they are transported from the source to receptor site results in a log-normal distribution for the ambient concentrations (Güllü, 1996).

Geometric mean concentrations of aerosols measured at Antalya (collected between 1992 and 1993), at Amasra (collected between 1995 and 1997), at Çubuk (collected between 1993 and 2000) and at Uludağ (collected between 1993 and 1994) are given in Table 3.1.

The mean concentration of each element is statistically compared with the same element in the other station by using student-t test using Stat Graphics program. This test determines whether two means from two independent and normally distributed samples differ within a certain statistical confidence level. For this test confidence level was taken as 95%. The test has shown that the average concentrations of most

Table 3.1. Geometric mean concentrations of sampling sites Antalya, Amasra, Çubuk and Uludağ

	Antalya	Amasra	Çubuk	Uludağ
Elements and Ions	ng/m ³	ng/m ³	ng/m ³	ng/m ³
SO ₄ ²⁻	4250	4150	1150	1480
NO ₃	810	790	290	610
NH ₄ ⁺	800	1180	340	670
Mg	280	110	100	50
K	250	135	175	45
Ca	1550	270	365	830
Cl	1010	215		260
Na	750	300		350
V	1.82	2.12	1.34	
Pb	14.30	12.06	7.03	
Al	300	900		
Sc	0.06	0.04		
Tl	26.6	20.3		
Cr	2.60	0.87		
Mn	6.11	8.68		
Fe	230	200		
Co	0.14	0.13		
Ni	1.63	1.13		
Zn	7.49	10.46		
As	1.20	1.15		
Se	0.23	0.29		
Br	14.2	6.5		
Rb	0.62	0.62		
Mo	0.33	0.35		
Cd		0.21	96.9	
Sb	0.29	0.30		
Cs	0.069	0.090		
La	0.20	0.15		
Ce	0.38	0.17		
Sm	0.028	0.021		
Nd	0.31	0.84		
Eu	0.0062	0.012		
Tb	0.0031	0.0158		
Dy	0.034	0.036		
Yb	0.011	0.0084		
Lu	0.0019	0.0013		
Hf	0.015	0.014		
Hg	0.041	0.037		
Th	0.054	0.040		
NO ₂			2230	
TSP		37500		16200
HNO ₃			235	
NH ₃			225	

element pairs are different from each other. The results of t-test are given in Table 3.2. Concentrations of crustal elements, Co, Dy, Hf, Lu and Ti as well as concentrations of anthropogenic species As, Sb and NH_4^+ were found to be the same in Antalya and Amasra stations. Concentrations of K and V are statistically similar in Antalya and Çubuk stations. Those of Mg and NO_3^- were the same in Amasra and Uludağ stations and Pb has the similar concentrations at Amasra and Çubuk stations.

Table 3.2. The results of student t-test of elements which do not have statistically significant difference between their average concentrations within 95% confidence level

Station Sites	Elements and Ions
Antalya-Amasra	Co, Dy, Hf, Lu, Ti, Sb, NH_4^+ , As and V
Antalya-Çubuk	K and V
Amasra-Uludağ	Mg and NO_3^-
Amasra-Çubuk	Pb

3.1.1. Comparison of Geometric Mean Concentrations

Preliminary investigation of the data in all stations indicated that all elements are log-normally distributed, as can be expected in atmospheric data sets. Consequently, lack of similarity in the mean concentrations of elements pointed out in the previous section can be due to high influence of outliers on average concentrations. Comparison of values of elements in different stations may be a better indicator for the similarities or differences between data populations at different stations. In this study, median values of elements at different stations were compared using Mann-Whitney w test, which combines the two data populations that are being compared, sort them from largest to smallest and compare the

average ranks of the two elements in the combined data. Using this test, median values were compared pair wise at every combination of stations.

In this section the term “similar” means that there is no statistically significant difference between the median values of the specie at the indicated two stations with 95% confidence. The term “different” indicates the existence of statistically significant difference in the mean concentrations of two test element at indicated two stations.

Species like SO_4^{2-} , NO_3^- , NH_4^+ , Pb, V, Zn, As, Se, Mo, Cd, Sb, Hg are known to have anthropogenic sources. Generally contribution of natural sources on observed concentrations of these elements are negligible (Gordon, 1980).

General comparison of anthropogenic elements and ions based on the geometric mean values have showed that species measured in Antalya and Amasra stations have higher concentrations than those in Uludağ and Çubuk stations.

Concentrations of SO_4^{2-} , NO_3^- , As, Mo, Hg and V in Antalya and Amasra stations are very close to each other and are statistically similar. This means that the influence of pollution regions for above species have similar influence on these receptor sites.

However, lead concentration in Antalya is statistically higher than those observed in Amasra. The main source of lead in the atmosphere is leaded fuel and smelter activities. This shows that Antalya region is affected more strongly by these sources. Concentrations of NH_4^+ , Zn and Se observed higher in Amasra station.

Concentration differences of elements and ions for Antalya and Amasra stations are considerably “smaller” than differences observed between these stations and Çubuk and Uludağ stations. Besides it should be

noted that concentrations of all measured anthropogenic parameters, SO_4^{2-} , NO_3^- and NH_4^+ in Çubuk and Uludağ stations and Pb and V also in Çubuk station are significantly “smaller” than concentrations determined in Antalya and Amasra stations.

Only anthropogenic parameters measured in Uludağ station are SO_4^{2-} , NO_3^- and NH_4^+ ions. Their concentrations are “similar” to concentrations measured in Çubuk station; but substantially lower than corresponding concentrations measured at Amasra and Antalya.

This comparison indicates that both of the coastal regions are under similar influence of pollution load. This could be due to two factors. First of all, the oscillatory motion of pollutants back and forth between the sea and the coast in a circular mode can result in accumulation of pollutants at coastal areas. Such local systems are observed in Iberian Peninsula (Millan et al., 1991; Gangoiti et al., 2001) and on the coast of Israel (Tov et al., 1997; Ranmar et al., 2002). Even though, there is not re-circular analysis performed coastal regions in Turkey, such process may be occurring along the Mediterranean and Black Sea coasts, resulting in higher concentrations of pollutants along the coast. Secondly, high altitude regions in the Anatolian Plateau are not influenced from pollution transport as much as coastal areas, due to differences in flow patterns in the central and coastal locations.

Fairly large number of soil related elements (Al, K, Mg, Ca, Sc, Ti, Fe, Co, Rb, Cs, La, Ce, Sm, Nd, Eu, Tb, Dy, Yb, Lu, Hf and Th) is measured in the Amasra and Antalya stations, which allows for a reliable comparison. However, comparison is limited to Mg, K and Ca in Çubuk and Uludağ station, as these are the only crustal species measured.

For Cs, Sc, Ti, Fe, Co, Yb, Rb, Lu, Hf, La, Sm, Dy and Th, the concentrations observed in the two coastal stations are “similar”.

Concentration values of Rb, Dy and Hf are almost identical in both stations whereas, except Cs, the rest of the elements listed above observed in slightly higher concentrations in the Mediterranean region. However, it should be noted that the Antalya/Amasra ratio for these elements vary between 0.8 and 1.4 and Mann-Whitney w-test indicated that medians of these elements are the same with 95% confidence.

Even though most of the soil related elemental concentrations are similar in two coastal regions, concentrations of K, Mg, Ca and Ce are observed “higher” in Antalya station whereas concentrations of “Al, Nd, Eu and Tb” are higher in Amasra station. Observed amounts of K and Mg expected to be higher in Antalya station because these elements could be partly from sea salt. Since Antalya station is close to the sea compared to Amasra station and since sea salt particles are mainly coarse particles, which settles out quickly, it is normal to observe such kind of trend.

High amount of calcium in Antalya station deserves a special attention since Ca concentration measured in Mediterranean region is about a factor of 6 higher than in Black Sea region. This trend can be either due to the calcareous nature of soil in the Mediterranean region or due to more frequent Saharan dust events to Antalya station. Although it is not directly related to this study, very substantial difference between Ca concentrations measured at the Black Sea and Mediterranean regions can have serious implications in terms of acid deposition. Sulfate concentrations measured at the Mediterranean and Black Sea are among the highest measured anywhere on the earth. Since SO_4^{2-} and NO_3^- are two ions that causes acidity in the rain water, high SO_4^{2-} concentration imply a very high potential for acid deposition and subsequently, damage to forest ecosystem. However, acidity in rain water is neutralized by CaCO_3 in the soil aerosol, due to highly calcareous nature of soil in Turkey. Lower Ca concentrations measured at the Black Sea station

indicates that acid buffering capacity of particles in the Black Sea atmosphere is not as high as anticipated and there may be more serious acid rain threat to forest ecosystem in the Black Sea than there is in the Mediterranean region. Concentrations of Al, Nd, Eu and Tb in Amasra station are 3 times that measured in Antalya station.

Potassium concentration at Uludağ is significantly lower than corresponding concentrations at other three stations. Calcium concentration in Çubuk station is comparable to Amasra station, however concentration measured in Uludağ for Ca is about a factor of 3 higher than these two stations.

Marine elements observed in higher concentrations in Antalya station than Amasra and Uludağ stations with a factor that ranges between 5 for Cl and 3 for Br and Na. This is expected since Antalya station is by the sea side whereas the other two stations are located some distance away from the coast. Concentrations of marine elements observed in Amasra and Uludağ stations are statistically similar.

Elements Cr, Mn, Br and Ni have mixed sources. Some of their observed concentrations are accounted by crustal material some by anthropogenic sources. These elements are measured only at Antalya and Amasra stations. Higher concentrations of Cr and Ni in Antalya are expected, because the soil in the Mediterranean is known to be enriched by these elements (Kubilay and Saydam, 1995). High Mn concentration in Amasra station was also observed by Hacısalıhoğlu et al., 1992 during ship-borne sampling on the Black Sea and attributed to close proximity of the region to dense ferromanganese industries at the Central Russia.

3.1.2. Comparison of Seasonal Variations of Elements

Elements and ions measured in the stations are categorized into 3 groups namely crustal, marine and anthropogenic and comparison of

seasonal variations of elements between the stations is made according to this classification. The main purpose of comparing the seasonal variations of elements is to identify the periods that the pollutants effecting each region.

Monthly geometric mean concentrations of the crustal elements for each station are given in Figure 3.1. Only the crustal elements K and Ca were measured in all stations and Al and Fe were measured only in the Antalya and Amasra stations. At coastal stations since samples were analyzed with INAA technique, besides Al and Fe, there are also data for concentrations of approximately 30 crustal elements. However, these elements are not included in the figure, because their monthly patterns are very similar with those of Al and Fe.

In all of the stations, crustal elements have higher concentrations during summer season. The seasonal variation of crustal aerosols can be explained by the seasonal variation of the emissions from the soil. In each of the station, soil is either covered with ice and snow or in mud form. Under such conditions, aerosol formation from the soil is minimized. However, during summer months, in all stations, including Uludağ, soil is dry and aerosol generation can even occur with very low wind speeds.

Monthly geometric mean concentrations of marine elements, namely Na, Cl and Mg are given in Figure 3.2. The mechanism that forms the marine aerosols is called bubble bursting (Piazzola and Despiou, 1997). This mechanism occurs at the sea surface and is related to the wind velocity (Blanchard, 1963; Blanchard and Woodcock, 1980; Chabas and Lefevre, 2000). Since wind velocity is the controlling parameter for the formation of marine aerosols, concentrations of marine elements are expected to be higher during winter months and lower in summer months. However, the expected trend is only observed in Antalya station. In Amasra and Uludağ, seasonal variations for marine elements are not so clear; and no

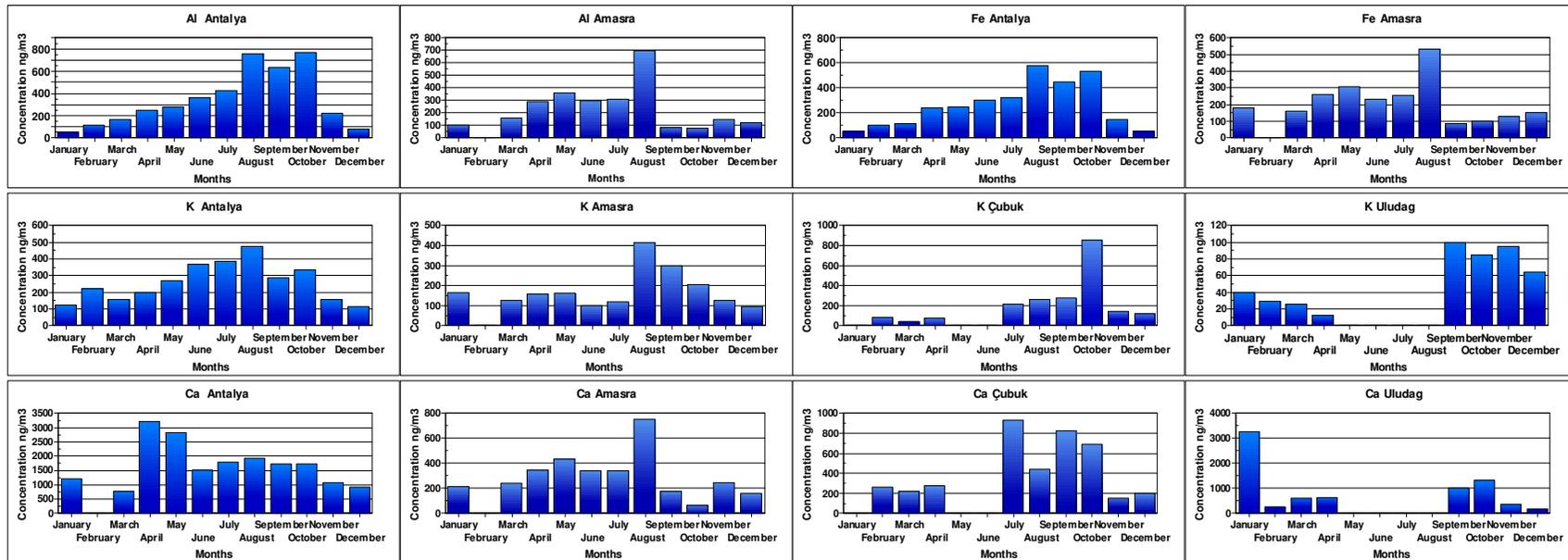


Figure 3.1. Monthly geometric mean concentrations of the K and Ca for each station and Al and Fe for Antalya and Amasra stations

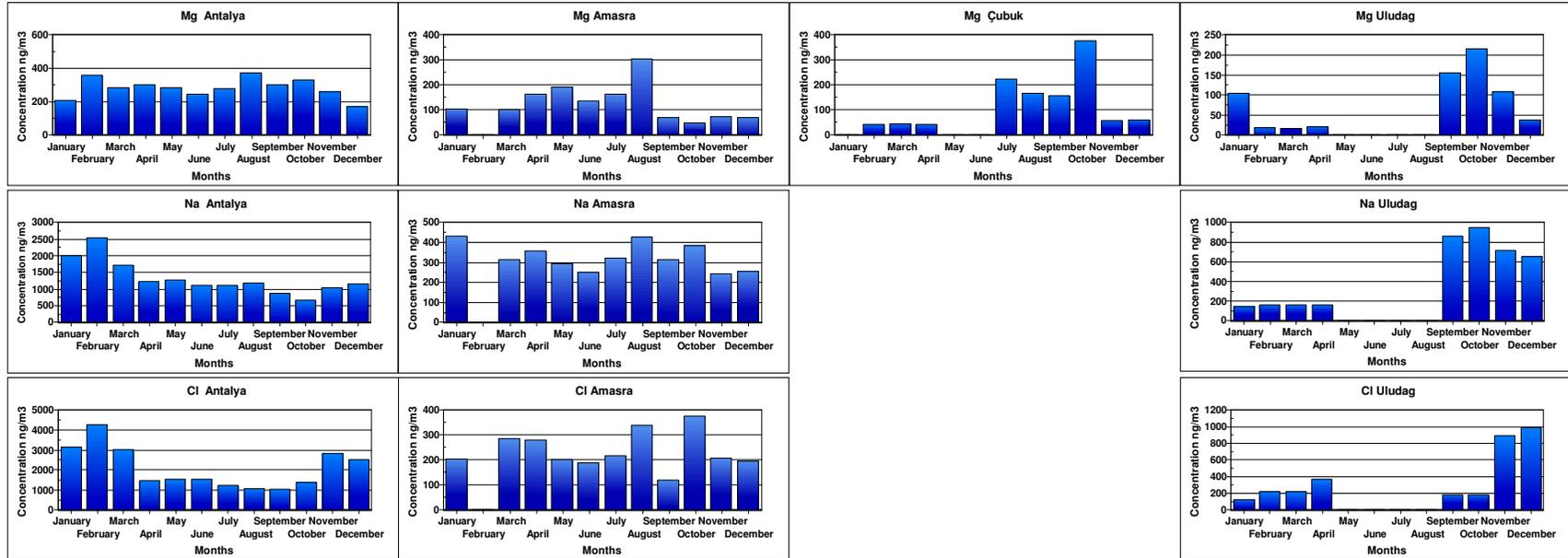


Figure 3.2. Monthly geometric mean concentrations of Mg for each station and Na and Cl for Antalya, Amasra and Uludağ stations

judgment could be made for Çubuk station since the indicator element for marine element, Na, is not measured. The reason of this difference between the Antalya station and other two stations is that Antalya station is on the sea side while the others are away from the coastal lines. Sea salt aerosols are coarse particles and they are removed from the atmosphere by dry deposition processes within very small distances. Therefore, stations away from coastal stations are not affected from sea salt as much as the stations at the coast. On the other hand, a significant fraction of measured Na concentrations can be accounted for the crustal material at the stations that are not under direct influence of the sea. Since the crustal Na is peaking during summer months, a seasonal variation for the Na concentration could not be observed at stations that are not at the immediate vicinity of the sea. Due to the fact that Antalya station is on the coast, sea salt is the dominating source of measured Na concentration.

Geometric mean values of monthly concentrations of elements and ions with anthropogenic sources given in Figure 3.3. The seasonal variation of anthropogenic elements and ions are not as clear as crustal elements. The main reason is the close proximity of crustal sources to sampling stations. Even a small change in the emission strength of these elements could also be observed in the stations. However, anthropogenic elements are transported from distant sources. Therefore, variations in the emissions are smoothed out during transport. Furthermore seasonal patterns observed in concentrations of anthropogenic elements are also strongly affected by seasonal variations in the transport pattern and seasonal variations in precipitation pattern. With so many factors affecting seasonal variations are smoothed out.

Anthropogenic elements and ions show different seasonal trends in different stations and even with opposite seasonal variations in each

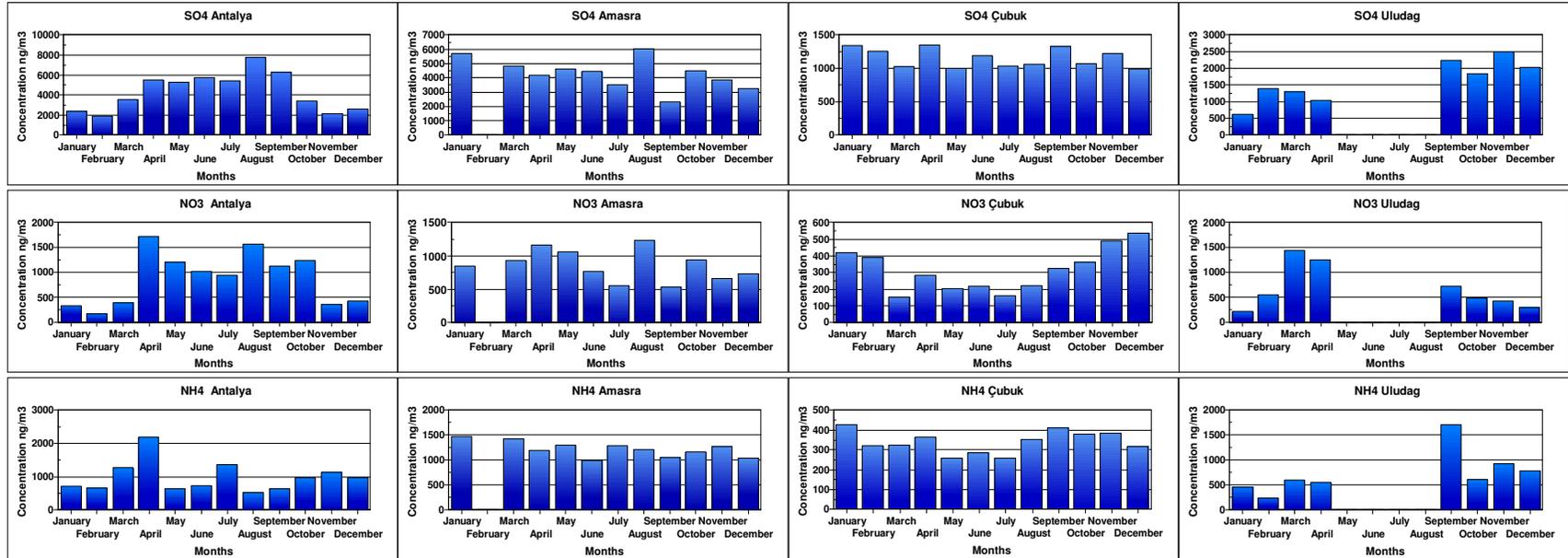


Figure 3.3. Monthly geometric mean concentrations of anthropogenic elements and ions for each station

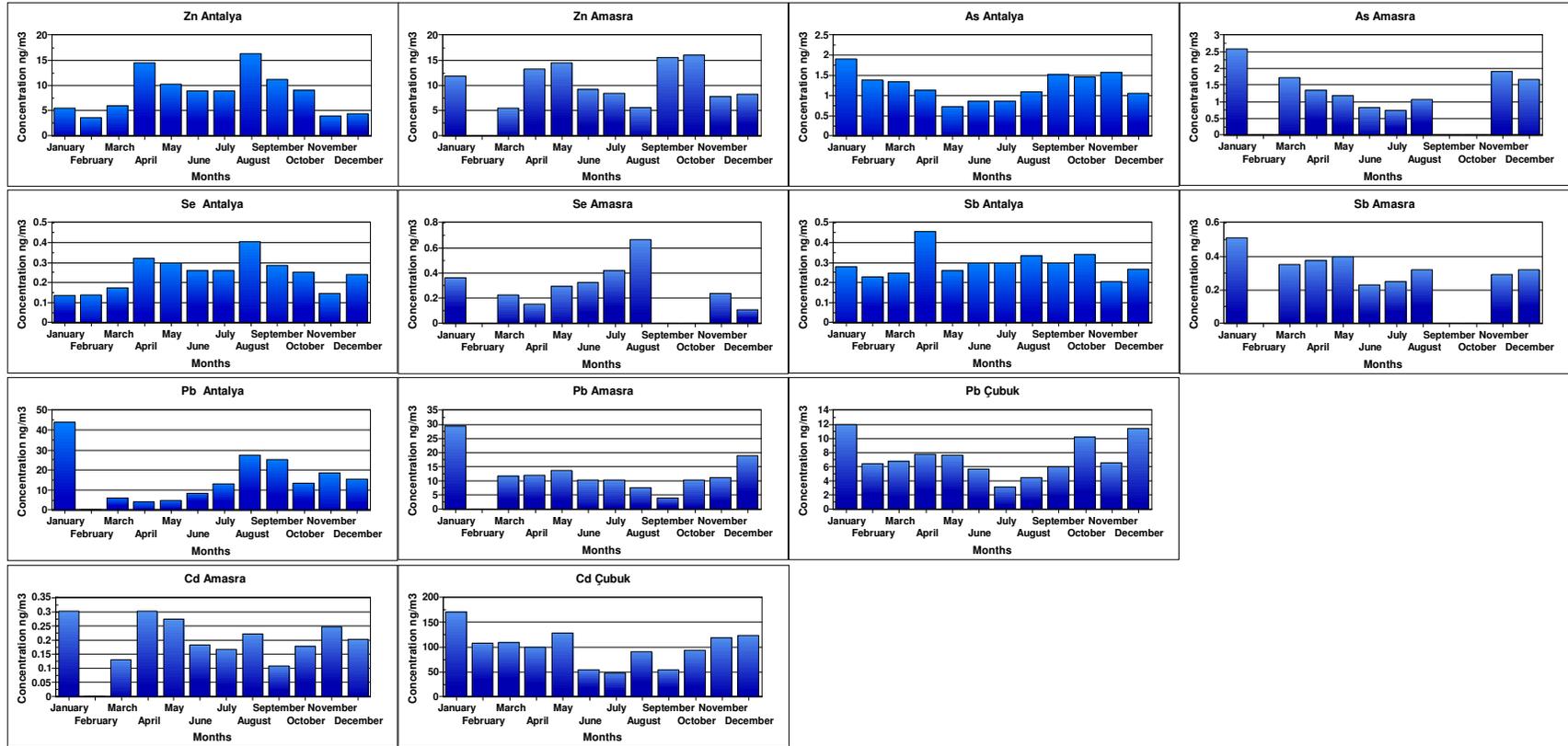


Figure 3.3. Cont'd.

station. If one can understand the mechanism resulting in observed seasonal variations in concentrations of anthropogenic elements substantial information can be obtained about their source. Before the evaluation of the seasonal trends of elements, the general factors that effect the seasonal variations should be well known.

First of all, an element has a local source and its emission is not changing in time, it is expected to have higher concentration during winter months, because mixing height is lower during in winter months than in summer months which confine particles to smaller volume and increase their concentrations.

Secondly, the most distinctive parameter that controls the concentration of elements and ions at the station site is the washing out of the particles from the air with rain. So, pollutants, which are from distant sources, can meet with the rain during their one to five day traveling time and removed from the atmosphere. Since during winter months, more frequent rain events occur in all Europe, concentrations of pollutants at the receptor is expected to be lower during winter months.

Finally, ions, which formed photochemical mechanisms like SO_4^{2-} , NO_3^- and NH_4^+ , are expected to have higher concentrations during summer months due to their higher production as a result of increase of solar flux. Therefore, elements and ions whose concentrations are higher during summer months are either have sources far from the station site so that their transportation time is long and hence their scavenging is efficient or their photochemical production is an important factor on their observed concentrations. On the contrary concentrations of elements that have local sources are expected to be higher in winter or at least comparable in both seasons, because transit time (time between emission and interception point at the station) is short and rain scavenging is less effective.

Zn and Se concentrations in Amasra and Antalya stations are higher in summer and lower in winter months indicating that these two elements are transported from distant sources for both of the stations.

For Sb, there is no significant seasonal variation at Antalya and Amasra stations. However, for As, at both coastal stations, for Cd, at Amasra and Çubuk stations, for Pb at Antalya, Amasra and Çubuk stations, winter concentrations are higher than those observed during summer months.

Sulfate showed a seasonal pattern with higher concentrations in summer only at Antalya station. In all other stations there is not such a significant seasonal variation in SO_4^{2-} concentration. For NO_3^- ion, both in Antalya and Uludağ stations, higher concentrations are observed during summer season whereas in Çubuk station, a SO_4^{2-} maximum was observed in winter period. On the other hand, there is not any seasonal variation for the Black Sea station for NO_3^- . For NH_4^+ , none of the stations shows any seasonal variation.

3.2. Comparison of Background Concentrations

Background concentrations in a region are regionally uniform concentrations of elements that exist in the absence of direct input from immediate emission sources. Information on regional background levels of elements and ions can be important because the difference between background and average concentrations is an indication of pollution input specific to the sampling point.

There are two types of background concentration definitions, global background concentrations and regional background concentrations of species. People have attempted to define and determine global background or baseline concentrations of elements and ions in the last 30 years. Global baseline concentrations of elements and ions (also other pollutants) are theoretical concentrations that are assumed to exist

uniformly around the globe. At each location concentrations characteristic for that region are superimposed on this background levels. A global background level can not be determined experimentally, because wherever you collect your samples, those samples will be influenced by locally generated aerosols. Ice-covered regions in the Antarctic and Arctic, mountaintops, well above the permanent snow level or islands in the middle of Pacific and Atlantic Oceans had been used to understand the composition of background particles.

Regional background concentrations of elements are calculated experimentally assuming that these observed concentrations are uniform for a given region. Regional background levels are interesting because they show the continuous input to the region and also show how much the source types affecting the region.

The difference between the regional background concentration and the geometric mean concentration of the station shows the impact of episodic transport to the station site.

There are different ways of calculating the regional background concentrations of elements. These are:

1. Manually deleting all the peak values of the data set,
2. After fitting a curve to frequency distribution of the data, the maximum point for this curve is defined as the background level,
3. Getting the most frequently occurring value as the background concentration.

In this study the second method is used to get the background concentration of the station sites. In Table 3.3, calculated regional background concentrations of elements and ions are given for Antalya, Amasra, Çubuk and Uludağ stations. In order to compare the baseline

concentrations visually, they are also given in Figure 3.4. The data given in both Table 3.3 and Figure 3.4 shows how much each observed parameter is effected from continuous and episodic inputs to four regions in Turkey investigated in this study.

The comparison of the data set with respect to baseline concentrations for Amasra and Antalya stations are straightforward due to high number of elements measured in these stations. However, it is harder to compare the results for Uludağ and Çubuk stations because of small number of parameters investigated.

For major crustal elements, like Al, Fe and K, the baseline concentrations of elements and ions are comparable to each other for Amasra and Antalya stations. This shows that the soil input for these two coastal stations are not so different from each other. The background concentration of Ca in Antalya is higher since, although the soil input is the same, the soil in Mediterranean region is more calcareous.

The baseline concentrations of some of the soil originated trace elements, for instance Co, Sc, Cs, Sm and Th, are similar for both of the coastal stations. However, trace elements such as Ce, Eu, Lu, Tb and Hf have different background concentration levels. As mentioned previously, this is because of the difference in the soil profiles affecting each region. The difference in the soil profiles does not affect the major elemental concentrations of the regions significantly but, this can effect the trace element compositions. Crustal elements measured in Uludağ and Çubuk stations are K and Ca and their baseline concentrations are lower than those observed in Antalya and Amasra satiations.

The highest background concentrations for marine elements are observed in Antalya station. The minimum background concentration for

Table 3.3. Calculated regional background concentrations of each element and ion (ng/m³)

Elements and Ions	Antalya	Amasra	Çubuk	Uludağ
SO ₄ ²⁻	2400	3150	300	625
NO ₃ ⁻	260	590	73	195
NH ₄ ⁺	112.5	875	88	215
Mg	175	60	20	7.5
K	115	80	37	18
Ca	800	93	80	160
Cl	330	105	-	70
Na	305	185	-	90
V	0.82	1.4	0.45	-
Pb	3.5	5	0.9	-
Al	80	85	-	-
Sc	0.015	0.0175	-	-
Ti	11	7.5	-	-
Cr	0.9	0.35	-	-
Mn	2.4	5.2	-	-
Fe	65	95	-	-
Co	0.045	0.035	-	-
Ni	0.575	0.55	-	-
Zn	3.7	3.75	-	-
As	0.65	0.63	-	-
Se	0.15	0.1	-	-
Br	9.5	5	-	-
Rb	0.27	0.08	-	-
Mo	0.011	0.215	-	-
Cd	-	0.13	17	-
Sb	0.2	0.21	-	-
Cs	0.0325	0.025	-	-
La	0.0525	0.075	-	-
Ce	0.125	0.05	-	-
Sm	0.0075	0.009	-	-
Nd	0.08	0.215	-	-
Eu	0.0015	0.003	-	-
Tb	0.0006	0.006	-	-
Dy	0.012	0.015	-	-
Yb	0.0025	0.0035	-	-
Lu	0.0005	0.0003	-	-
Hf	0.0036	0.0015	-	-
Hg	0.0075	0.021	-	-
Th	0.0125	0.01	-	-
NO ₂	-	-	1150	-
TSP	-	1550	-	7100
HNO ₃	-	-	75	-
NH ₃	-	-	65	-

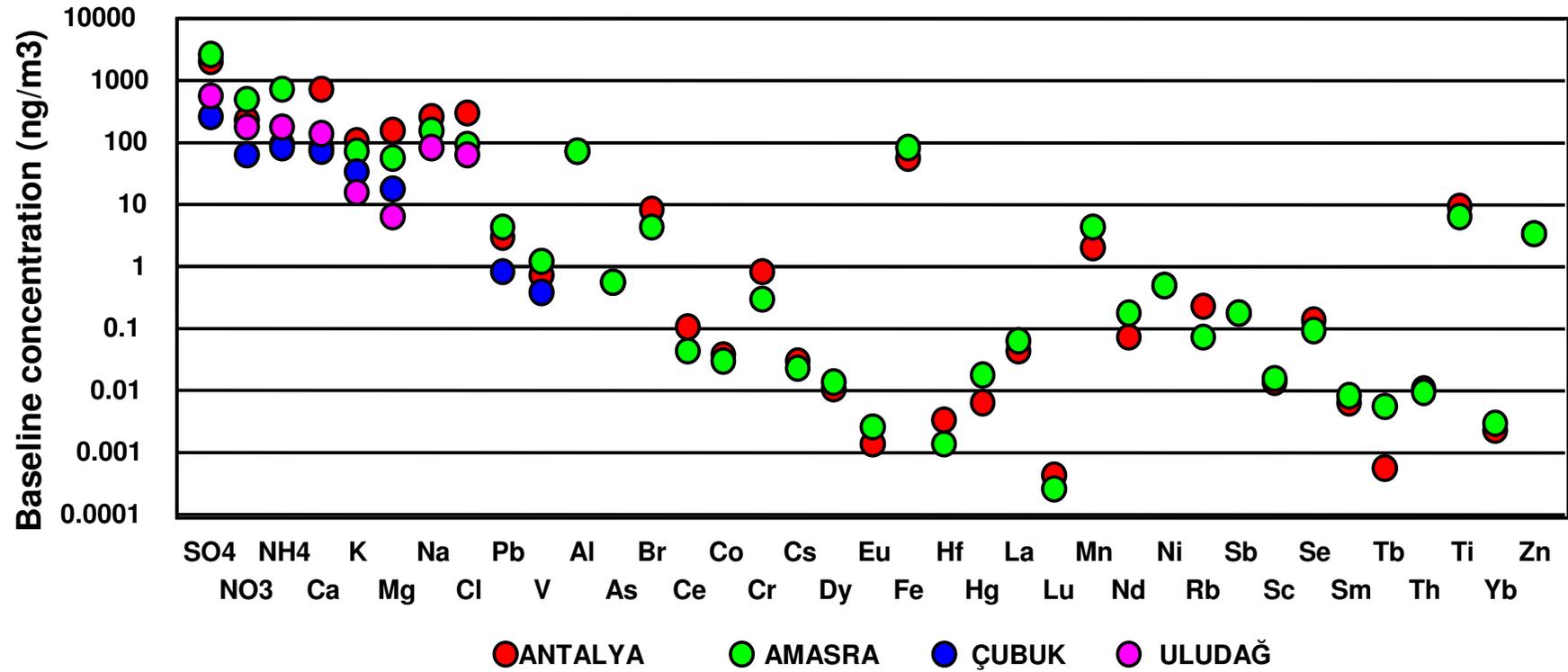


Figure 3.4. Calculated regional background concentrations of elements in each station

this group of element was measured in Çubuk station. This trend is expected; as the station is closer to the sea side, sea salt influence to the station increases. Therefore, since Antalya station is on the coast of Mediterranean sea, the influence of marine environment to the station is the highest for marine elements. Obviously regional uniformity is not valid for the elements that are very strongly affected from local sources.

For anthropogenic elements and ions, like Pb, As, Sb, Zn, SO_4^{2-} and NH_4^+ , there is not any significant difference calculated for the baseline concentrations between two coastal stations. However, Sb in Antalya station and Hg and NO_3^- in Amasra station have higher background concentrations. For Çubuk and Uludağ stations, the baseline concentrations of anthropogenic elements and ions observed as much lower than Amasra and Antalya stations.

The results obtained for anthropogenic elements and ions from the comparison of baseline concentrations of elements and the comparison of geometric mean concentration of elements do not fully confirm each other.

Most of this discussion indicates that expected regional uniformity of regional baseline concentrations is not observed throughout Turkey. There may be some uniformity in smaller scale, but calculated background concentrations are not uniform through the basin. The difference between the geometric mean and the baseline concentrations of the elements shows how the episodes effect the elemental concentrations.

The contributions of episodes to different element groups are given for each station in Table 3.4. For the calculation of episodes, each elements baseline concentration is divided to the elements average concentration, then this ratio is then subtracted form unity and multiplied with hundred to

figure out the effect of the episodes. The values of each element groups in the table are generated by averaging the episode contribution of each group element. If the contributions of episodes are high then the site is said to be affected from local sources. This is because if the source of the element is close to station site, then there will be a strong episodic transport when the air parcels are moving from the source to station site or wind is blowing from the source site. However, if the element is only transported from distant sources, then the episodes become smoother, with smaller maximum values.

Table 3.4. Contribution of episodes on average concentrations of element groups

	Antalya (%)	Amasra (%)	Çubuk (%)	Uludağ (%)
All	75.0 ± 13.4	67.0 ± 17.1	87.3 ± 4.3	82.2 ± 7.7
Crustal	80.5 ± 8.3	78.5 ± 9.8	88.5 ± 1.1	80.9 ± 9.2
Marine	70.0 ± 10.6	58.9 ± 14.5	89.5 ± 0.0	88.5
Anthropogenic	68.8 ± 17.7	54.5 ± 16.2	87.9 ± 4.5	76.8 ± 4.2
Mixed	68.2 ± 10.6	53.4 ± 14.5	80.1	

For Uludağ and Çubuk stations, in general, the contributions of episodes to elemental concentrations are around 80 to 90%. For the coastal stations, the contribution of episodes is around 70%. The observed results showed that Çubuk and Uludağ stations are under stronger influence of local sources more than Amasra and Antalya stations. The effect of local emissions from highly populated settlement areas to observed concentrations of some elements are documented for both Çubuk (Yörük, 2004) and Uludağ (Tuncel et al., 1994). The higher average to background ratio observed at two high altitude stations can be

an indication of higher contribution of relatively local sources on observed concentrations of elements at the Anatolian Plateau. Although contribution of episodic transport to the coastal sites is smaller than that observed to central Anatolian, 65-70% of observed concentrations can be accounted for episodic transport.

When each element group is considered separately, it is observed that crustal elements at Antalya and Amasra regions are more episodic than anthropogenic elements. This is not so surprising since in both of the stations; because most of the crustal aerosols are locally derived at the immediate vicinity of stations and since the elemental concentrations of these elements are strongly related to wind speed, the episodic input should be higher. In these two stations, for marine, anthropogenic and mixed elements and ions episodic inputs to geometric concentrations are 10 to 15% less than observed for crustal elements. This is expected for anthropogenic elements and elements with mixed sources because when although episodes do occur in concentrations of anthropogenic elements, they are not as strong as those observed in concentrations of elements with local sources.

Especially for Antalya station, the contribution of episodes to marine elements is expected to be higher. Because sea salt is a local source and sea salt in the atmosphere, as in the case of crustal elements, depends on wind speed. However, the results in Table 3.4 indicate that, such expected episodic nature is not observed in an annual basis. Time series plots prepared for Amasra and Antalya stations in earlier studies indicate that concentrations of sea salt elements, such as Na and Cl show a highly episodic behavior, but only during winter months. With relatively low wind speed in summer, sea salt generation is at minimum and episodes do not occur. When averaged over the whole year, this

dramatic difference between summer and winter, results is lower than expected average to background ratio.

For Uludağ and Çubuk stations, there is not any significant difference between the different element groups. On the other hand, since the number of elements measured in these stations is low, the differences between the different elemental groups are not so statistically meaningful.

Episodic ratio in elemental basis for each station is given in Figure 3.5. The difference in anthropogenic elements for Antalya and Amasra especially for Hg, NO_3^- and NH_4^+ are clearly observed. For these element and ions the episodicity ratio in Amasra are between 30 and 50% whereas this ratio is around 80-90% for Antalya station. Reason of such kind of high difference is not known very well. However, since the fertilizer use is the main source of NO_3^- and NH_4^+ ions and since fertilizer use in Mediterranean region is higher than that in the Black Sea region, presence of stronger local emissions at the Antalya station can be at least one of the reasons.

The ratio is smaller for Pb and SO_4^{2-} for Antalya and Amasra stations. Sb and As have almost same degree episodic. However, for Se and Zn, the ratio shows that Amasra station is under influence of more local sources which is opposite to general trend. The episodic contribution of SO_4^{2-} , NO_3^- , NH_4^+ and Pb for Uludağ and Çubuk stations are similar to the observed values in Antalya station.

3.3. Comparison of Correlation between Parameters

The correlations between the concentrations of elements provide useful information as it indicates both similarities of sources and relations between elements due to transport. However, binary correlation coefficients themselves, whatever their values, do not always show a valid relation between parameters. Correlation between two parameters

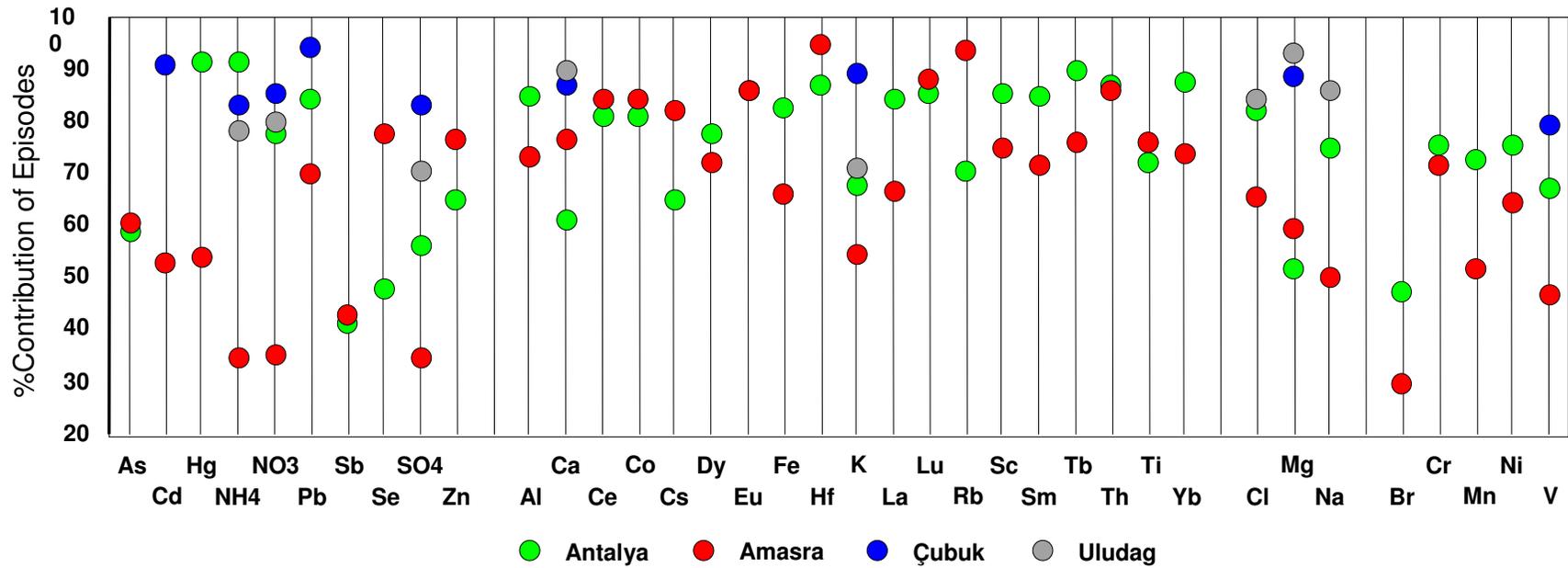


Figure 3.5. Contribution of episodes on average concentrations of elements and ions in each station

can only be statistically significant if “probability of chance correlation” is less than 5% [$P(r, n) < 0.05$]. In this section the term “correlated” means that there is statistically significant correlation between parameters; i.e. [$P(r, n) < 0.05$] and terms “not correlated” or “there is no correlation” means that [$P(r, n) > 0.05$]. The correlations of elements and ions are calculated using Microsoft Office Excel 2003 program.

The correlations of elements and ions for Amasra, Antalya, Çubuk and Uludağ stations are given in Tables 3.5, 3.6, 3.7 and 3.8 respectively. Crustal elements as expected are generally well correlated in all stations.

Bromine correlates well with most of the crustal elements in Amasra station indicating that certain fraction of Br originate from soil. Similar correlations of Br with crustal elements are not observed in Antalya station. Sea salt in Antalya is a dominating component in aerosol; consequently, sea salt Br can easily mask any Br originating from soil.

Crustal elements in Antalya station correlate with Pb. It can be concluded as Pb observed in Amasra is originating from long range transport, whereas Pb in Antalya has a greater local component, due to the close proximity of the road that connects Antalya to Finike to our station. This road holds a heavy traffic load in summer season. Therefore, a well documented road dust, which is soil enriched in motor vehicle emissions, is a component in the Antalya station. In Amasra the station is approximately 2 km away from any road, and the road that connects Amasra to Kurucaşile is nowhere as crowded as the road passing by the Antalya station. It can be concluded that Pb observed in Amasra is originating from long range transport, whereas Pb in Antalya has greater local component, but it should be noted that road dust is not the only source of Pb in Antalya as will be discussed later in the manuscript.

Table 3.5. Correlations between measured parameters in Antalya station.

(Only statistically significant ($[P(r,n)<0.05]$) correlations are shown)

	Ca	Al	Sc	Ti	Fe	Co	La	Ce	Sm	Eu	Tb	Dy	Yb	Lu	Hf	Th	V	Cr	Mn	Ni	Br	
Ca	Ca	0.39			0.45						0.41						0.34	0.45	0.54	0.40		
Al		Al	0.91	0.96	0.92	0.48	0.77	0.89	0.89	0.90	0.83	0.92	0.87	0.90	0.82	0.90	0.58	0.40	0.95	0.45		
Sc			Sc	0.90	0.99	0.60	0.78	0.99	0.98	0.99	0.93	0.91	0.97	0.99	0.92	0.98	0.71	0.41	0.86	0.49		
Ti				Ti	0.88	0.58	0.75	0.88	0.88	0.90	0.82	0.93	0.86	0.89	0.81	0.89	0.72	0.34	0.91			
Fe					Fe	0.61	0.74	0.99	0.98	0.98	0.93	0.90	0.97	0.99	0.92	0.98	0.58	0.45	0.84	0.53		
Co						Co	0.55	0.60	0.60	0.68	0.61	0.61	0.70	0.68	0.71	0.69	0.46		0.44		0.63	
La							La	0.76	0.77	0.74	0.63	0.68	0.73	0.75	0.73	0.80	0.61	0.31	0.75	0.43		
Ce								Ce	0.98	0.99	0.93	0.90	0.97	0.98	0.93	0.98	0.68	0.40	0.82	0.42		
Sm									Sm	0.97	0.92	0.91	0.95	0.97	0.89	0.96	0.67	0.39	0.81	0.39		
Eu										Eu	0.95	0.92	0.98	0.99	0.92	0.98	0.68	0.41	0.83	0.38		
Tb											Tb	0.84	0.94	0.92	0.86	0.93	0.64	0.34	0.77	0.59		
Dy												Dy	0.88	0.92	0.83	0.89	0.66	0.38	0.85			
Yb													Yb	0.99	0.94	0.97	0.69	0.40	0.82			
Lu														Lu	0.94	0.98	0.70	0.42	0.84	0.68		
Hf															Hf	0.93	0.65	0.41	0.77	0.52		
Th																Th	0.70	0.42	0.86	0.52		
V																	V	0.34	0.80	0.51		
Cr																		Cr	0.39	0.55		
Mn																			Mn	0.38		
Ni																				Ni		
Br																						Br

Table 3.5. Cont'd.

	K	Mg	Na	Cl	SO ₄	NO ₃	NH ₄	Zn	As	Se	Sb	Hg	Pb	Mo
Ca	0.30	0.42				0.31		0.31				0.45		
Al	0.59	0.57				0.33								
Sc	0.64	0.48				0.34				0.33	0.30		0.49	
Ti	0.62	0.67											0.71	
Fe	0.59	0.52				0.35		0.36		0.35	0.33			
Co	0.56	0.64	0.36	0.36									0.45	
La	0.56	0.51				0.32							0.45	
Ce	0.62	0.48				0.31		0.30		0.32			0.41	
Sm	0.60	0.50				0.30				0.32			0.50	
Eu	0.63	0.52				0.30				0.36			0.54	
Tb	0.59	0.51				0.28				0.39			0.43	
Dy	0.56	0.64												
Yb	0.61	0.53				0.33		0.32		0.40			0.47	
Lu	0.63	0.53				0.33		0.32		0.39			0.55	
Hf	0.58	0.52				0.30				0.35			0.59	
Th	0.64	0.51				0.33		0.32		0.34			0.50	
V	0.48	0.39			0.53	0.59		0.56		0.58				
Cr								0.30						
Mn	0.66	0.49				0.44		0.40		0.34			0.40	
Ni	0.30				0.55	0.40		0.45	0.47	0.37	0.41			
Br		0.66	0.75	0.78										0.39
	K	0.43				0.34		0.31						
		Mg	0.72	0.58										
			Na	0.87										0.31
				Cl										0.35
					SO₄	0.63	0.38	0.60		0.57				
						NO₃	0.17	0.60		0.61				
							NH₄	0.58		0.55				
								Zn		0.67	0.33		0.45	
									As		0.49		0.51	
										Se			0.45	
											Sb		0.63	
												Hg		
													Pb	
														Mo

Table 3.6. Correlations between measured parameters in Amasra station.

(Only statistically significant ($[P(r,n)<0.05]$) correlations are shown)

	Ca	Al	Sc	Ti	Fe	Co	La	Ce	Sm	Eu	Tb	Dy	Yb	Th	V	Cr	Mn	Ni	Br
Ca	Ca	0.82	0.81	0.75	0.77	0.4	0.8	0.81	0.8	0.82	0.38	0.73	0.81	0.74		0.4	0.56	0.41	0.36
Al		Al	0.97	0.91	0.93	0.46	0.95	0.93	0.95	0.87	0.39	0.82	0.9	0.86	0.33	0.5	0.77	0.41	0.46
Sc			Sc	0.91	0.96	0.5	0.99	0.97	0.99	0.92	0.42	0.89	0.95	0.92	0.33	0.51	0.75	0.49	0.43
Ti				Ti	0.89	0.53	0.91	0.9	0.91	0.87	0.86	0.86	0.91	0.85	0.33	0.58	0.71	0.5	0.5
Fe					Fe	0.47	0.95	0.94	0.95	0.91	0.39	0.86	0.93	0.88	0.43	0.55	0.8	0.53	0.47
Co						Co	0.49	0.5	0.49	0.79	0.4	0.47	0.6	0.61	0.32		0.34	0.34	0.32
La							La	0.98	1	0.92	0.41	0.9	0.96	0.92	0.34	0.49	0.74	0.47	0.44
Ce								Ce	0.98	0.92	0.86	0.89	0.96	0.92	0.34	0.49	0.7	0.49	0.42
Sm									Sm	0.92	0.42	0.9	0.96	0.92	0.32	0.48	0.73	0.45	0.42
Eu										Eu	1	0.95	0.93	0.91	0.9	0.76	0.84	0.85	0.58
Tb											Tb	0.99	0.43	0.86	0.41	0.46	0.41		0.42
Dy												Dy	0.88	0.89	0.43	0.6	0.74	0.69	0.41
Yb													Yb	0.94	0.4	0.52	0.7	0.55	0.5
Th														Th	0.34	0.45	0.7	0.54	0.4
V															V	0.42	0.51	0.67	0.48
Cr																Cr	0.49	0.49	0.51
Mn																	Mn	0.45	0.39
Ni																		Ni	0.47
Br																			Br

Table 3.6. Cont'd.

	K	Mg	Na	Cl	SO ₄	NO ₃	NH ₄	Zn	As	Se	Cd	Sb	Hg	Pb	Mo	SPM
Ca	0.44	0.85				0.39										0.40
Al	0.48	0.85				0.42										0.40
Sc	0.85	0.79		0.30		0.51										0.39
Ti	0.81	0.75	0.35	0.40		0.51										0.39
Fe	0.49	0.77				0.47										0.36
Co	0.42	0.38								0.35						
La	0.84	0.77		0.32		0.51										0.38
Ce	0.82	0.75	0.31	0.33		0.48										0.33
Sm	0.84	0.76		0.31		0.49										0.37
Eu	0.83	0.74	0.80	0.75		0.78		0.33	0.45	0.34	0.68					0.78
Tb	0.42	0.45	0.77		0.33	0.32			0.68		0.30			0.33		
Dy	0.84	0.65	0.37	0.42		0.55										0.57
Yb	0.83	0.74	0.43	0.47		0.54										0.31
Th	0.80	0.66	0.42	0.45		0.54				0.34						0.38
V					0.50	0.44	0.40	0.47	0.62		0.39	0.47		0.52		
Cr		0.51						0.30	0.36			0.30		0.42		0.36
Mn	0.71	0.62			0.30	0.53		0.36		0.38	0.34					0.37
Ni	0.36	0.33			0.30	0.45		0.32	0.51		0.40	0.37		0.42		
Br	0.48	0.55	0.56	0.52		0.60			0.46		0.38			0.40		
	K	0.36	0.31			0.32										
		Mg	0.43	0.32		0.48										0.37
			Na	0.77		0.49										
				Cl		0.50										
					SO₄	0.32	0.67		0.42	0.35	0.45	0.31		0.39		
						NO₃			0.33							0.41
							NH₄	0.30	0.41	0.30	0.48	0.34		0.49		
								Zn			0.38			0.42		
									As		0.64	0.46		0.58		
										Se						
											Cd	0.47		0.54		0.35
												Sb	0.27	0.35		
													Hg			
														Pb		
															Mo	
																SPM

Table 3.7. Correlations between measured parameters in Çubuk station.
(Only statistically significant ($[P(r,n)<0.05]$) correlations are shown)

	Mg	K	Ca	V	SO ₄	NO ₃	NH ₄	Pb	Cd	NO ₂	HNO ₃	NH ₃
Mg	Mg	0.58	0.70	0.34							0.34	0.30
K		K	0.46									
Ca			Ca	0.33							0.40	0.30
V				V								
SO ₄					SO ₄	0.50	0.83			0.30	0.39	
NO ₃						NO ₃	0.56	0.30		0.43		
NH ₄							NH ₄			0.35	0.42	
Pb								Pb				
Cd									Cd			
NO ₂										NO ₂		
HNO ₃											HNO ₃	0.40
NH ₃												NH ₃

Table 3.8. Correlations between measured parameters in Uludağ station.
(Only statistically significant ($[P(r,n)<0.05]$) correlations are shown)

	Mg	K	Ca	SO ₄	NO ₃	NH ₄	Cl	Na
Mg	Mg	0.31	0.56					0.91
K		K		0.48		0.44		
Ca			Ca					
SO ₄				SO ₄		0.43	0.52	
NO ₃					NO ₃			
NH ₄						NH ₄		
Cl							Cl	
Na								Na

Similarly, in Antalya station crustal elements correlates also with Zn but comparable correlation is not observed in Amasra station. Some portion of Zn can be due to traffic (Adachi and Tainosho, 2004). Therefore, some portion of Zn in Antalya, as in the case of Pb, can be due to road dust. However, in Amasra, both Zn and Pb are due transport from distant sources to the region. Nevertheless, in both of the stations there are similar correlations between Zn and Pb. Studies performed in urban atmosphere have demonstrated that a small fraction of Zn can originate from traffic, due to engine year. However, traffic is not the main source of Zn even in urban areas, where traffic activity is very high. Consequently, observed correlation between Pb and Zn in both Antalya and Amasra stations should be transport generated, due to mixing of emissions during several day long transport. This issue will be discussed in details in PMF section.

In both of the coastal stations, sea salt elements Na and Cl do correlate well, as expected. Also, for these two stations Na and Cl correlate well with Mg and Br. This observation is also expected, because sea water concentration of Mg and Br are fairly high (Güllü et al., 1998; Qin and Oduyemi, 2003) and these two elements are important components of sea salt aerosols. Concentrations of Na and Cl are also correlated with K and Ca due to same reason in Amasra and Çubuk stations. In Antalya, there is no correlation between Na and Cl with K and Ca, as soil source of K and Ca is dominating over the region. Sodium and chloride is not measured at Çubuk station.

An interesting point in Amasra station is that Na and Cl show good correlation with the majority of crustal elements. This is due to the fact that Amasra station is 3 km away from the coast and sea salt does not have dominating effect at the station site due to scavenging of particles within that 3 km. Consequently, significant part of the Na and Cl are from

soil. For Antalya station, there is not significant correlation between Na and Cl with the crustal elements. Antalya station is on the coast and because of this contribution of crustal material on Na and Cl concentration is negligible.

Anthropogenic elements and ions in both stations are generally correlates with each other. However, there are some noticeable similarities and differences between these correlations.

Sulfate concentrations at both Amasra and Antalya stations generally correlate with secondary ions, NO_3^- and NH_4^+ , with elements that have mixed sources, such as, V, Ni, Mn and with purely anthropogenic elements. However, this general pattern is modified for selected element at each station. The only exception to this general trend is the Zn; SO_4^{2-} is not correlated with Zn at Antalya station. At Antalya station SO_4^{2-} is also not correlated with As, Sb and Pb. Sulfate is generally considered as specie that reaches to station as a result of long range transport. Its correlation with other elements can be an indication of distant sources of other elements. This relation will be discussed in more detail in subsequent sections where results of PMF analysis are presented. The lack of correlation between SO_4^{2-} and As, Sb and Pb in Antalya station is an indication that concentrations of these three elements can be accounted for by local sources. This conclusion is also supported by PMF analysis.

NO_3^- ion in both coastal stations also shows interesting correlations. In both of the coastal stations, NO_3^- correlates with SO_4^{2-} and Se, which is also reported in other studies in literature (Raymond et al., 2004).

The interesting point is that NO_3^- show a relationship with crustal and marine elements as well. In Black Sea station, NO_3^- correlates with all marine and crustal elements. In Mediterranean station, although NO_3^-

correlates with soil originated elements; it does not show correlation with marine elements like Na and Cl. Normally, NO_3^- is expected to correlate with SO_4^{2-} and NH_4^+ which are also secondary pollutants. However, the relation between SO_4^{2-} and crustal and marine elements arise from following two reactions that occurs on the surfaces of soil and sea salt particles:



Although association of NO_3^- with sea salt is frequently reported in the literature (Pakkanen, 1996; Wu and Okada, 1994; Solomon et al., 1992; Poor et al., 2001; Yeatman et al., 2001), its association with soil particles and the occurrence of the second reaction is not as common and reported in only few publications (Pakkanen et al., 1996; Wolff, 1984). The correlation of NO_3^- with soil originated elements in both coastal stations confirms that there is a secondary NO_3^- over the regions and NO_3^- accumulates on the surfaces of the crustal aerosols. Size separated aerosol samples collected by cascade impactors at Antalya station showed that NO_3^- is associated with coarse crustal particles and does not related marine aerosols (Kuloğlu, 1997). Although Antalya station is on the coast and aerosol is dominated by sea salt, there is no correlation observed between NO_3^- and marine aerosols. Although the reason for observed lack of relation between NO_3^- and marine elements at Antalya station is not very clear, one reason may be freshness of the marine aerosol reaching the station. Since the station is on the coast collected sea salt aerosol is generated at the immediate vicinity of the station and mostly consists of large particles. There may not be enough time between generation of particles and their interception at the station for the reaction 1 to convert gas-phase HNO_3 into particle bound NaNO_3 . However, at the Amasra station, there is some time between particle

generation and their subsequent transport to the station, which is approximately 3 km from the coast. The short time (approximately 30 minutes to 90 minutes) may be enough for the reaction to generate NaNO_3 on the surface of sampled sea salt particles.

At Amasra station, except for Se, all anthropogenic elements are correlated with each other. This is typical for long range transport. When the air masses are transported from distant sources, the pollutants mixed well and, whatever the sources, they show correlation with each other. This feature can also be used to discriminate anthropogenic elements that can potentially have local sources, as they will not be correlated with the long-range transported group. These type of correlations or lack of correlations between elements only provide preliminary information and the conclusions reached can not be conclusive, because generally different sources contribute observed concentration of a given element. The correlation coefficients obtained in a simple correlation analysis gives an overall picture and use of more sophisticated statistical tools are necessary to differentiate between different sources. When different sources equally contribute to the concentration of a given element, the element may not correlate with marker elements for either of the sources. The conclusions derived in this section should be viewed with this point in mind. In Antalya station the situation is slightly different than that observed at Amasra station. In the Mediterranean aerosol, anthropogenic elements can be divided into two groups depending on the correlations. Sulfate, NO_3^- , NH_4^+ , Zn and Se make up the first group, as they correlate with each other. The second group of anthropogenic elements are Pb, As and Sb. This group also shows correlation with each other and they do not show any relationship with the first group of pollutants. This shows that Mediterranean aerosols composed of two anthropogenic groups, however, for the Black Sea aerosols, such differentiation is not possible from correlation coefficients alone.

One interesting point with the correlations of anthropogenic elements is that some of these elements correlate with crustal elements. For Antalya station, Se, Zn and Pb correlate with crustal elements. The correlations of Pb and Zn with crustal elements are discussed previously and explained as some portion of these elements are from road dust. Other than these two elements Se, in both stations, correlates with crustal elements, especially with rare earths. The reason of such correlation is unknown, but such correlations are observed regularly.

Vanadium, chromium, manganese and nickel, correlate both anthropogenic and crustal elements in both coastal stations. This observation is not surprising, because these elements have anthropogenic sources, and also their concentrations are high in the crustal material.

In Uludağ and Çubuk stations, since the number of parameters is restricted, an extensive comparison of the correlation is difficult and conclusions reached are uncertain.

Crustal elements, Mg, Ca, K and V, in Çubuk station correlates with each other. Major secondary ions also correlate with each other. Besides, these ions do correlate well with gaseous phased pollutants, NO_2 , HNO_3 and SO_2 , in the atmosphere. Observed correlation between major ions, SO_4^{2-} and NO_3^- and gaseous pollutants should be expected, because these gaseous pollutants, namely SO_2 , HNO_3 and NO_2 are precursors of SO_4^{2-} and NO_3^- . When there is high concentration of, say, SO_2 in an air mass it is very likely that there will also be high concentration of SO_4^{2-} ion.

The discussion of correlations between elements at each station indicates that there are similarities as well as differences between stations. Crustal elements correlates with each other in all stations,

indicating a common soil source in aerosols sampled at different parts of Turkey. The correlation between marine elements are not the same at all stations, they are correlated with each other indicating a common marine source at all stations (this assessment is not valid for Çubuk station, because Na and Cl, which are marker elements to differentiate sea salt aerosol are not measured in this station). However, in the Black Sea data, Na and Cl are also correlated with crustal elements, indicating the marine component in the Black Sea aerosol population is not as overwhelming as in the Mediterranean aerosol population.

Binary correlations between anthropogenic elements depicted different patterns in different stations. They indicated a local and a long-range transported components in the Mediterranean at Antalya aerosol population, correlations in Black Sea data set, on the other hand, indicated one unique anthropogenic component. It should be noted that these conclusions are based on binary correlations alone.

Multivariate statistics, which will be discussed later in the manuscript revealed six different anthropogenic components in the Black Sea aerosol population, clearly demonstrating that, conclusions based on binary correlation coefficients are only preliminary in nature.

Parameters measured at Çubuk and Uludağ stations, were too few to discuss anthropogenic components at Central Anatolia using correlation coefficients.

Even though Pb and Cd are anthropogenic elements, they do not show statistically significant correlation with other pollutants. The reason of such behavior is not so clear.

In Uludağ station, crustal elements do correlate well with each other. However, since there is only anthropogenic ion measurements, yielding a result will not be so correct.

3.4. Comparison of Flow Climatology of Stations

One of the important reasons for observing differences in the aerosol compositions between the stations is the differences in flow climatology of the regions. Air climatology can be described as the percent contribution of upper atmospheric air flow from each wind direction sectors to the receptor sites. If the stations have completely different flow climatology, then it is expected that the pollutants in these air masses are different from each other. On the other hand, stations located few hundred kilometers from each other are likely to be affected from similar wind sectors and therefore the observed aerosol compositions are expected to be similar. Consequently, the flow climatology of the regions should be well known to be able to discuss similarities and differences in sources and source regions affecting composition of particles in different stations.

Flow climatology of Mediterranean, Black Sea and Central Anatolia are calculated. Flow climatologies of these three sites were calculated using isentropic, 5.5 day long backtrajectories which were computed using ECMWF model. One backtrajectory was calculated for every day in which an aerosol sample is collected. Starting point of the backtrajectory was the mid-point of the sampling duration. In this way a second data set composed of backtrajectories were created for the each measurement day for each station.

The most common approach used to calculate flow climatology for a given site involves visual inspection of trajectories to assign them to one of the wind sectors (Katsoulis, 1999). Although, this method is widely used, it has some disadvantages. The calculated backtrajectories are rarely derived from a single wind sector and reach to the receptor site. Most of them arrive to receptor point after spending some time in more than one wind sectors within 5.5 days. Assigning such trajectories to a

certain sector as if they spend all of their time in that sector can produce incorrect results in both flow climatology analysis and also in the site determining location of emission sources affecting the site.

In this study, in order to avoid the problem stated above, back trajectories are divided into hourly segments. A total of 132 segments, with known coordinates, were obtained from each 5.5 day-long backtrajectory and percent contribution of each sector on the flow pattern at the receptor is calculated by counting trajectory segments in each sector, using GIS software. The total number of the segments in each wind sector shows the time that air masses spent in that sector during the sampling period. Since the sampling period of each station is different, in order to compare the results, the calculated air masses are presented as percents of total air mass residence time.

The back trajectories calculated for each sampling day includes three different trajectories with different starting altitudes of 900 mb (950 m), 850 mb (1400 m) and 700 mb (2960 m). Since all of the three trajectories are included in flow climatology calculations, calculated flow pattern at each station represents altitudes between 900 – 700 mb, where the long-range transport of pollutants are expected to occur.

Flow climatologies for Çubuk, Amasra and Antalya stations are given in Figure 3.6 as trajectory roses. As seen from the figure, the flow patterns are generally similar in all three stations. However, there are some differences in details.

In all of three stations, most frequent, flows are from W, WNW, NW and NNW sectors. These four sectors accounts for approximately 46% of total flow at the Central Anatolia and 50% of total flow at Mediterranean and Black sea regions. This pattern indicates that pollution sources located in

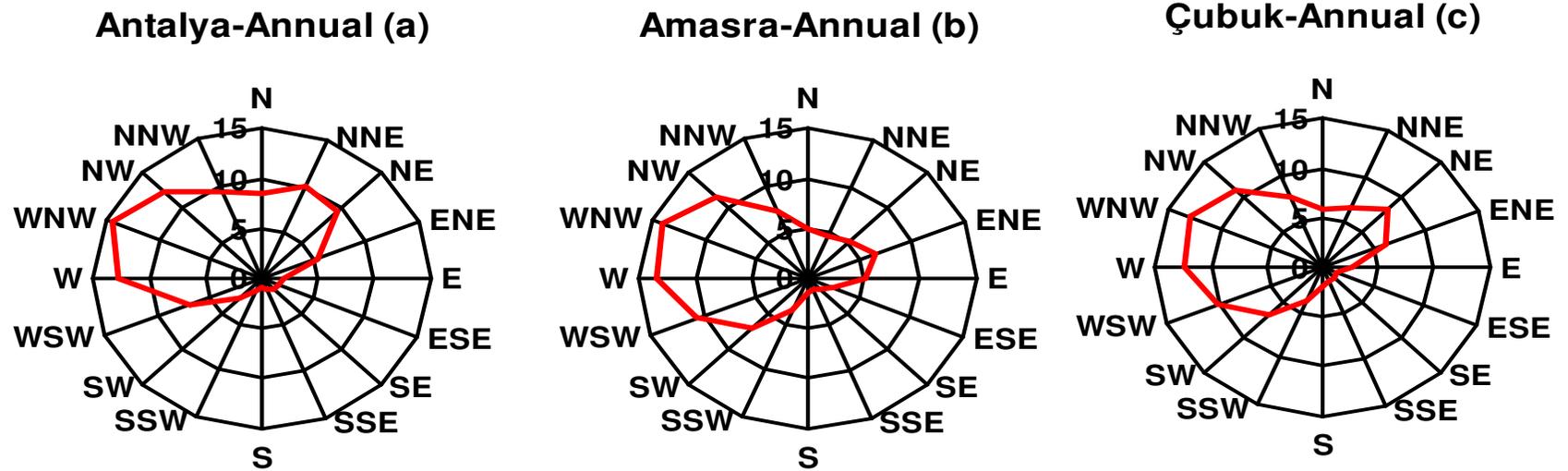


Figure 3.6. Flow climatologies of Antalya (a), Amasra (b) and Çubuk (c) stations as trajectory roses

these four sectors are more influential in determining composition of particles in the Mediterranean, Black Sea and Central Anatolia regions.

Countries located in each wind sector are depicted in Figure 3.7 for each receptor region. The sectors stated above include almost all parts of Europe. High emission regions in Spain for Mediterranean station and both in Spain and in Italy for Central Anatolia and Black Sea stations are outside the four wind sectors from which the transport is the most frequent. However, almost all parts of Ukraine are in the W and NNW sectors for Central Anatolia and Black Sea stations. But for Mediterranean station, only a small part of Ukraine takes place in these four sectors. Black sea and Central Anatolia regions are affected less from emission in Italy and Spain compared to their impact on the Mediterranean region. The influence of Eastern European countries, like Ukraine and Belarus, to the Black Sea and Central Anatolia regions is higher than their effect on Eastern Mediterranean region. Furthermore, since sources in Turkey are closer to stations, their impacts on aerosol composition are expected to be higher than the impact of sources that are away. High flow frequency wind sectors include all western part of Turkey for Antalya station whereas for the other two stations, these sectors include a small portion of Turkey. As western Turkey contains important emission sources such as İstanbul area, İzmir area and thermal power plants at Soma and Kütahya, its effect to Antalya region is expected to be higher than other two stations. Even though the flow diagrams of the stations look like similar and contributions of wind sectors W-NNW are approximately similar, the source regions affecting each region are not completely identical because regions in similar wind directions are not the same. For example, Aegean coast which is an important source region lies in the W and NW sectors for Antalya, WSW and SW sectors for Çubuk and SW to SSW sectors for Amasra stations. Since flow is more frequent from W and WNW sectors compared to SW

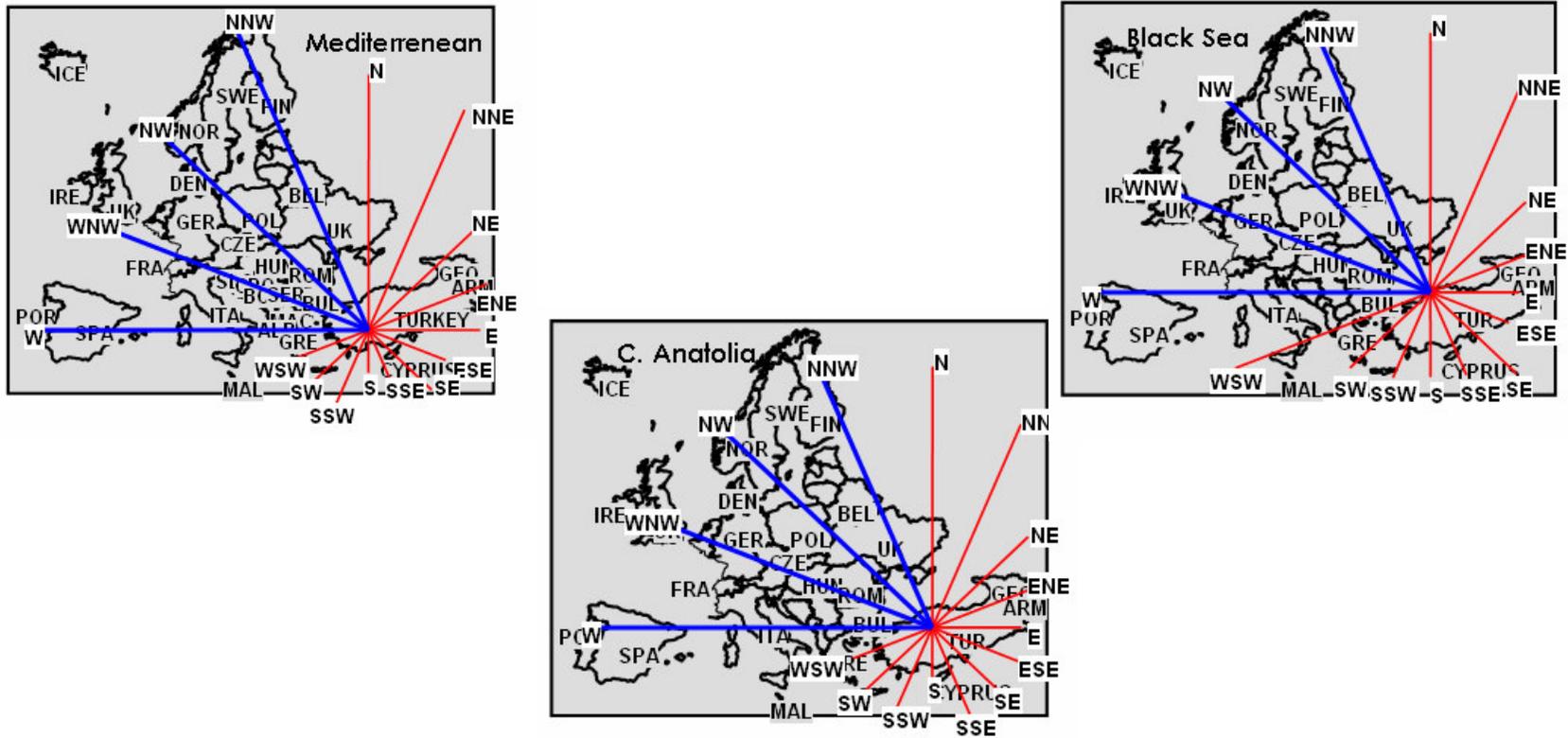


Figure 3.7. Countries in each wind sector

and SSW sectors, although the flow patterns are pretty similar in all three stations, impact of sources in the Aegean coast on the Mediterranean region will be more pronounced compared to the impact of the same sources on Central Anatolia and Black Sea.

In all three stations, the contribution of sectors SSW, S, SSE, SE, SSE to the total flow are fairly lower than the other sectors. The total flow contributions of these five sectors to each station are 6%, 9% and 8% for Mediterranean, Black Sea and Central Anatolia, respectively.

The residence times of air masses in the WSW and SW wind sectors show some differences between stations. The contribution of the sum of these two sectors to the total flow is around 13% for Black Sea and Central Anatolia regions and 6% for Mediterranean region. These sectors cover western part of Turkey and countries like Greece and Italy. As discussed previously, for the W and NNW sectors, it was concluded as the emissions from these sectors do not have much contribution to Central Anatolia and Black Sea regions, but, since flow frequency from sectors WSW and SW accounts for approximately 13-14% of total flow, sources at the western part of Turkey such as İzmir, Greece and Italy is expected to have at least a minor impact on aerosol characteristics in these regions.

North, NNE, NE and ENE sectors are important because the area covers Russia and the countries that are in located in the western of Russia. This region includes important emission sources. The contributions of these sectors to the stations are 20 %, 27% and 36 % for Black Sea, Central Anatolia and Mediterranean regions, respectively. These contributions are relatively high and they indicate that the emissions form sources of Russia are expected to effect the aerosol compositions of all three regions. The air masses reaching to the Mediterranean region from N, NNE, NE and ENE pass through eastern and central parts of Turkey

and consequently, carries the pollutants emitted from these regions as well as emissions from further north. Northerly flow intercepted at Amasra and Çubuk stations, on the other hand, do not include emissions from northern and eastern parts of Turkey.

As discussed previously, some of the measured species show seasonal variation whereas some do not. This was explained with the seasonal variation in wet scavenging. In addition, the seasonal variations in the calculated flow frequencies may also contribute to the observed seasonal variation of the concentrations of elements and ions. For this reason, seasonal variation of the flow climatology of each region should be evaluated. The flow climatology of each station calculated for summer and winter seasons are represented in Figure 3.8. Months from May to October are considered as summer season and the rest of the months are assumed to make up winter season. Such a division was based on distribution of rain in Antalya station. The winter season was considered as the period in which 80% of total precipitation to the Mediterranean region occurs. Even though the precipitation regime is different in each station, to be able to compare the results, same periods were used for all of the three stations.

In all of the stations, the flow climatology show variations between summer and winter seasons. This difference is significantly high for Central Anatolia and Black Sea stations, but smaller at the Mediterranean station. For Amasra and Çubuk stations, transport from SW, W, W and WNW sectors are considerably higher in winter than in summer. On the contrary, air mass flow frequency from NW, NNW, N, NNE, NE and ENE sectors are higher in summer season. For Mediterranean region, although the difference is not as high, when compared with other two stations, transport from W, WNW and NW sectors are higher in winter months. In contrast, there are significant differences between the

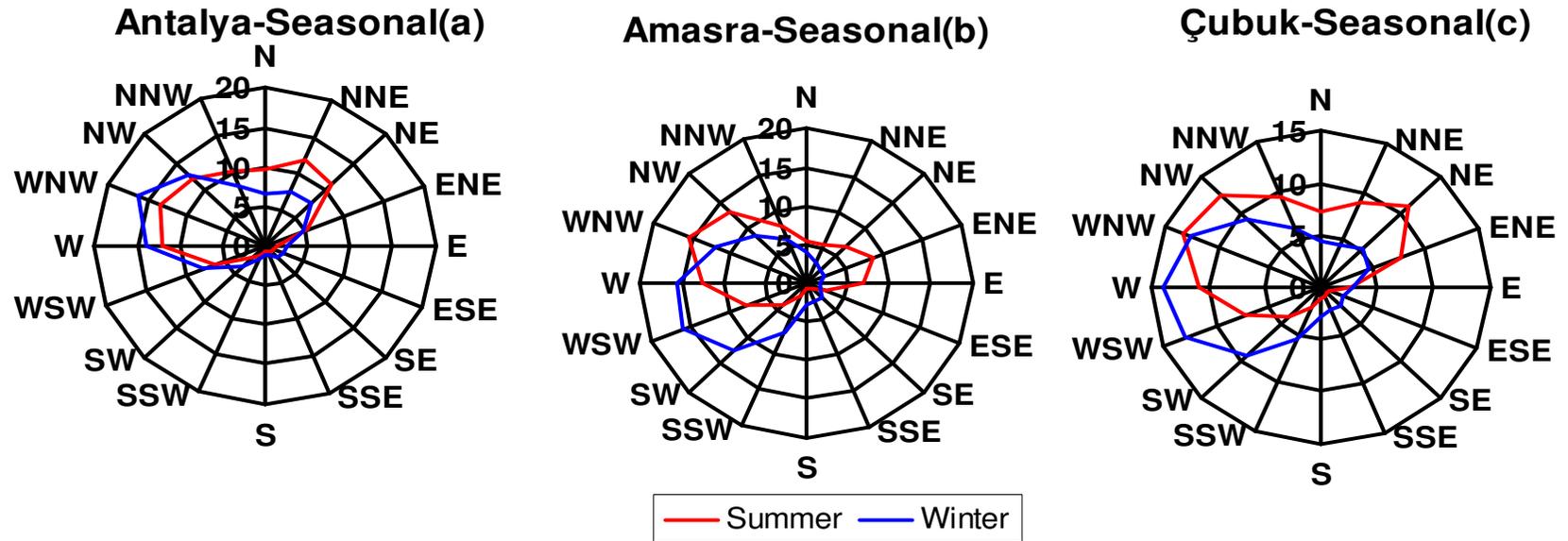


Figure 3.8. Seasonal variations in flow climatologies of Antalya (a), Amasra (b) and Çubuk (c) stations as trajectory roses

transport from N, NNE, NE and ENE sectors which are high in summer season.

The differences in the flow frequencies between summer and winter may create serious implications in terms of pollutant transport to the regions. This is depicted in Figure 3.9. For this station, NW sector divides Europe into two parts, namely Western and Eastern Europe. The region under the NW sector line composed of mostly with countries in Western Europe. The region above this line is constituted of mainly Ex-Russia countries.

Thus, it can be concluded as for Central Anatolia and Black Sea regions, Western Europe has higher input during winter months whereas Eastern Europe has higher contribution during summer season. For Antalya station, this difference is not as significant.

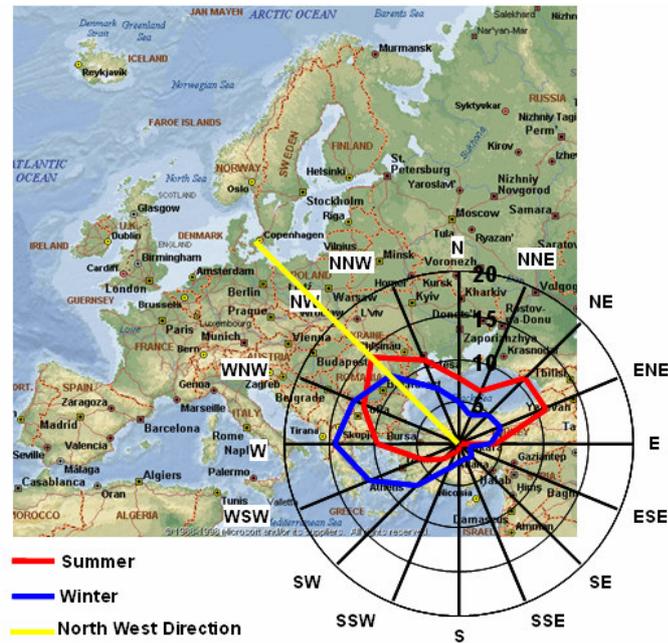


Figure 3.9. Seasonal contributions of eastern and western European countries to the seasonal variation of flow climatology in Çubuk.

The effect of different transport patterns between summer and winter seasons were investigated using $\text{SO}_4^{2-} / \text{NO}_3^-$ as a tracer. Sulfate-to-nitrate ratio is used as a tracer to differentiate between transport from eastern and western European countries, because $\text{SO}_4^{2-} / \text{NO}_3^-$ ratio differs significantly in air masses arriving from western and eastern European countries. The ratio is different due to different levels of SO_2 emission control applied in the western European and Eastern European (former USSR) countries. In Europe, SO_2 control was started in 1985 by ratification of Sulfur protocol by western European countries. After this year, SO_2 emissions from Western Europe started to decrease and as a consequence of this reduction in emissions, SO_4^{2-} concentrations in the Western Europe atmosphere decreased by 70% in last 10 years. This decrease in SO_4^{2-} concentrations in western part of Europe is depicted in Figure 3.10, where variation of SO_4^{2-} concentrations in selected EMEP stations located in the Western Europe are plotted between 1978 and 2000.

However, the situation in former USSR countries (Eastern European countries) is different. During USSR era, there were limited controls on SO_2 emissions in these countries. They also could not invest on SO_2 control technologies, after they became independent states, owing to poor economical slate they were in. Due to these developments, the decrease observed in SO_2 emissions and SO_4^{2-} concentrations, in the Western Europe was not observed in the Eastern European countries. The variation in SO_2 concentrations in the EMEP stations located at East European countries between 1978 and 2000 are depicted in Figure 10b. The difference between Figures 10a and 10b is very clear.

The situation is different for NO_x emissions and NO_3^- concentrations, since the control of NO_x emissions is more difficult than SO_2 emission control. NO_x emission control in Europe was started approximately 10

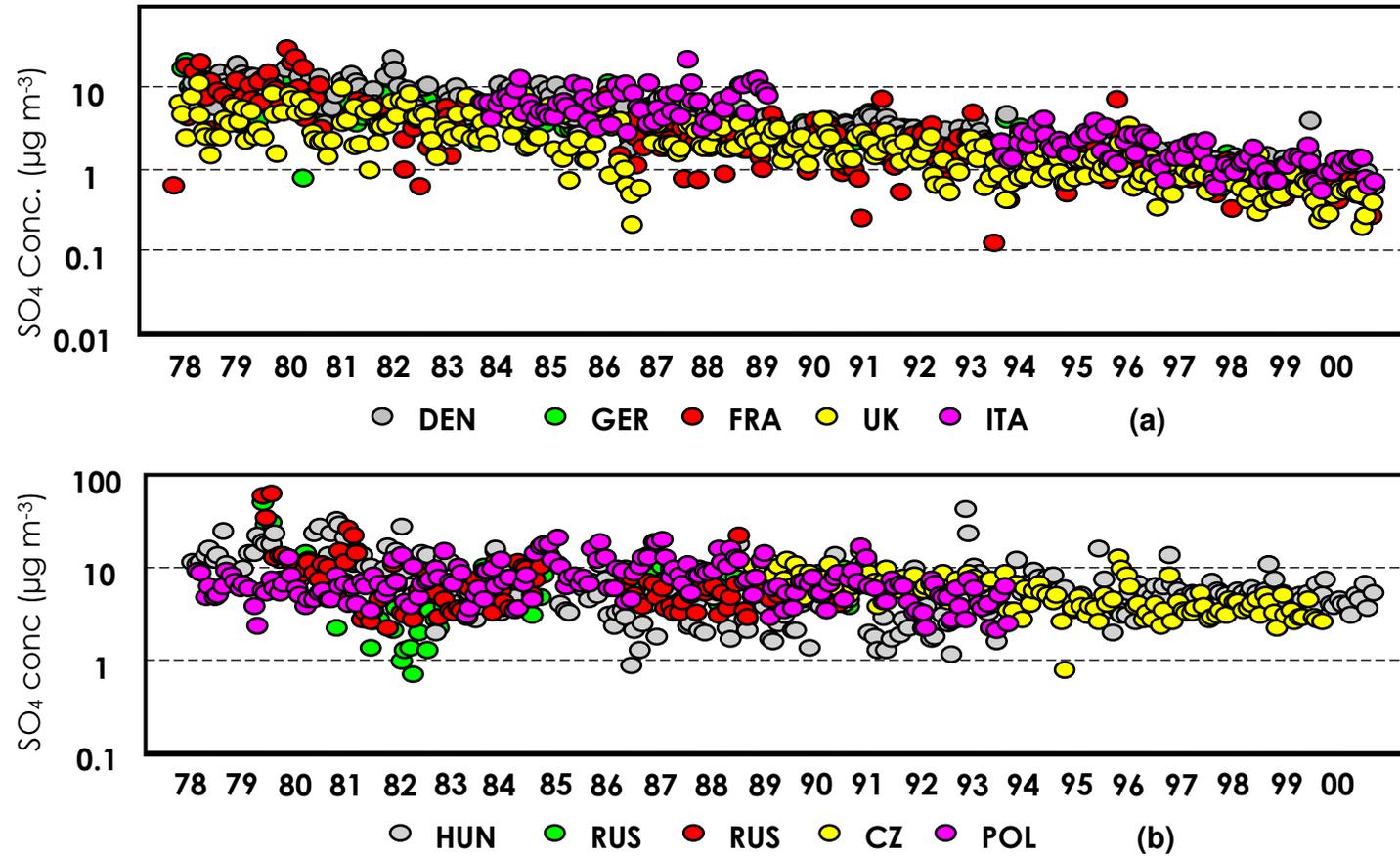


Figure 3.10. Variation of SO_4^{2-} concentrations in atmospheric aerosol in the western European (a) and former USSR countries (b), between 1978 and 2000

years later than initiation of SO₂ emission control. NO₃⁻ concentration in the European atmosphere started to decrease only recently. This statement is true for both Western and Eastern European countries. The variation of NO₃⁻ concentration in the Western and Eastern European countries are depicted in Figure 3.11 where NO₃⁻ concentrations measured in EMEP stations are plotted between 1979 and 2000. It is clear from the figure that decrease in NO₃⁻ levels in the Western European countries is much smaller and much more recent than the decrease observed in SO₂. No significant decrease in NO₃⁻ concentration was observed in the Eastern European countries.

From the above discussion, the SO₄²⁻ / NO₃⁻ ratio in the Western Europe is expected to be lower than the corresponding ratio in the Eastern Europe. Measured SO₄²⁻ / NO₃⁻ ratios for the EMEP stations in both Western and Eastern Europe are given in Figure 3.12. As can be seen from the figure, the SO₄²⁻ / NO₃⁻ ratio for Western Europe varies between 0.5 and 2 with an average of 1.3±0.7. For Eastern European countries, on the other hand, the ratio is significantly higher with an average value of 3.4±2.7. This difference in the SO₄²⁻/NO₃⁻ ratio in Western and Eastern European atmosphere provided us a convenient tracer to differentiate between air masses arriving from Western and Eastern European countries to Antalya, Amasra and Çubuk stations.

If the air masses intercepted in our stations are originating from Eastern Europe, then the SO₄²⁻ / NO₃⁻ ratio in the samples is expected to be high. On the other hand, if the air masses are transported from Western Europe, then this ratio is expected to be lower. As depicted in Figure 3.12, the average SO₄²⁻ / NO₃⁻ ratio in the samples collected at Antalya, Amasra and Çubuk stations are 4.8, 5.0 and 4.3, respectively. These high ratios indicate that Eastern European emissions or the local emissions within Turkey have higher influence in the aerosol compositions observed

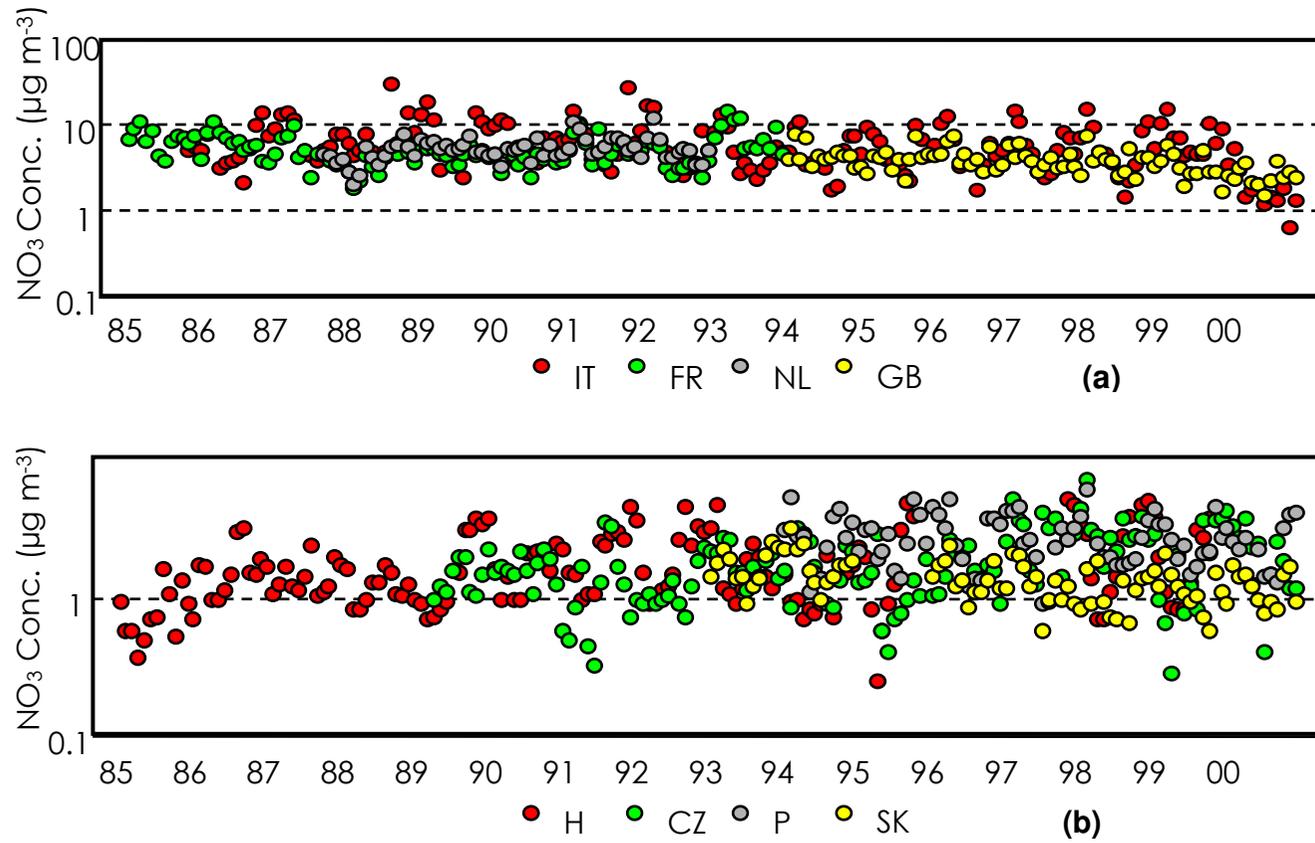


Figure 3.11. Variation of aerosol NO_3^- concentrations in Western Europe (a) and former USSR countries (b), between 1978 and 2000

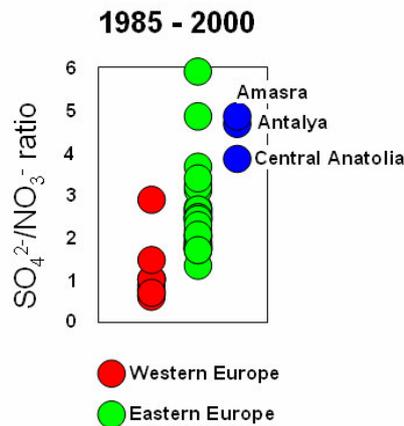


Figure 3.12. SO₄²⁻ to NO₃⁻ ratio at EMEP network and Turkish stations

in the stations than emissions in the Western European countries, which will be discussed later in the manuscript.

Monthly average concentrations of the SO₄²⁻ / NO₃⁻ ratio in Amasra, Antalya and Çubuk stations are given in Figure 3.13. The ratio varies between 4 and 6 at Antalya station and it does not show a significant seasonal variation. However, the SO₄²⁻ / NO₃⁻ ratios measured at Amasra and Çubuk stations do show clear seasonal patterns. In these two stations the ratio is as high as 6 – 7 in summer, but decreases to 2 to 3 in winter. The pattern is better defined in Çubuk station. This seasonal pattern in measured SO₄²⁻ / NO₃⁻ ratio indicates that transport from eastern Europe is dominating during summer months, but contributed strongly by transport from western parts of Europe in winter season.

The seasonal variations observed in SO₄²⁻ / NO₃⁻ ratios measured at Amasra, Çubuk and Antalya stations are in agreement with seasonal variations in flow climatology in these stations discussed previously and given in Figure 3.13. Seasonal variations in flow patterns indicated more frequent flow from WSW, W and WNW sectors during winter months at Amasra and Çubuk stations. Since these sectors include western

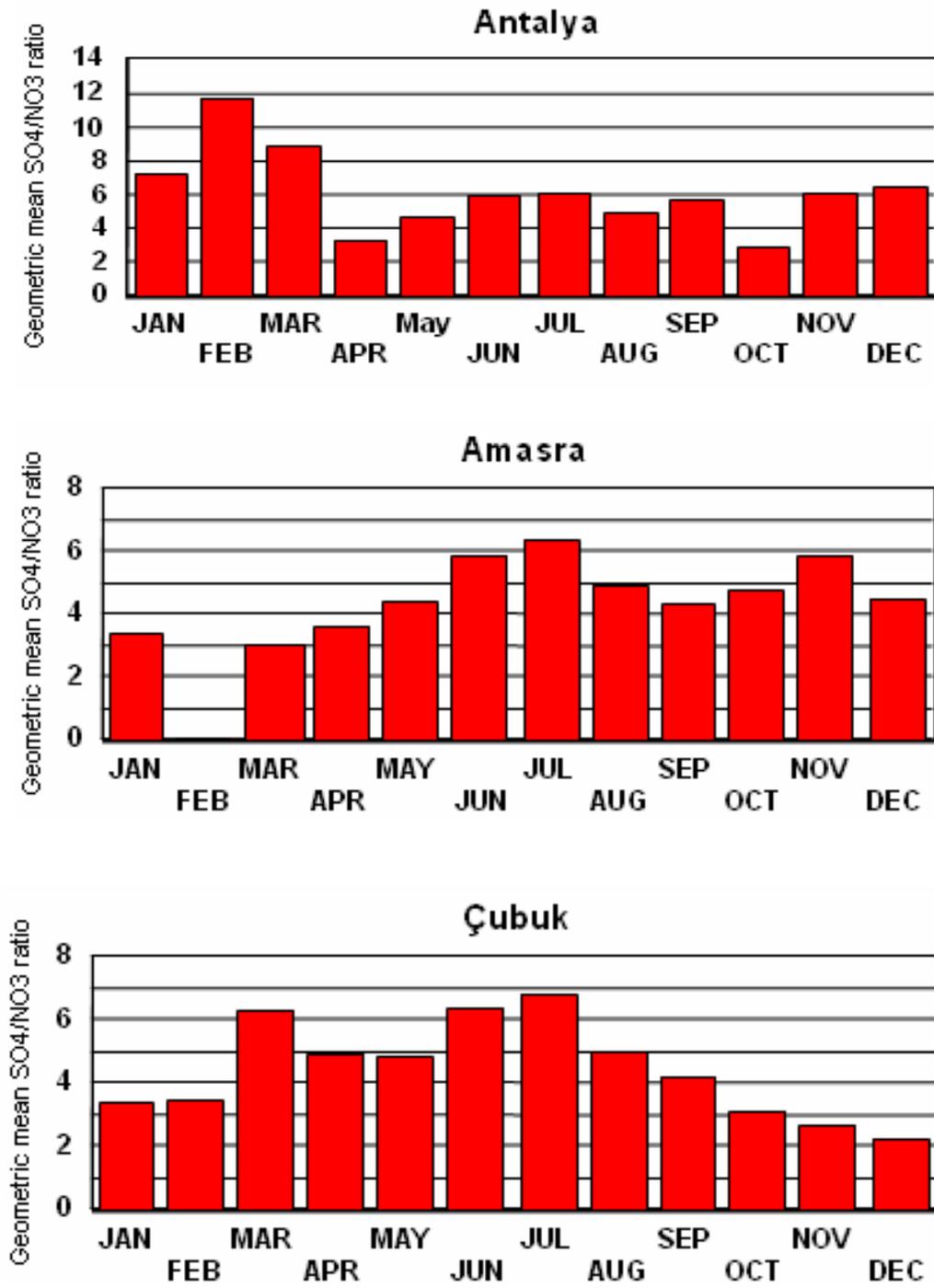


Figure 3.13. Monthly variation of SO_4^{2-} to NO_3^- ratio at Mediterranean, Black Sea and Central Anatolia

European countries, $\text{SO}_4^{2-}/\text{NO}_3^-$ ratio measured in these two stations are lower in winter. In the same stations flow from NE, NNE, N and ENE stations are more frequent during summer, resulting in higher $\text{SO}_4^{2-} / \text{NO}_3^-$ ratio during this period. The flow pattern do not show any seasonal variations at Antalya station, which agrees nicely with the lack of seasonal variation in the $\text{SO}_4^{2-} / \text{NO}_3^-$ ratio.

Similarities in the expected and observed $\text{SO}_4^{2-} / \text{NO}_3^-$ ratios showed that the seasonal variation in the concentrations of elements and ions depends not only on seasonal variation in precipitation frequency but also on the seasonal variations in the flow pattern in that region.

3.5. Comparison of Geological Locations of Potential Source Regions for Major Pollutants

In this study, PSCF approach is used to identify locations of the source regions that determine aerosol compositions at Black Sea, Mediterranean and Central Anatolia regions. Results of PSCF calculations were useful to answer weather composition of aerosol in three parts of Turkey are affected from similar source regions of pollutants or totally different source areas.

Since the PSCF is discussed in detail in Chapter 2, it is not further explained here. This technique has been used for a long time in our group and elsewhere. PSCF was applied to data sets of Çubuk, Antalya and Amasra regions (Yörük, 2004; Güllü, 1996; Karakaş, 1999). Statistical significance of the calculated PSCF values was not tested, as method used for such testing was not available at that time. In this study, PSCF values were recalculated and their statistical significance was testes using “bootstrap” technique and distribution maps were prepared using only statistically significant within 95% confidence interval PSCF values.

As discussed in Chapter 2, PSCF is based on dividing the working area into grids and dividing polluted trajectory segments to total trajectory segments in each grid. Therefore, when calculating the PSCF value in each grid, the uncertainty in the grid is completely depends on the total trajectory segments in the grid. If there is only one segment in the grid and by chance, if that segment was a part of a trajectory that is classified as polluted, then that grid becomes very strong source region. However, conclusion that bases on one segment will be highly uncertain. Since the starting points of all trajectories are coordinates of the stations, number of segments close to the in the station are high and the number of segments decreases going away from the station. Therefore, uncertainty problem is faced mainly at the edges of the study area.

The distribution maps of the conducted studies up to now were drawn without considering the statistical significance of the PSCF values. During last few years, it is realized that the statistical significance of the PSCF values can easily be tested by Bootstrap technique. In this study, the bootstrap technique is applied to the PSCF values calculated for Antalya, Amasra and Çubuk stations and distribution maps are prepared using only PSCF values that are statistically significant within 95% confidence interval. The effect of bootstrap technique is shown in Figure 3.14. This figure is prepared by using the SO_4^{2-} concentrations at Antalya station. Without bootstrap, almost all parts of the Europe appear to contribute to high SO_4^{2-} concentration in the Mediterranean region. However, PSCF values in large number of grids are not statistically significant. When the grids are removed by bootstrapping, maps become easier to interpret.

Secondly, in this study “polluted trajectory” definition is investigated. In the calculations of PSCF, the trajectories corresponding to high values of the specie are identified as polluted trajectories. The term “higher concentration” is tentative and can change from one study to another. In

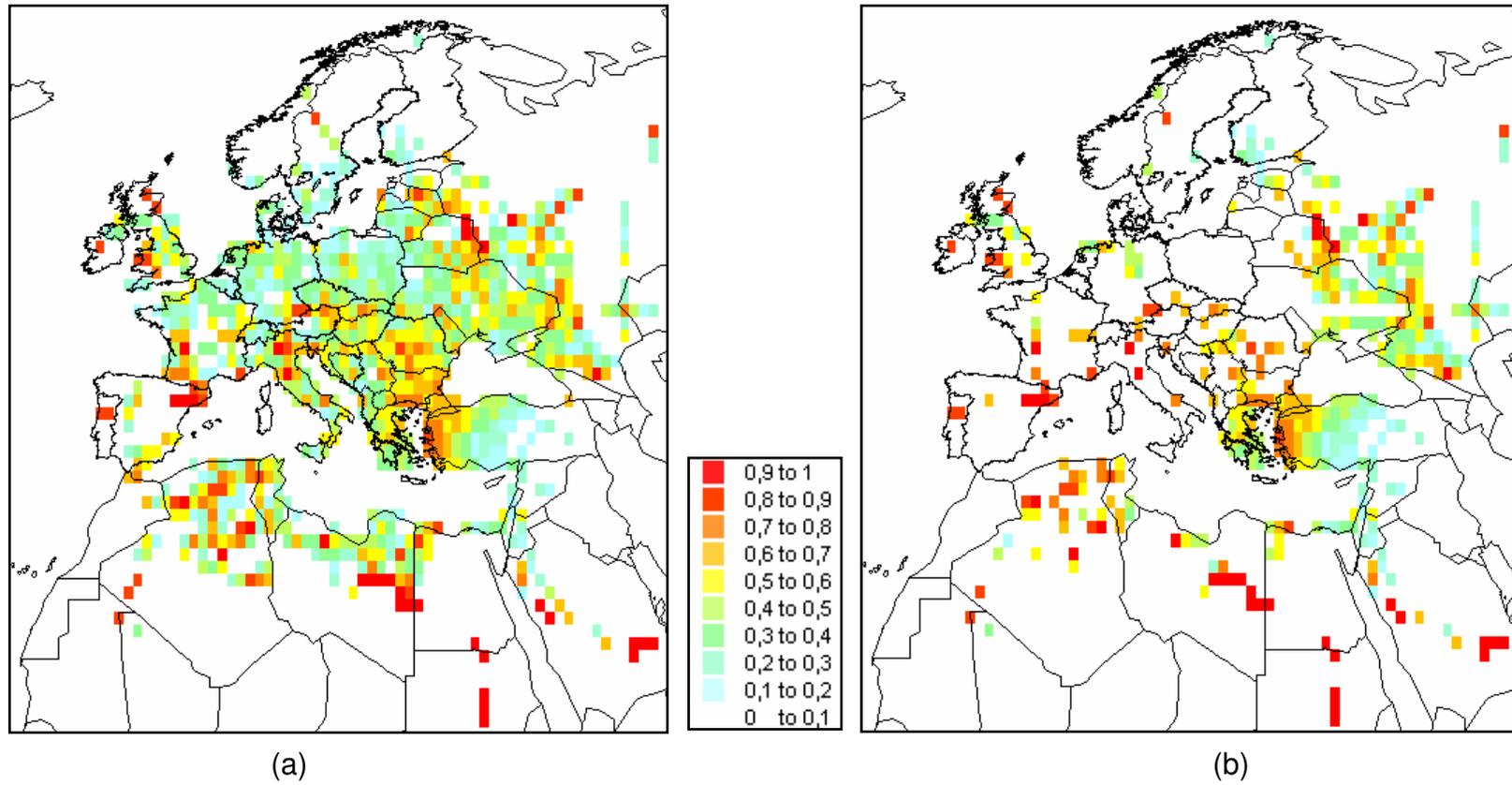


Figure 3.14. Effect of bootstrap to the potential SO_4^{2-} regions of Antalya region; without bootstrapped (a), with bootstrapped (b).

the previous studies, trajectories corresponding to highest 20% concentration are accepted as polluted. In this study, bootstrapped PSCF maps were prepared using different percentages of highest concentrations as “polluted” data set.

Bootstrapped- PSCF maps prepared using 20% and 40% of the highest SO_4^{2-} concentrations as polluted data set at the Antalya station is depicted in Figure 3.15. As can be seen from the figure, there is not much difference in the source regions. However, since the number of trajectories defined as polluted in the highest 20% case is smaller in number, the PSCF values turn out to be smaller. A better resolution of the source areas is obvious in the 40% case. The PSCF distributions of trajectories corresponding to the highest 20%, 30%, 40%, 50% and 60% SO_4^{2-} concentration as polluted are investigated and it is decided to use PSCF distributions of trajectories corresponding to highest 40% concentration as polluted for all of the PSCF calculations in this study.

In this study, another point that is investigated is whether the height of the trajectory has any affect on PSCF values. The vertical profile of the trajectories that corresponds to the highest 20 % concentration of SO_4^{2-} in Antalya are given in Figure 3.16. As can be seen from the figure, different trajectories pass through different heights from different grids. It is clear that a grid with a certain source in it will affect an air parcel at 1000 m altitude more than it effect an air parcel at 3000 m altitude. As expected, trajectory segments near the surface are more affected from the emissions than a segments at 3000 m. But this difference is not considered in PSCF calculations. In order to understand the effect of height in the determination of potential regions, only segments which are under 1000 m (882 mb), are taken and PSCF values of SO_4^{2-} are calculated accordingly. The result of this analysis is given in Figure 3.17. The figure demonstrates that using trajectory only segments below 1000

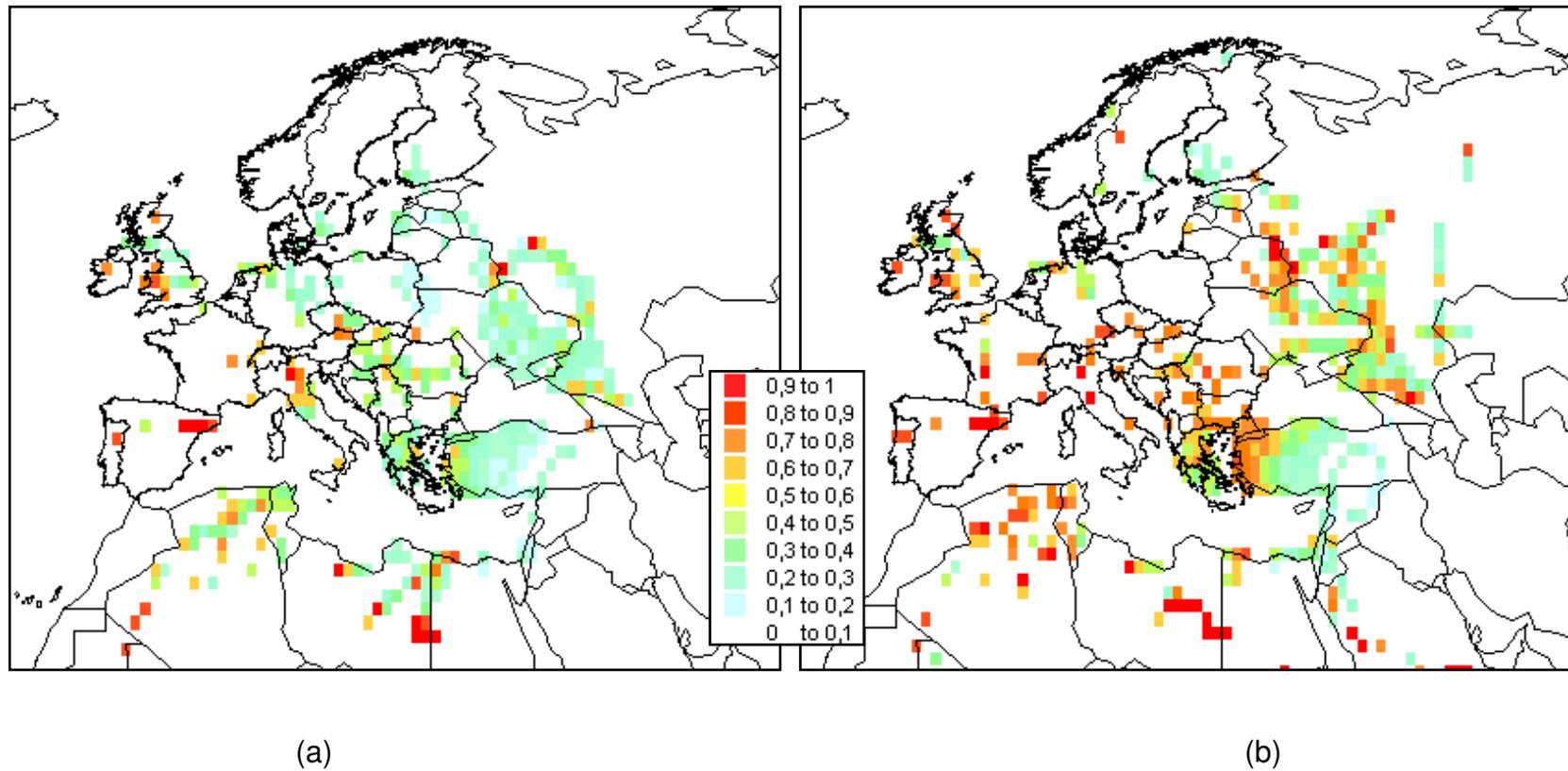


Figure 3.15. Comparison of the PSCF calculations performed defining highest 20% (a) and 40% (b) of measured concentrations as polluted of SO_4^{2-} in Antalya.

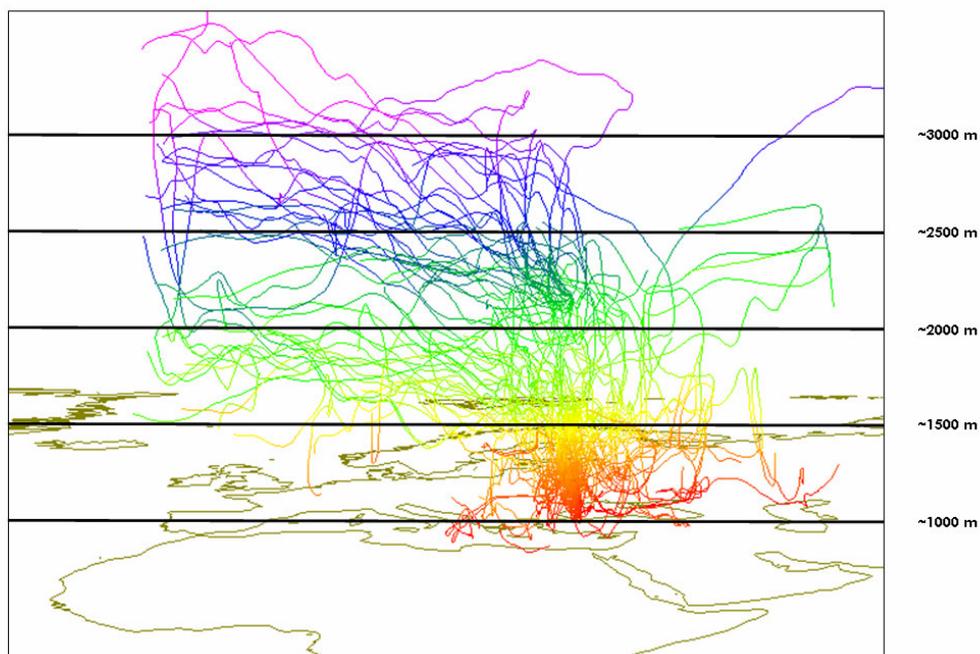


Figure 3.16. The vertical profile of the trajectories that corresponds to the highest 20 % concentration of SO_4^{2-} in Antalya

m, even without checking their statistical significance, clears up the map significantly compared to conventional distribution given in Figure 3.17a. The distribution of PSCF values calculated with segments <1000 m altitude closely resemble the distribution obtained by applying bootstrap technique to PSCF values calculated using all trajectory segments, which is given in Figure 3.17c.

Only difference between Figure 3.17a and 3.17c is that, in Figure 3.17a, some parts of Ukraine and Poland which were not identified as potential source regions in Figure 3.17c appear as potential source areas in Figure 3.17a. Distribution of statistically significant PSCF values, which were obtained by bootstrapping the PSCF values, obtained using only the

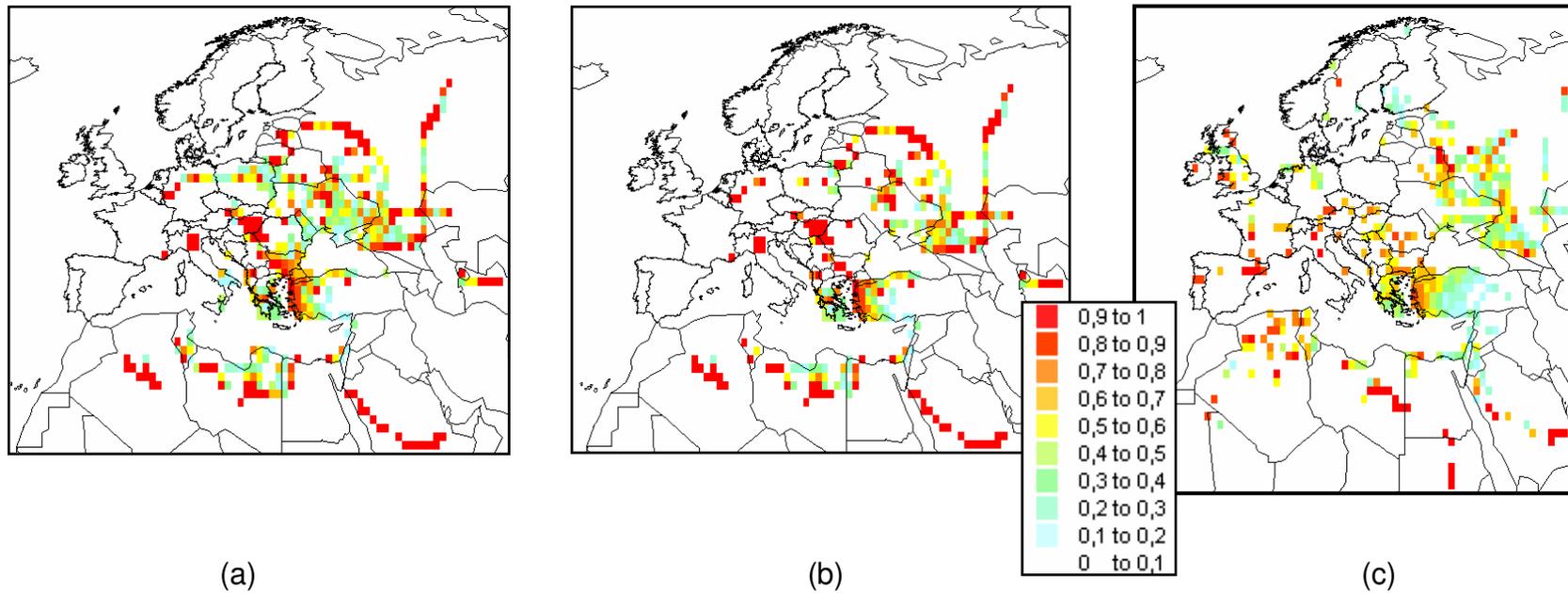


Figure 3.17. Calculation of PSCF for highest 40% of SO_4^{2-} concentrations at Antalya using only trajectory segments below 1000 m (a), same with bootstrapping (b) and using all trajectory segments and applying bootstrap with 3000 iteration (c)

segments below 1000 m altitude are given in Figure 3.17b. The agreement between distribution of PSCF values in bootstrapped, <1000 m case (Figure 3.17b) and bootstrapping, all segments case (Figure 3.17c) is fairly good. The source regions in Ukraine and Poland that appeared in Figure 3.17a were not statistically significant and removed in Figure 3.17b. Some of the potential source regions at central Anatolia and France that appears in Figure 3.17c are probably due to high altitude trajectory segments and do not appear in Figures 3.17a and 3.17b. The potential source regions affecting SO_4^{2-} concentrations at the Eastern Mediterranean atmosphere are much better defined when PSCF values are calculated using only segments below 1000 m and bootstrap is applied.

Nevertheless, there is something that is ignored in the calculations. If the PSCF are calculated only with segments below 1000 m, then it would be assumed that the trajectories which pass higher than 1000 m do not have any contribution to the long range transport. However, this is not the case. It is true that the surface emissions generally remain within the boundary layer, but some of the pollutants diffuse over the boundary layer and can be captured and transported by air masses above 1000 m. Consequently, trajectory segments over 1000 m, even they are less important than segments near to the surface, have a role in the long range transport of pollutants. Generally, trajectories, far from the receptor site, are in high altitudes and when just segments below 1000 m are to be used, then it is clear that the effect of source regions away from the station sites like Germany and UK will be underestimated. Weighting trajectory segments at different altitudes with different weighting factors would be a better way to obtain more realistic distributions of PSCF and more accurate assessment of source regions. However, determining appropriate weighting factors requires an extensive study which is beyond the scope of this work and it would extend the duration of this

study substantially. Consequently, further improvement of the method was not carried out in this work, but it will be further investigated as a separate research activity in our group.

All PSCF distribution maps in this study are prepared by using all of the trajectory segments. Statistical significance of the calculated PSCF values were checked using bootstrap technique with 3000 iterations which corresponds to 95% confidence interval.

Potential source contribution function calculations performed in all 3 stations for SO_4^{2-} , NO_3^- , NH_4^+ and Pb. There are some reasons for the calculation of PSCF values only for these 4 parameters: (1) These four species were measured in all three stations, (2) although many crustal and marine element were measured in Mediterranean and Black Sea regions, since the source regions are almost known, calculation of PSCF values would not be meaningful and (3) since the main objective of this study is to compare the similarities and differences in the source regions effecting each site, these 4 elements are enough to extract this information.

The distribution of PSCF values calculated for SO_4^{2-} ion in Mediterranean, Black Sea and Central Anatolia is given in Figure 3.18. The most important potential sources of SO_4^{2-} in Antalya are western part of Turkey, especially Aegean coast, Marmara and Trakya regions, Greece, particularly Athens and west coast, northeast coast of Black Sea, region between western Ukraine and central Russia, and Belarus-Russia border. Besides, Balkan countries mainly Romania and Bulgaria, countries like Italy, Czech Republic, Austria, France, England and Spain have certain source regions observed in particular grids.

The potential source regions of SO_4^{2-} for the Black Sea region are more limited. The western part of Turkey also observed as a potential source

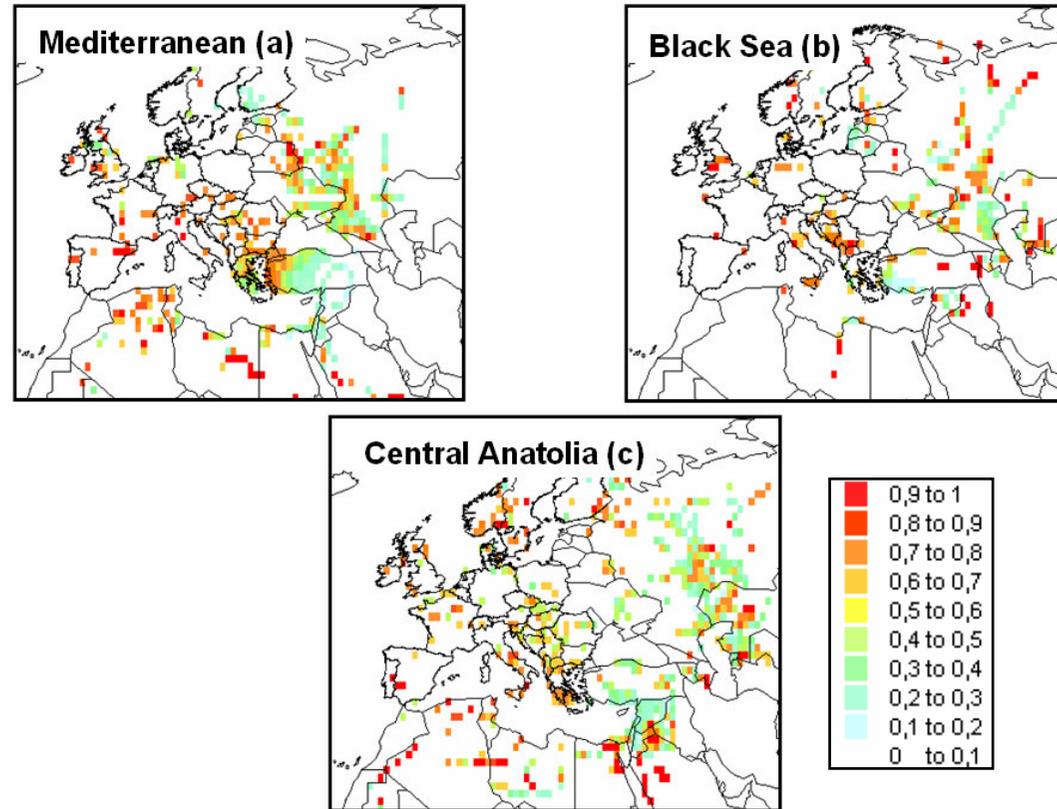


Figure 3.18. Distribution of SO_4^{2-} PSCF values in the Mediterranean (a), Black Sea (b) and Central Anatolia (c)
(Calculated for the highest 40% of measured concentrations)

region as in the case of Mediterranean station. However, the contribution of this region to SO_4^{2-} concentration to Black Sea aerosols is less when compared with the input to the Mediterranean station. Similar to the Mediterranean station, UK, northeast coast of Black Sea and central parts of Russia are also source regions of SO_4^{2-} . Furthermore, Balkan countries like Albania, Serbia and Italy, especially Sicily and Rome have potential sources of SO_4^{2-} observed in the region. Even though, there are some common source regions with Antalya station, such as potential source areas in the Russia, most of the source regions are different.

Potential sources of Central Anatolia for SO_4^{2-} cover central region of Russia which also affects the Black Sea region, Middle East, northern and eastern parts of Caspian Sea, Balkan countries especially, Greece and Serbia, and Italy. The source regions affecting the Central Anatolia are more distant than the source regions of Mediterranean and Black Sea regions. There are significant similarities between the source regions affecting central Anatolia and the Black Sea SO_4^{2-} levels, but SO_4^{2-} source regions for the Eastern Mediterranean are distinctly different.

Distribution of PSCF values calculated for NO_3^- ion in Mediterranean, Black Sea and Central Anatolia is presented in Figure 3.19. Nitrate source regions in the Mediterranean region, that lies to the north of Turkey are similar to SO_4^{2-} source regions. The potential sources of NO_3^- in the Mediterranean are located in Greece, Serbia and Italy. Besides, France and England are also important source regions. Even with lower potential, Central and Eastern Anatolia also contribute to the NO_3^- concentrations.

The potential regions effecting the concentration of NO_3^- in Black Sea are also similar SO_4^{2-} source regions. Middle East region is the most important potential source region for the Black Sea. Source regions of NO_3^- in Black Sea and Mediterranean Sea are different from each other.

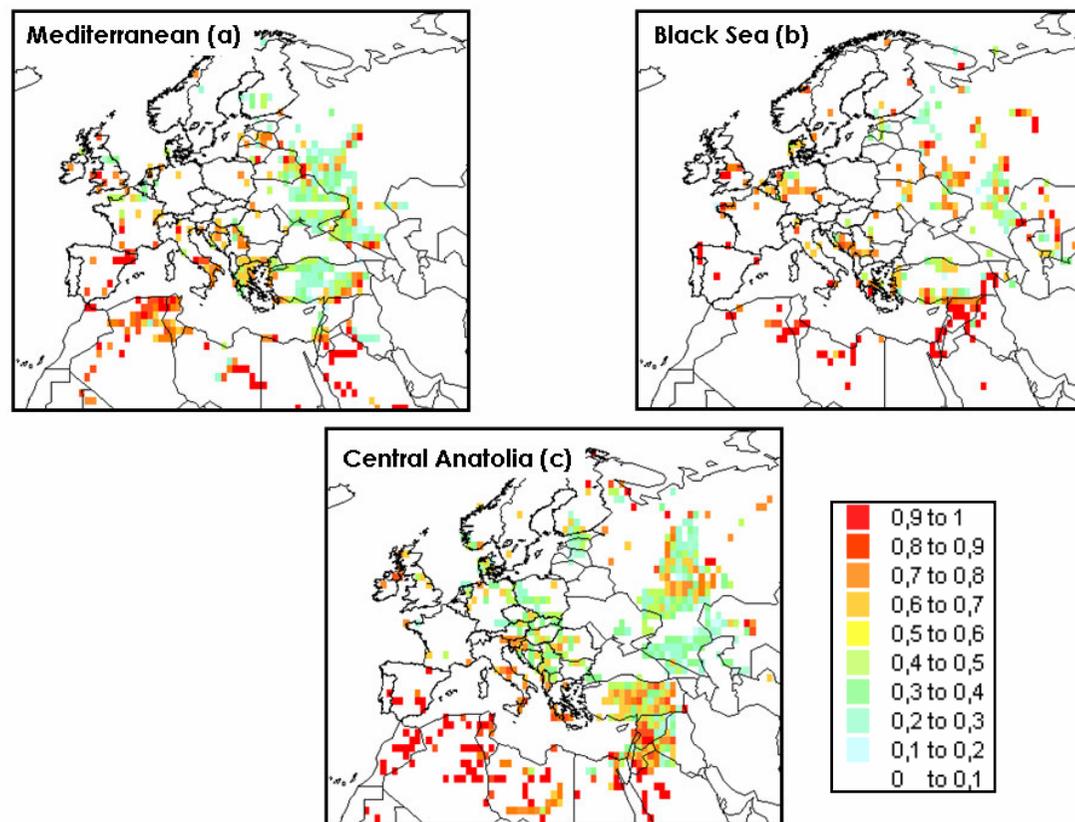


Figure 3.19. Distribution of NO_3^- PSCF values in the Mediterranean (a), Black Sea (b) and Central Anatolia (c) (calculated for the highest 40% of measured concentrations)

The regions identified by PSCF analyses showed that central and eastern Anatolia, Middle East regions have potential locations that may contribute to NO_3^- concentrations in the Central Anatolia. Aside from these, northeast coast of Black Sea, central part of Russia, Romania, Serbia, Italy, Czech Republic and Poland are significant potential source regions of NO_3^- ion in the Çubuk station. Northwest coasts of the Black Sea are a common NO_3^- source region for both the central Anatolia and Eastern Mediterranean.

Figure 3.20 shows the distribution of PSCF values calculated for NH_4^+ ion in Mediterranean, Black Sea and Central Anatolia regions. As in the cases of NO_3^- and SO_4^{2-} , NH_4^+ ion in Antalya station has potential sources in northeast Black Sea. Some regions of Turkey also contribute to the NH_4^+ concentration such as Marmara region and south eastern region. In addition to these, countries located in the central Europe also have significant potential contributions such as Czech Republic, Italy, Germany and Austria. England is also an important source region for the NH_4^+ in Antalya.

The most important potential region of NH_4^+ in Amasra is the southern regions of Turkey. Other potential regions of NH_4^+ are central parts of Russia, region in the Russia-Belarus border, eastern parts of Caspian Sea and England. The contribution of southern part of Turkey to the Black Sea station is higher than the Mediterranean station. The other source regions are different than those found for the Antalya station.

Balkan countries, except Bulgaria and Romania, have high potential regions of NH_4^+ in the Central Anatolia. Central Italy, some parts in Germany and England and northern and eastern regions of Caspian Sea are other important potential source regions of NH_4^+ ion in the Çubuk station. Besides, southern Turkey has certain contribution; however, this

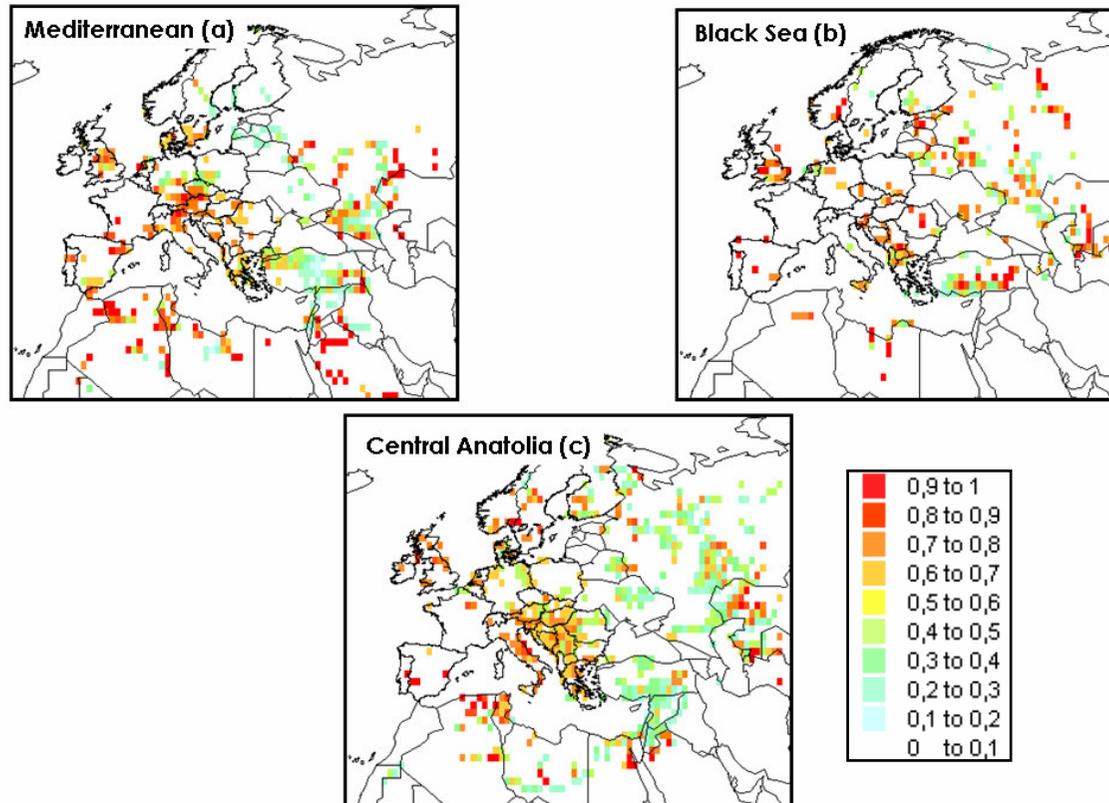


Figure 3.20. Distribution of NH_4^+ PSCF values in the Mediterranean (a), Black Sea (b) and Central Anatolia (c) (calculated for the highest 40% of measured concentrations)

contribution is very low when compared with the contribution of this region to Black Sea and Mediterranean stations.

The distribution of PSCF values calculated for Pb ion in Mediterranean, Black Sea and Central Anatolia is given in Figure 3.21. Possible regions of Pb in Mediterranean region are central and eastern parts of Turkey, Israel, northeast Black Sea coast, region between Ukraine-Belarus border, Serbia and Latvia. The potential of sources in the Turkey are higher than the others. There is a road with heavy traffic during summer, approximately 150 m from the sampling point, consequently, most of the lead measured at Antalya station may originate from this local source. When there is such a strong local source, the distant Pb sources may not be determined accurately, because no matter from which direction trajectories come from, they have to pick up locally generated Pb.

Potential regions of Pb in Amasra are Israel, with a higher contribution than Mediterranean, central parts of Anatolia, with less contribution than Antalya, central parts of Russia, all of the Balkan countries and the Central European countries particularly, Austria, Slovakia, Czech Republic and Germany.

The regions identified by PSCF analyses showed that northeast Anatolia, central Russia, central European and Balkan countries are potential source locations that contributes to Pb concentrations in the Central Anatolia. Aside from these, northern and eastern Caspian Sea, Middle East region, France and Germany are other significant potential source regions of Pb in the Çubuk station. The source regions of Pb in the central Europe and Balkans are common for both Black Sea and Central Anatolia.

As a result, source regions effecting Mediterranean, Black Sea and Central Anatolia regions have some similarities. Especially emissions to

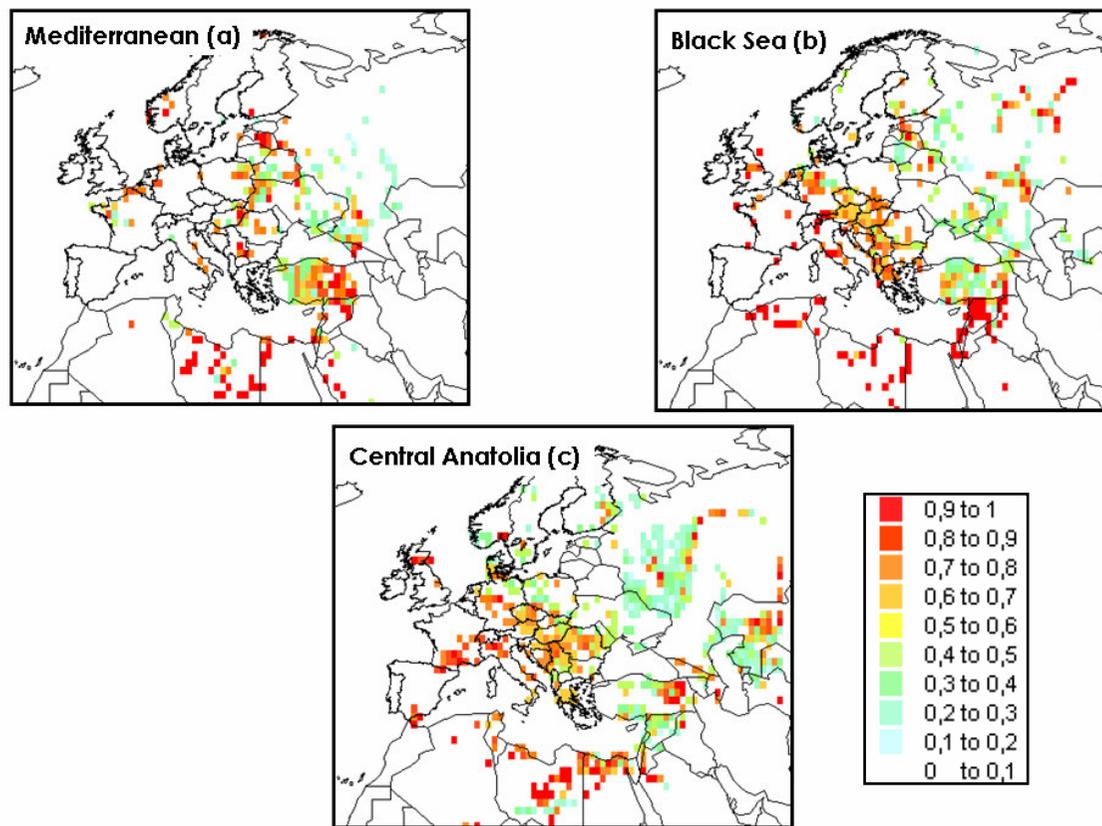


Figure 3.21. Distribution of Pb PSCF values in the Mediterranean (a), Black Sea (b) and Central Anatolia (c) (calculated for the highest 40% of measured concentrations)

the atmosphere in some regions in the Russia have effects on three stations. Similarly, releases of pollutants in some Balkan countries are also affecting all of the three stations. However, the differences in the source regions affecting these stations are more than their similarities. The source regions calculated for Central Anatolia and Black Sea resemble each other, but potential source areas effecting regions are clearly different.

The major part of the pollutants measured in Mediterranean region is due to Aegean coast, whereas Central Anatolia and Black Sea stations are not affected from the same region as much as the Antalya station does. A similar conclusion was also reached during the discussion of the flow climatologies.

3.6. Source Apportionment and Quantification

There are numerous models developed for the identification of the sources affecting a region. These models which have found widespread use in air pollution studies include chemical mass balance, linear regression, temporal and spatial correlation eigenvectors, neural networks, edge detection, aerosol evaluation and gas/particle equilibrium (Watson et al., 2002). Quite the opposite to dispersion models, these techniques are based on analysis of ambient air samples and chemical characterization of source emissions rather than measurement of source emission rates and application of atmospheric dispersion and transport equations. In this study, as discussed previously, a receptor oriented method; positive matrix factorization is used for the apportionment and the quantification of the sources in the Mediterranean, Black Sea regions. The results of these two stations are compared with the PMF result of Çubuk region (Yörük, 2004). The apportionment study was not applied for Uludağ station because of low number of measurements in the region.

3.6.1. Treatment of Values and Extraction of Factors

As mentioned in Chapter 2, the main advantage of PMF over other receptor oriented methods is its ability to use larger number of missing values by assigning them high uncertainties and thus reducing their influence on the least square fit. Consequently, calculation of uncertainties in each measured parameter is a crucial parameter in the PMF analysis. If the analytical method do produce the uncertainty in each measurement, then these values can be directly included in the PMF. Some analytical methods, such as those that rely on x-rays, γ -rays or mass spectrometric detection do produce measurement uncertainties due to counting statistics. However, it should be noted that counting statistics is only one of the components in total measurement uncertainty. Other components in measurement uncertainty, such as those arising from blank subtraction, weighting, volume measurements etc should also be known to assess the overall uncertainty in the measured value. Unfortunately, uncertainties from these components are not as readily accessible as the counting statistics. In any case, the overall uncertainty in measurements must be computed and an uncertainty matrix must be generated and used in the PMF analysis. The uncertainties must be such that:

Uncertainties in measured values must be realistic and represent true uncertainty in their measurement. The influence of the species in determining factors in the PMF analysis depends on their uncertainties. Species with smaller uncertainty are more influential in the fit. Different elements are generally measured with different uncertainties by different analytical methods, meaning that the least square fit used in the PMF will rely on different species depending on analytical method used.

Missing values (values that are not measured due to some reason) should be differentiated and should be given a very high uncertainty value so that it will not affect the fit.

Below detection value should be differentiated and should be given similar high uncertainty value for the same reason.

Outliers, values that are very high and very low should also be given a high uncertainty. Environmental data is in generally show log-normal distribution, which means unusual high values are real and not an artifact. Although high measurement results are real, they should be given a high uncertainty value, because otherwise one very high value can dominate the fit and determine the composition of the whole factor.

In this study, uncertainties of the measured parameters were calculated by the method proposed by Paatero et al., 2002, which is described in Chapter 2. The approach used in Polissar et al (2001), were used to assign uncertainties to missing values and below detection limit values, where missing values are replaced by the geometric mean value of that specie in the whole data set and uncertainties are assigned as the four times the geometric mean. Below detection values (BDL) are replaced with half of the detection limit of that specie and 5/6 of the detection limit value was assigned as the uncertainty of the BDL value. In this way, minimum contribution of BDL and missing values on the PMF fit was ensured.

PMF analysis was performed using PMF version 4.2 software compiled by Paatero, 2002. The global minimum of the PMF solutions were tested by using different seeds for the pseudo-random initial values. In this study robust mode was used to reduce the influence of possible outliers on the PMF solution. That is, a data point is processed as an outlier if the residual exceeds α times the standard deviation. The α value of 2.0 was

used for Antalya and Amasra data sets while for Çubuk data set, of 4.0 produced better fits (Yörük, 2004). This minimized the effect of extreme high values on the fit, which is one of the drawbacks in FA other multivariate statistical tools, such as factor analysis. To control the rotations a parameter called FPEAK is used in the PMF algorithm. PMF is run several times with different FPEAK values to find out a range within which the objective function Q value does not change much. For all of the station sites three to nine factor solutions were extracted and the final acceptable rotations were determined by trial and error and based on the evaluation of the resulting scaled residuals, Q values and source profiles.

To be able to figure out the most reasonable solution, crustal enrichment factors are calculated for each of the solution by using F-loading values of each factor. For the crustal enrichment factor calculations, in most of the cases, Al is used for the reference element. Besides, in some of the factors, Sc is also used for the reference element. However, in some of the factors, where contributions of crustal component are very low, Al is underpredicted. In such cases Sc, which is also purely crustal is used on reference in EF_c calculations.

Explained variance of each element in each factor was also used to identify sources represented by factors. The software also produce so called "G-factor matrix", which consists of factor score values (one score for every measurement day) for each factor. Factor scores are the weight of each factor in sampling days. Daily concentrations of elements due to each factor are computed by multiplying factor score for that particular day with the factor profile. Summation of the concentration of an element due to all factors should be the same with the measured concentration of that element in that particular day. By using that data set, seasonal variations of factor scores are also calculated. Also from the G-loading results, highest 20% contributions the factors are extracted

and the backtrajectories corresponding to those days are plotted using PloTra2.1 software. For the each factor, PSCF values were calculated using the highest 40% of the factor scores as polluted data set and drawn using program MapInfo 6.5. Bootstrap method was used for the calculation of PSCF values with 3000 iterations. All of these calculations were used to identify physical meanings of extracted factors.

3.6.2. Antalya PMF Results

Factor profile, variance explained, enrichment factors with Al and Sc and monthly average factor scores of Factor 1 are given in Figure 3.22. Enrichment factors are calculated taking both Al and also Sc as the reference elements. Aluminum concentration is underpredicted in some factors, where crustal contribution low, to avoid this EFc's of elements are calculated using both Al and Sc as reference elements. In Factor 1, the calculated enrichment factors are same for both of the reference elements. In this factor, NH_4^+ explains most of the variance. When the F>Loading values are considered, the main components of this factor are found to be SO_4^{2-} and NH_4^+ ions with some Mg. From the EFc values of this factor, it is observed that SO_4^{2-} , Mg, Br, Se and Pb are enriched (EFc>10) and the rest of the elements have lower EFc values.

Different anthropogenic species are enriched in Factor 1 which implies a long range transport. The combination of SO_4^{2-} and NH_4^+ ions in this factor confirm this. But, there are some points that suggest that this factor may not be related to a long range transport. The enrichment of Pb and Se do not necessarily indicate long range transport. These two elements are enriched in almost all factors which suggest a relatively local source. No matter from which direction trajectories comes in, they capture local crustal aerosols generated near the station and due to this reason, lithophilic elements are observed in each factor. Behavior of Pb and Se are

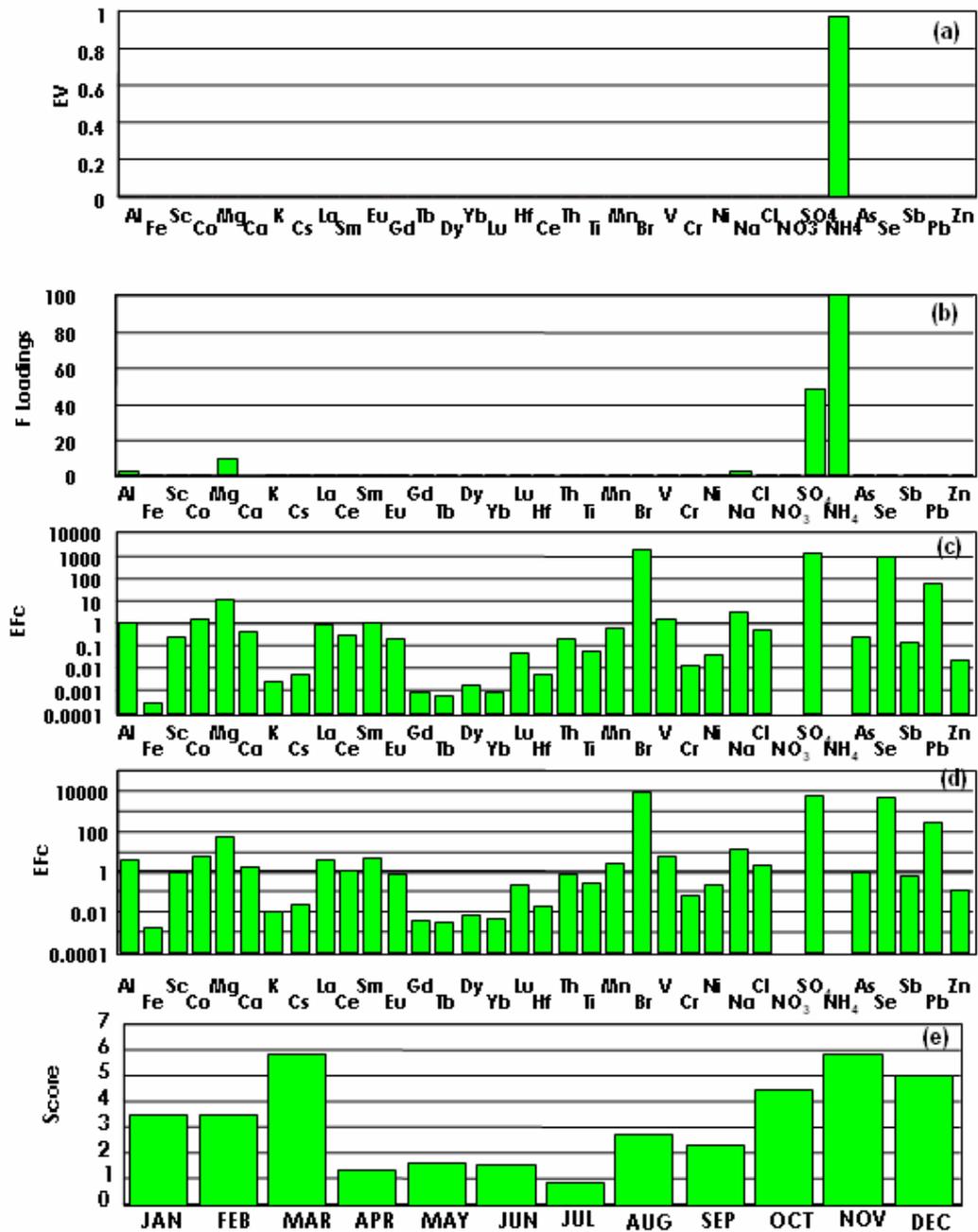
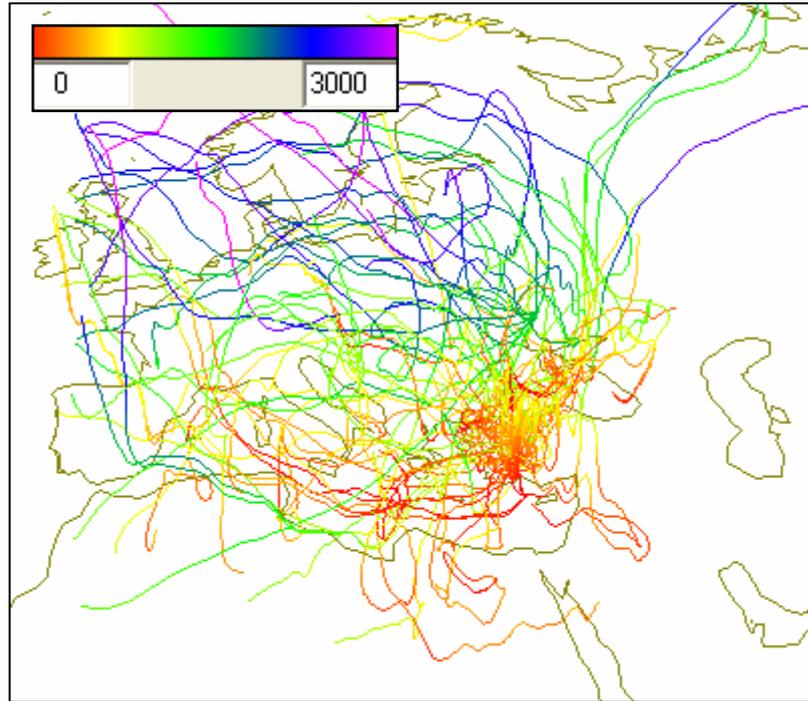


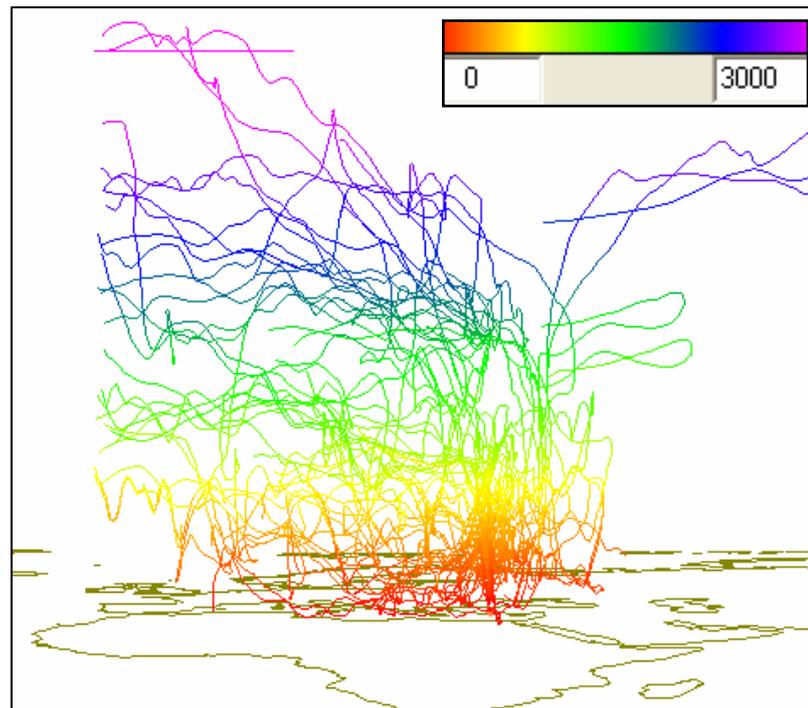
Figure 3.22. Explained Variation (a), Floading (b), Calculated Enrichment Factor with reference element Al(c) and Sc (d) and Monthly Variation in Factor Scores (e) of Antalya Factor 1

very similar to the behavior of lithophilic elements. Such behavior is expected for Pb, because Antalya-Finike highway is located approximately 250 m from the station. Therefore, road dust containing Pb can be picked up by all trajectories. However, there is no known local source for Se, but similar behavior of this element with Pb and lithophilic elements suggests a similar source.

The backtrajectories corresponding to highest 20% contribution to the Factor 1 is presented in Figure 3.23. The top view shows that the trajectories move from west sector. This is not specific for Factor 1. Similar flow patterns are also observed in trajectories associated with other factors due to the flow climatology in the region. However, since the emissions in W and NW sectors, from where the trajectories are approaching, are high, the air masses coming from these sectors are expected to bring higher concentrations of species that are observed in Factor 1. Vertical profiles of the trajectories, which are given in Figure 3.23b, shows that most of the trajectories advect to the surface around and over the Turkey, indicating that relatively local sources can have significant impact on Factor 1. Advection of trajectories to the surface can not be a conclusive evidence of local sources. However, it is observed that trajectories that are associated with species that are expected to originate from distant sources do not advect to surface in the vicinity of the station. Comparison of different factors and trajectories associated with them lead us to believe that low-lying trajectories, which are indicated by red coloration in the figures are the important ones in determining composition and physical meaning of the factors. Consequently, the advection of these low level trajectories to the surface or lack of such advection is used as a piece of evidence for local and distant sources associated with factors, throughout the discussion of PMF factors. Moreover, high factor scores (Figure 3.22e) during winter and lower during summer also supports that Factor 1 represent emissions



(a)



(b)

Figure 3.23. Top (a) and side view (b) of backtrajectories corresponding to highest 20% of the factor scores of Factor 1 of Antalya

from relatively local sources. The factor is heavily loaded with NH_4^+ . The amount of SO_4^{2-} in Factor 1 is not enough to account for all of the NH_4^+ in the factor. Main sources of NH_4^+ in the atmosphere are animal grazing and fertilizer use. In the Mediterranean region fertilizer use is expected to be more important source than animal grazing. In fertilizer applications a mixture of NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$ are used. The NH_4^+ ion applied as fertilizer is reduced to NH_3 and some of which evaporates to atmosphere. In the atmosphere it is oxidized back to NH_4^+ and collected. Extensive use of NH_4^+ containing fertilizers in the Antalya region, local sources suggested by vertical profiles of factor scores and higher scores in winter suggests that Factor 1 in the Mediterranean region represent emissions from fertilizer applications. Factor profile, variance explained, enrichment factors values and monthly average factor scores of Factor 2 are given in Figure 3.24. Factor 2 is clearly a sea salt factor. This factor has high loading of Na and Cl, which are well known markers for sea salt. Besides, loadings of Mg, Ca, K and SO_4^{2-} are also high. All of these elements and ions are known to have high concentrations in the marine aerosols.

The ratios of elements to Sc in Factor 2 are compared with corresponding ratios of Mason (1966) compilation of global average soil and given in Figure 3.25. Small amounts of soil component do exist in all factors generated by PMF, not only in Antalya station, but in Çubuk and Amasra stations as well. Soil particles are an obvious component of aerosol everywhere (unless samples are collected at ice-covered locations, such as mountaintops or in polar regions and at islands far from main land masses). Consequently no matter from where the air masses come to our stations they pick up soil particles in the atmosphere, either at the sampling point or during transport, because of this a soil component appear in all factors. The comparison between X/Sc, X/Fe and X/Al ratios in Factor 2 with the same ratios in the Mason composition showed that

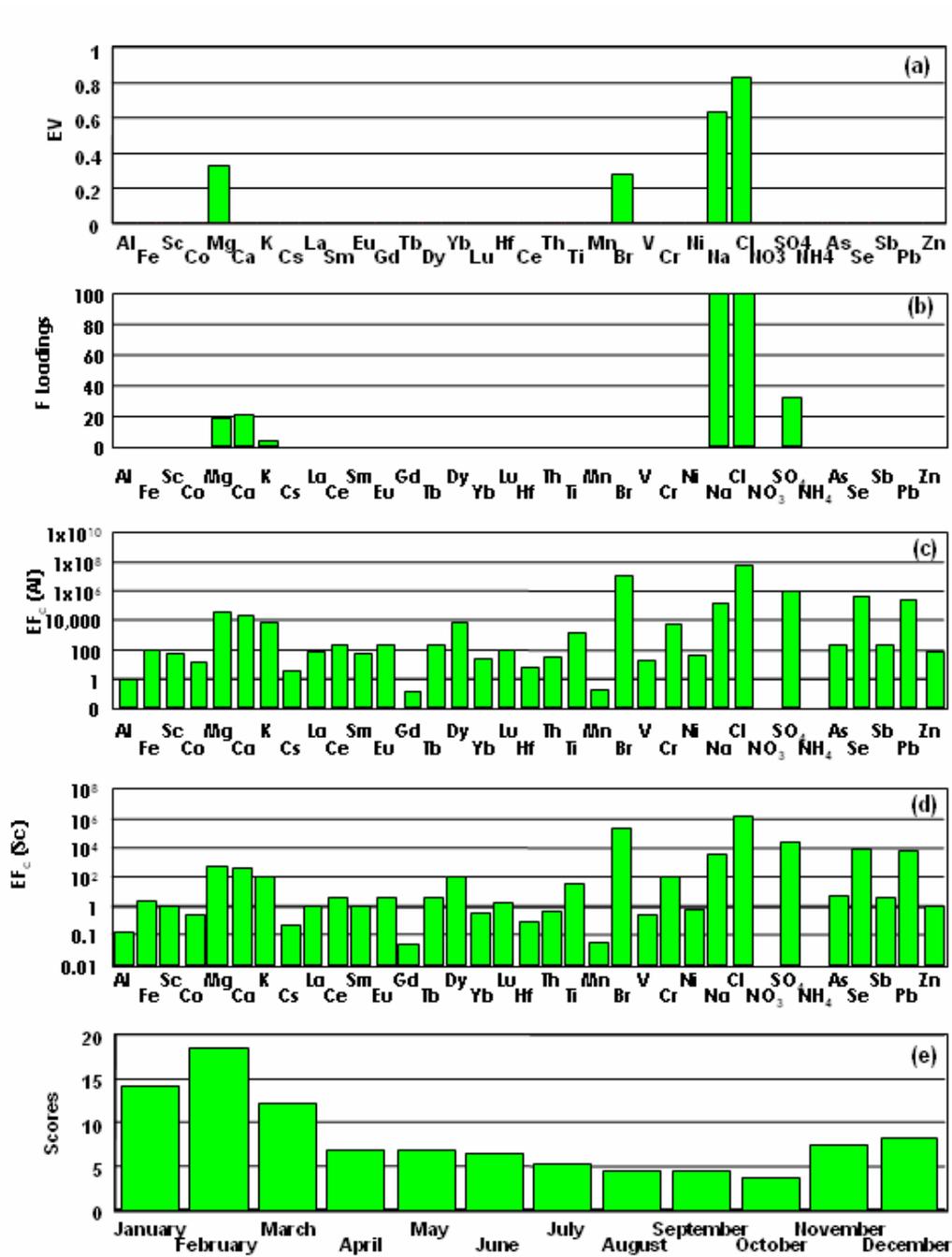


Figure 3.24. Explained Variation (a), Floading (b), Calculated Enrichment Factor with reference element Al(c) and Sc (d) and Monthly Variation in Factor Scores (e) of Antalya Factor 2

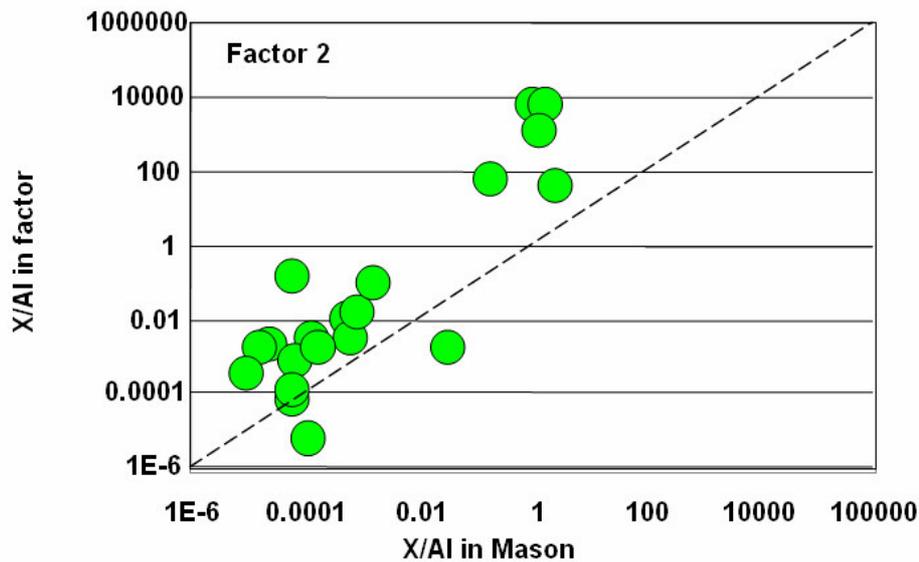
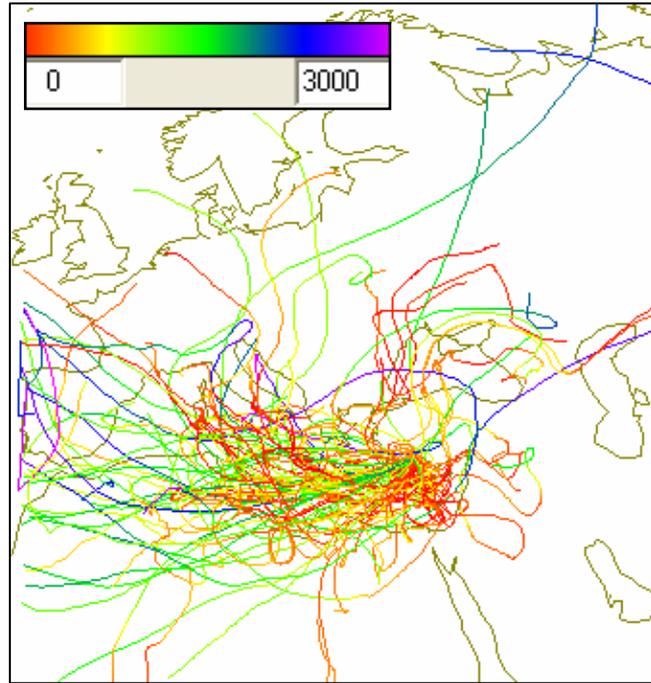


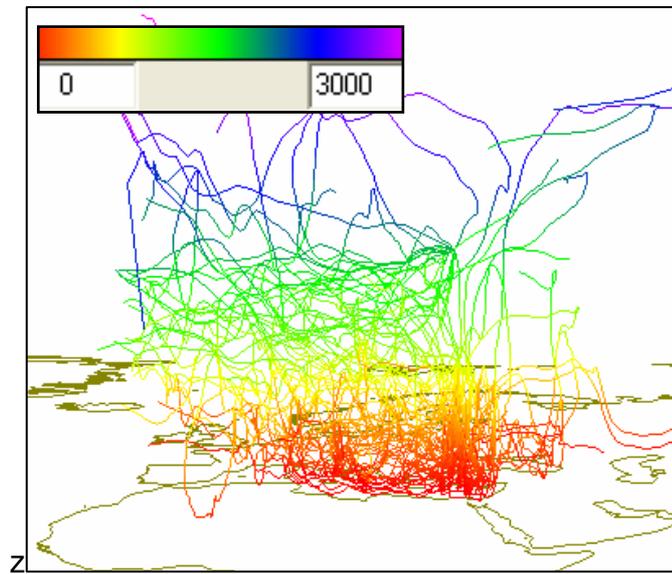
Figure 3.25. Correlation of ratios between lithophilic elements Al ratio in Factor 2 and in Mason

the soil composition in the factor generally agrees with the Mason's (1966) composition but some elements have quite different ratios. This may be due to different crustal compositions in the factor, or high uncertainty of the calculation of minor concentrations of crustal material by PMF.

The top view and vertical profiles of backtrajectories corresponding to the highest 20 % of Factor 2 scores are given in Figure 3.26. The top view of the trajectories do not show any indication that the factor is related to marine emissions. The top views of trajectories associated with Factor 2 are more concentrated over Mediterranean Sea; but, there are also many trajectories that are arriving to the station from regions away from sea. However, vertical profiles of the same trajectories clearly show that Factor 2 is a marine factor. No matter from where they originate all of the trajectories shown in the figure advects to the surface of the Mediterranean or the Black Sea at one time during their 5.5 day long



(a)



(b)

Figure 3.26. Top (a) and side view (b) of backtrajectories corresponding to highest 20% of the factor scores of Factor 2 of Antalya

transport to the sampling point. The figure is the most convincing evidence that low lying trajectories and advection of high trajectories to surface is much more important than overall distribution of trajectories in determining the composition of factors and composition of aerosols in general. Higher factor scores in winter also supports that the factor is a sea salt factor (because generation of sea salt aerosol is enhanced during stormy winter season).

Factor profile, variance explained, enrichment factors with Al and Sc and monthly average factor scores of Factor 3 are given in Figure 3.27. Factor 3 explains large fraction of variance in the concentrations of most crustal elements. F-Loadings showed that Al and Fe are the most significant elements. The EF_c values of this factor do not change much when the reference element is different. The EF_c for all species, including anthropogenic elements, have values around unity. Therefore, Factor 3 is a clear crustal factor and it represent crustal component of the soil originated in the Eastern Mediterranean atmosphere.

Factor scores are higher during summer months which is expected crustal behavior, since the soil is dry during summer months, the soil particles can easily re-suspended in the air causing higher contribution in this season. This factor is considered as Saharan dust factor. The reasons of this are going to be discussed in details later in this section.

The variance explained, F-Loadings, the EF_c values of elements and seasonal variations of factor scores for Factor 4 are presented in Figure 3.28. The fourth factor represents an anthropogenic component in the aerosols of the Eastern Mediterranean Sea. Most of the variance of this factor is explained by V, NO₃⁻, SO₄²⁻, Se and Zn. The F-Loading values show the highest concentrations contributing to this factor as SO₄²⁻, NO₃⁻ and Na. When Sc is taken as the reference element for the calculation of EF_c, crustal elements EF_c values are

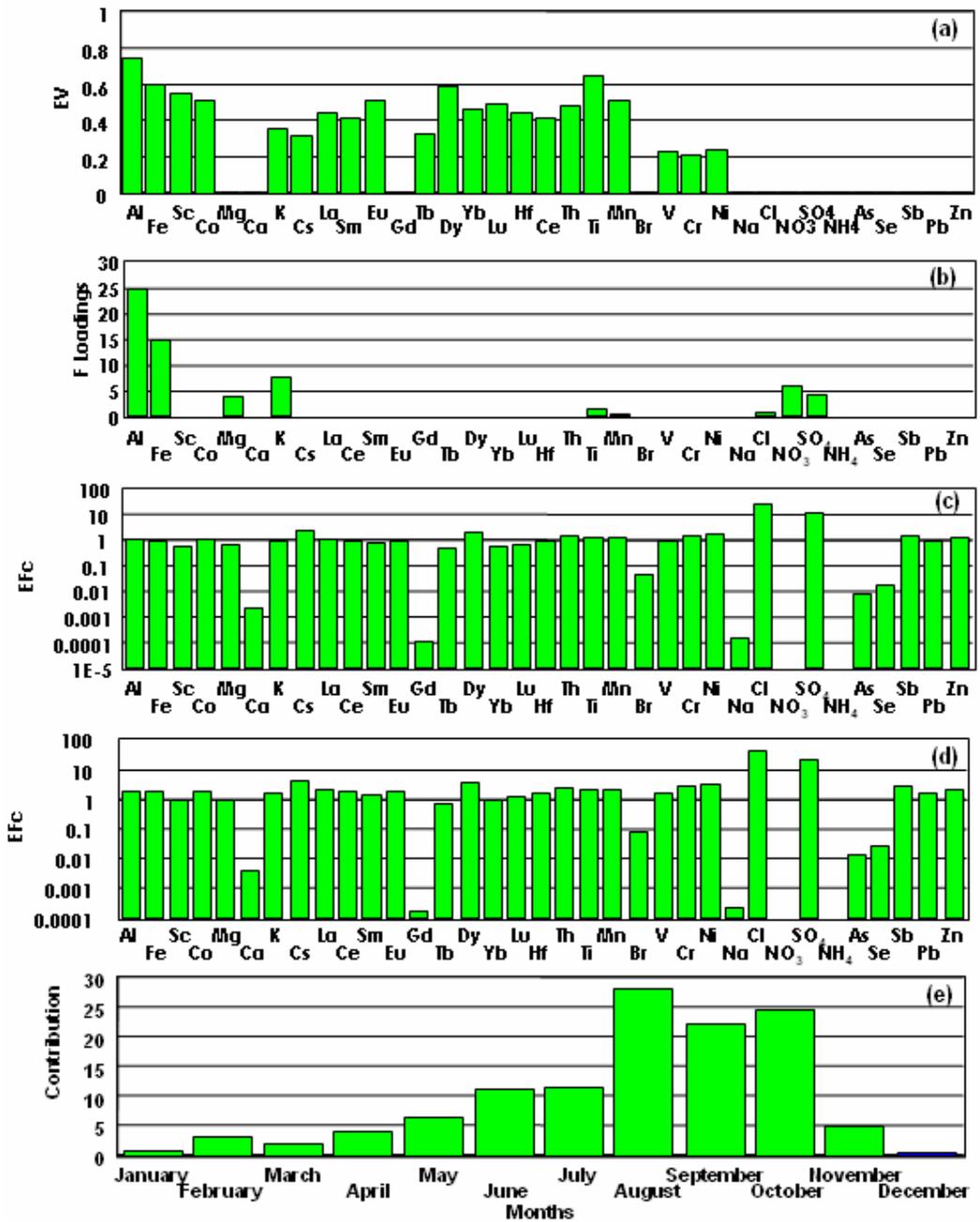


Figure 3.27. Explained Variation (a), Floading (b), Calculated Enrichment Factor with reference element Al(c) and Sc (d) and Monthly Variation in Factor Scores (e) of Antalya Factor 3

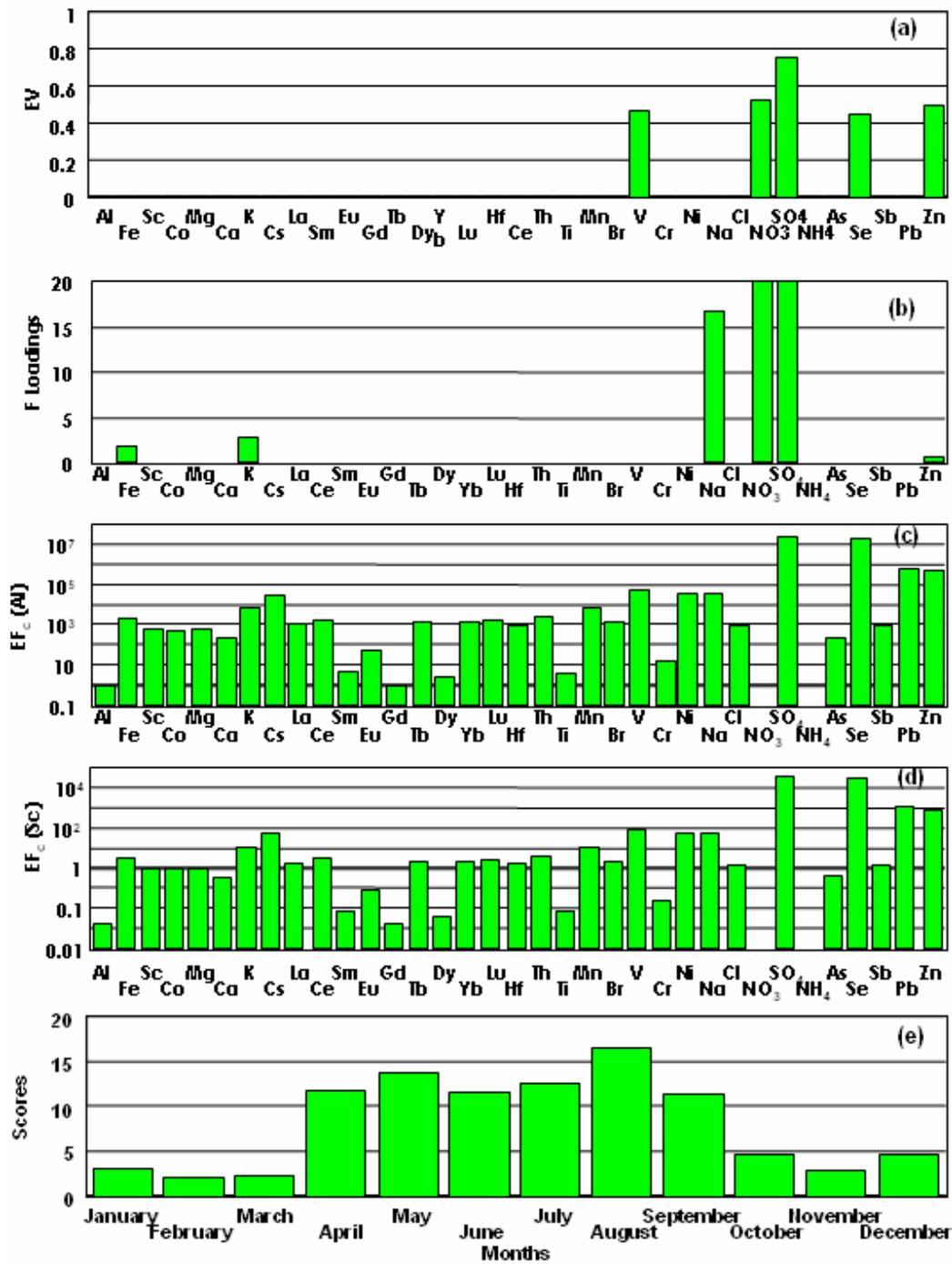


Figure 3.28. Explained Variation (a), Flooding (b), Calculated Enrichment Factor with reference element Al(c) and Sc (d) and Monthly Variation in Factor Scores (e) of Antalya Factor 4

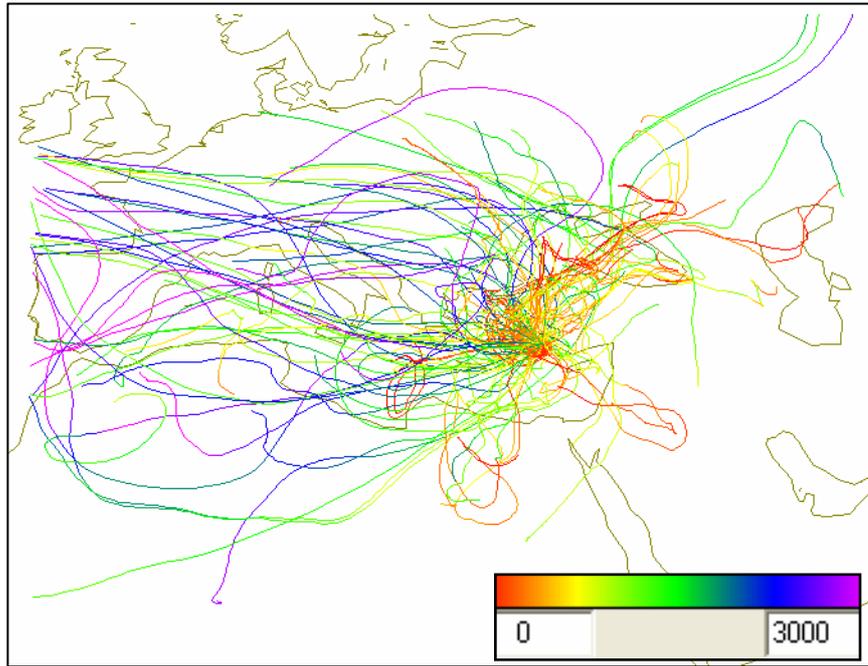
observed to be closer to unity. Even though the factor is an anthropogenic factor, some soil intrusions are also observed as discussed before. However, the contribution of soil particles to this factor is very low. Concentration of crustal material in Factor 4 is approximately 10 ng/m^3 calculated assuming all of the measured Sc comes from soil and soil component in the factor has similar composition with Mason (1966) global average soil. On the other hand, concentrations of SO_4^{2-} and NO_3^- in this factor are 400 ng/m^3 and 65 ng/m^3 , respectively.

The factor scores are higher during summer months, but the difference between summer and winter months are not as high as the difference observed in soil factor. The seasonal variation Factor 4 scores is similar to the seasonal variation in SO_4^{2-} concentration. Observed seasonal pattern is attributed to effective removal of aerosols by wash out process during long range transport in winter (Güllü et al., 1998).

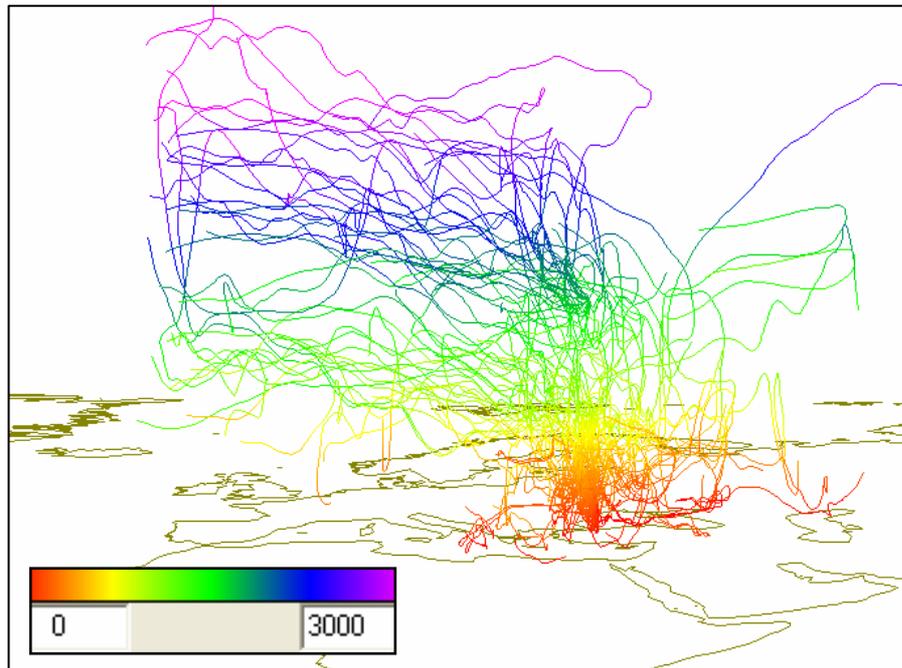
The backtrajectories corresponding to highest 20 % of the Factor 4 scores are given in Figure 3.29. The backtrajectories of the highest factor scores contributing this factor derive usually from southwest and northwest sectors. These sectors include strong anthropogenic emission sources.

The vertical profile of the same trajectories is rather interesting. Trajectories, with few exceptions, do not descent lower than the starting height, 900 mb level. This shows that the air masses of this factor are not affected from local sources.

By considering all of the discussions for the fourth factor, this factor can be considered as “long range transport” factor and shows the pollutants that are transported from distant sources. In order to locate the emission sources of this factor, PSCF is applied to the factor scores. The result is presented in Figure 3.30. The distributions of PSCF values are same as



(a)



(b)

Figure 3.29. Top (a) and side view (b) of backtrajectories corresponding to highest 20% of the factor scores of Factor 4 of Antalya

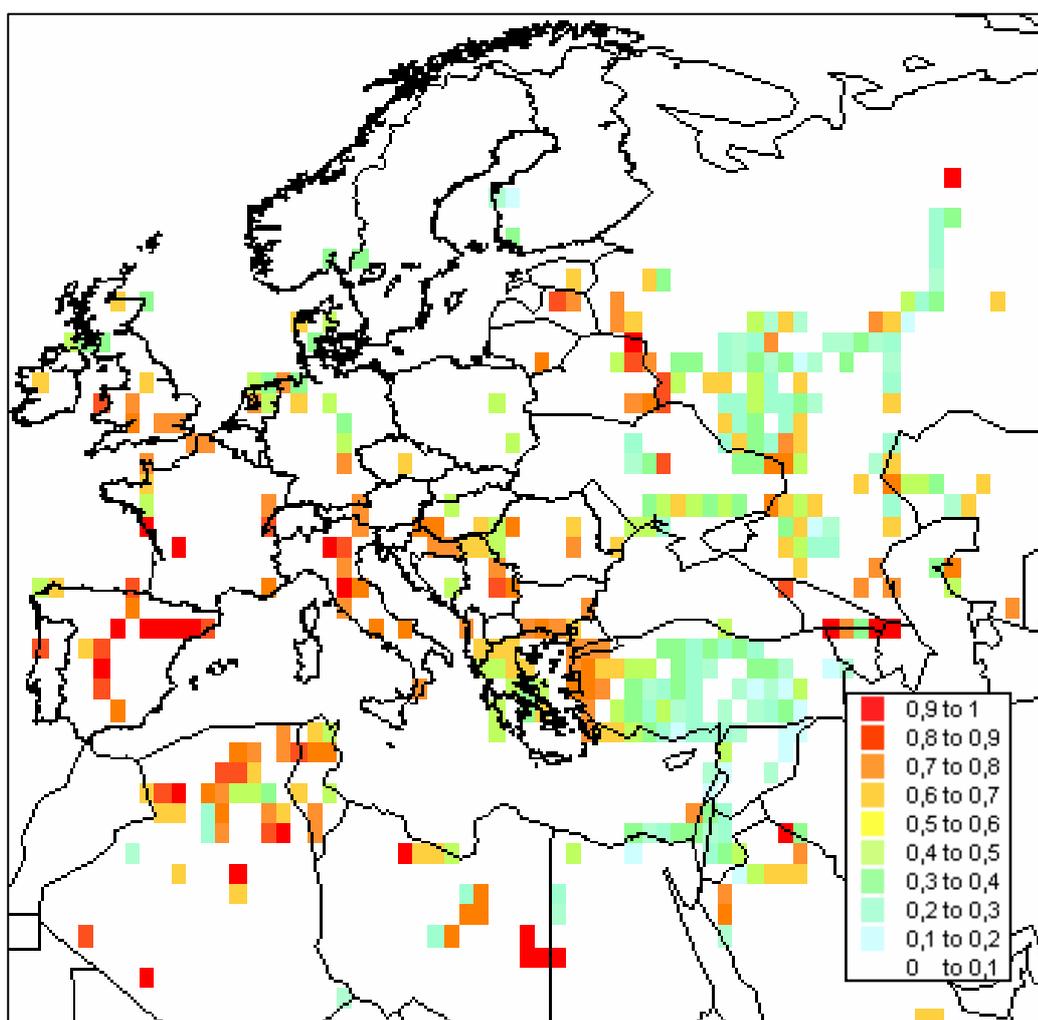


Figure 3.30. Calculated PSCF values for highest 40% factor scores of Factor 4 of Antalya

the PSCF values calculated for SO_4^{2-} concentrations in the previous section. The major contributions to this factor are from Aegean coast, Marmara region, Balkan countries, Ukraine and regions located northern part of Ukraine.

The variance explained, F-Loadings, the EF_c values of elements and seasonal variations of factor scores for Factor 5 are given in Figure 3.31. Factor 5 explains most of the variances of Cr, Ni, Sb and Zn.

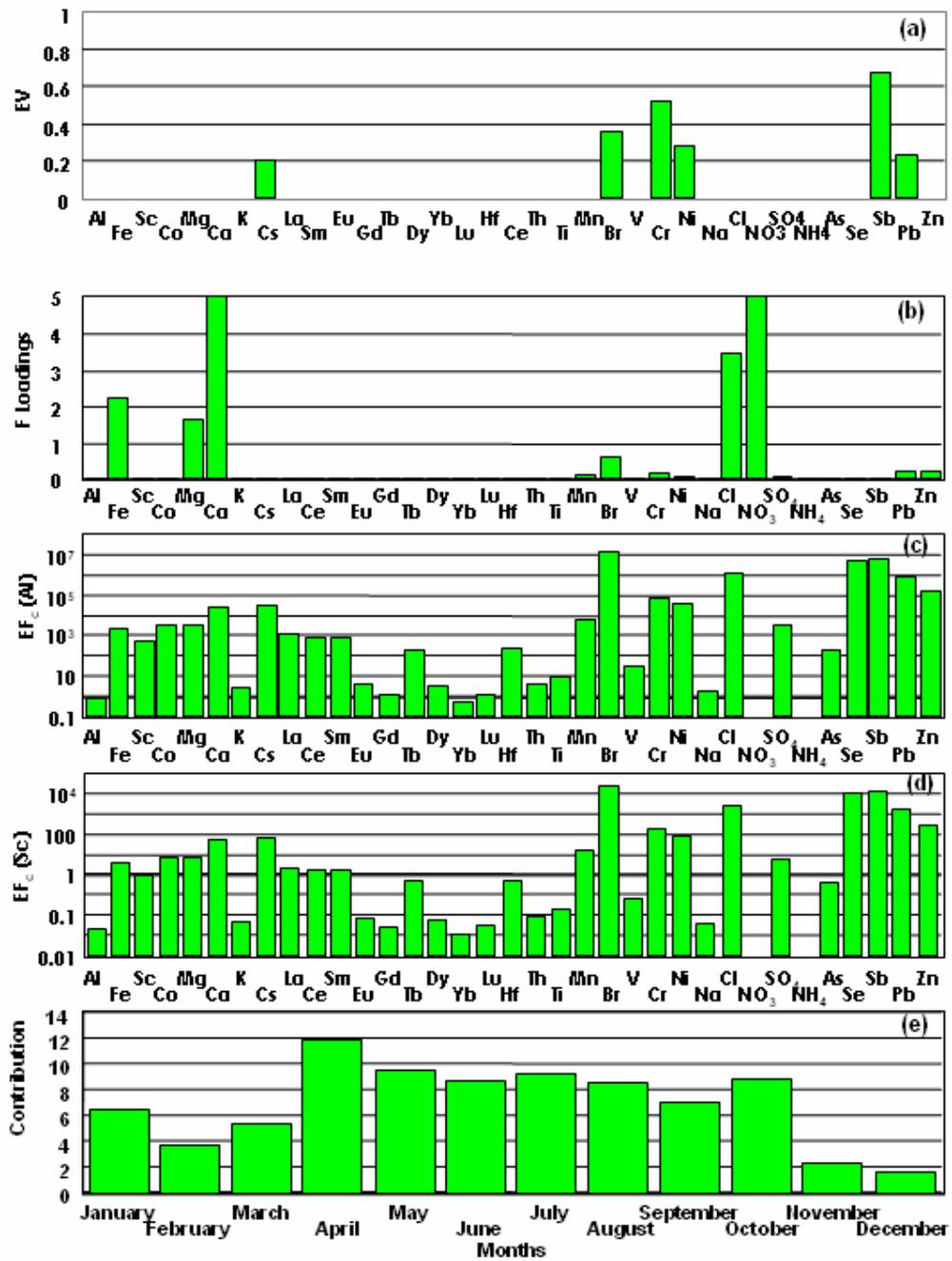


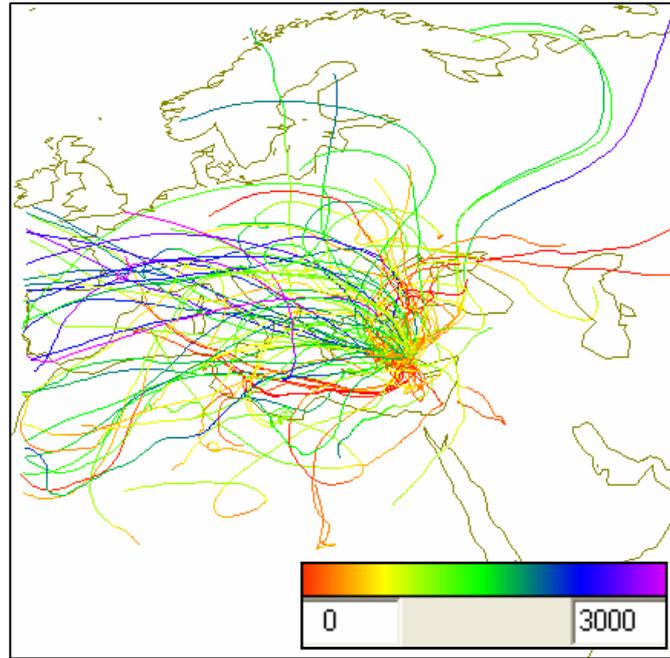
Figure 3.31. Explained Variation (a), Flooding (b), Calculated Enrichment Factor with reference element Al(c) and Sc (d) and Monthly Variation in Factor Scores (e) of Antalya Factor 5

Concentrations of Cl, NO₃⁻, Ca, Mg and Fe are high. As in the previous factors, the anthropogenic components are mixed with small amount of crustal particles. The soil composition in this factor does not fully match with the composition of Mason (1966). The reason of this can be both the difference between the soil compositions and also the high uncertainty of PMF for very low concentrations. NO₃⁻, Br, Cr, Ni, Cl, Se, Sb, Pb and Zn are enriched in this factor. Factor 5 is identified as a metal factor. The factor score values are higher during summer months suggesting effective scavenging during winter and consequently distant sources.

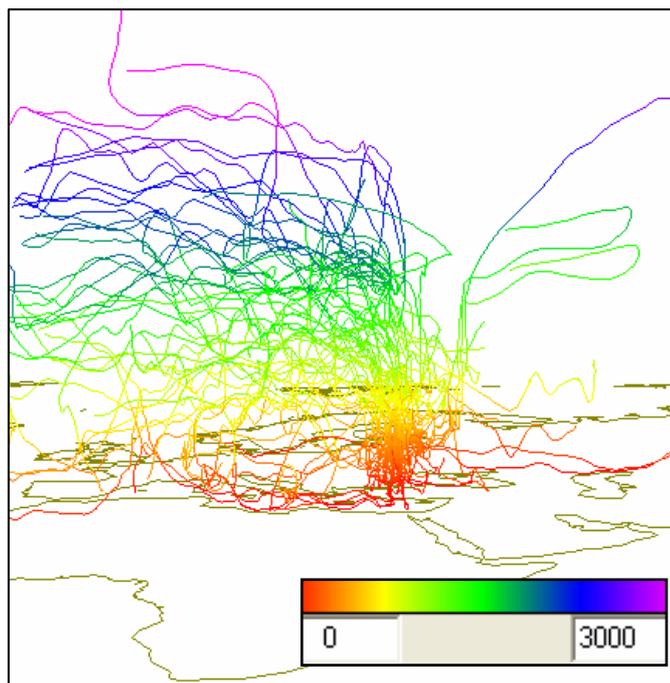
The backtrajectories of the highest 20% of Factor 5 scores are given in Figure 3.32. From the top view, it is observed that the trajectories originate from north and northwest sectors. Although, these sectors are include high emission regions; thus, this supports the presence of anthropogenic metals in the fifth factor. It should be also noted that flow direction of trajectories are not significantly different from flow directions observed in previously discussed factors.

Vertical profiles of the same trajectories show that trajectories do not advect to the surface in the vicinity of the station suggesting that the influence of local sources should be minimal on composition of Factor 5. High factor scores during summer period also confirm this conclusion.

PSCF values calculated for Factor 5 are given in Figure 3.33. Unlike in Factor 4, metal factor is affected from emissions in the eastern parts of Turkey. There is not much specific emission sources in the Eastern Turkey. However, higher PSCF values in the South Eastern Turkey indicate that Afşin-Elbistan power plant can be an effective source for this factor. The other source regions effecting metal factor are Bulgaria, Romania, Ukraine, Belarus and the region that is in the northern part of Ukraine.



(a)



(b)

Figure 3.32. Top (a) and side view (b) of backtrajectories corresponding to highest 20% of the factor scores of Factor 5 of Antalya

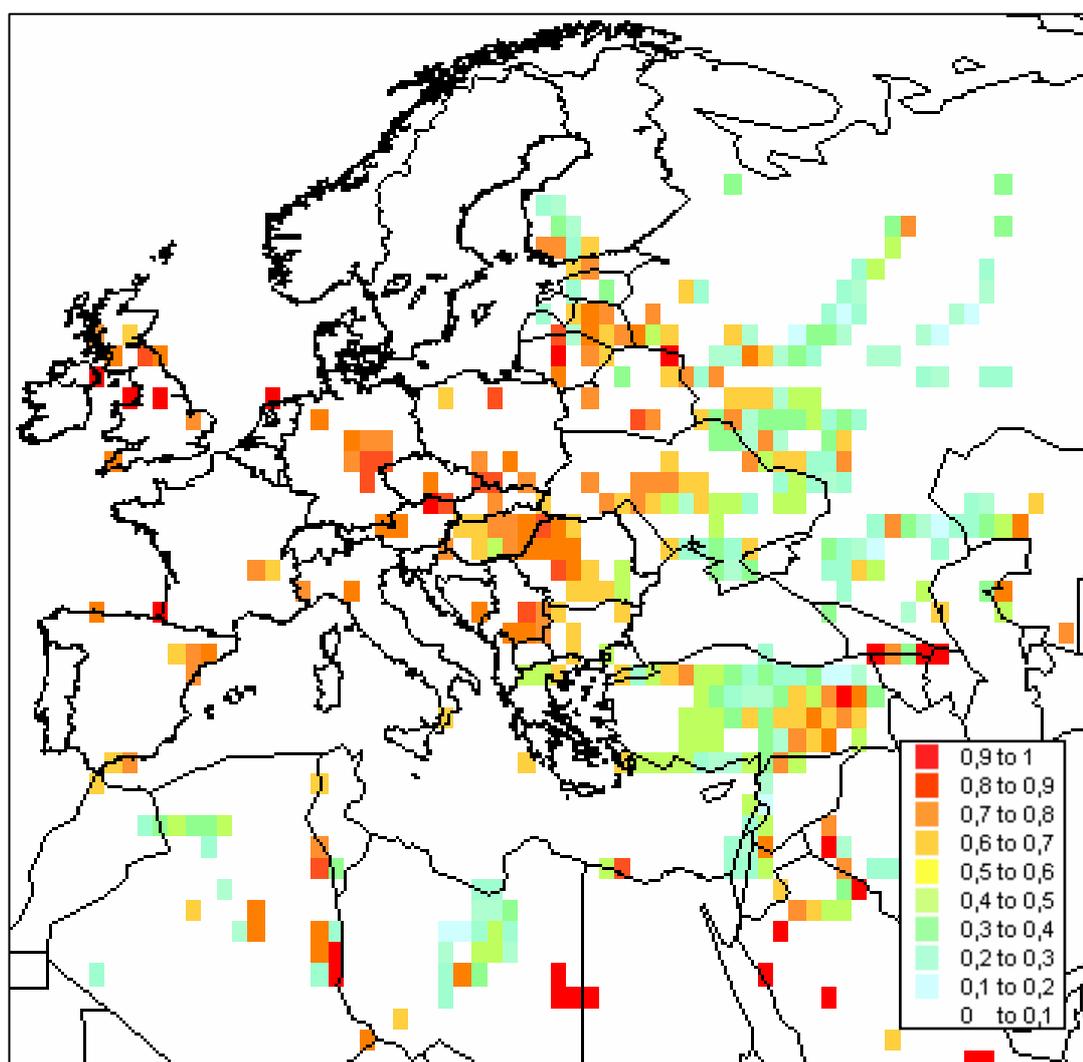


Figure 3.33. Calculated PSCF values for highest 40% factor scores of Factor 5 of Antalya

The variance explained, F-Loadings, the EFC values of elements and seasonal variations of factor scores for Factor 6 are presented in Figure 3.34. This factor shows the existence of a second crustal factor in the Eastern Mediterranean aerosols. Factor 6 explains variances of lithophilic elements Sc, Ca, La, Sm, Eu, Gd, Tb, Yb, Hf, Ce and Th. The EFC values of most of the elements are around unity. However, different from Factor 3, this factor is highly enriched with Br, Se, Sb and Pb and this shows

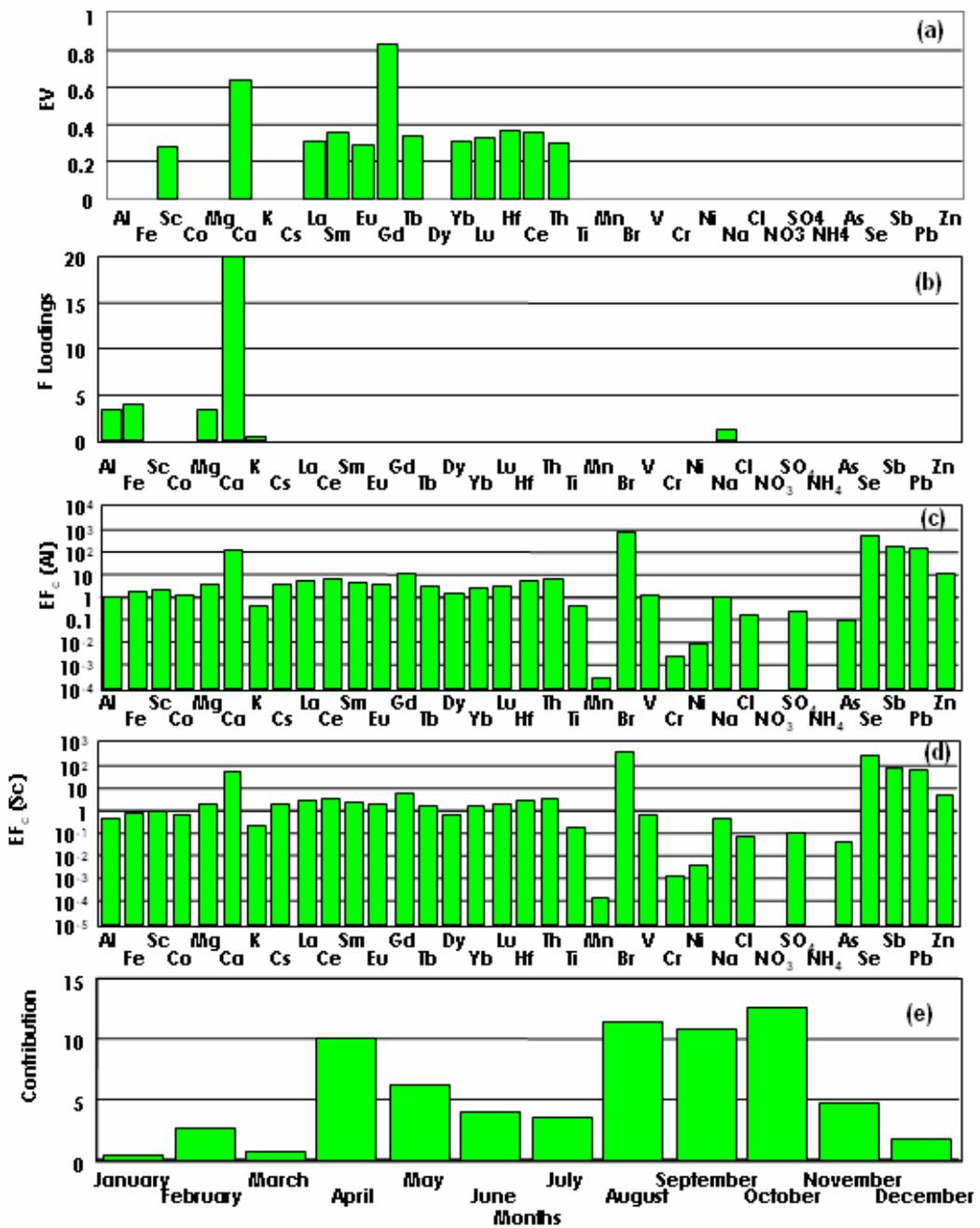


Figure 3.34. Explained Variation (a), Flooding (b), Calculated Enrichment Factor with reference element Al(c) and Sc (d) and Monthly Variation in Factor Scores (e) of Antalya Factor 6

that the anthropogenic particles are intruded to soil particles. This factor is identified as local soil factor. In the following parts of this section, two crustal factors are compared in details.

The variance explained, F-Loadings, the EF_c values of elements and seasonal variations of factor scores for Factor 7 are given in Figure 3.35. Factor explains variances of As, Sb and K. The species with high concentrations in this factor includes Cl, NO₃⁻ Ca and K. As observed in all of the factors, crustal aerosols are also mixed in the Factor 7. Calcium, K, Cl, SO₄²⁻, As, Se, Sb and Pb are enriched in this factor.

This factor is named as As factor because it explains most of the variance As concentrations in the data set and it is clear that it is an anthropogenic factor. However, physical source of this factor is not fully understood. The backtrajectories of the highest 20% contributing days for Factor 7 scores are given in Figure 3.36. From the top view, the trajectories arriving to the station site mainly approaches from west and south west sectors. These two sectors include Mediterranean Sea and Africa, however, in these regions there are not such strong anthropogenic emission sources. However, when vertical profiles of the trajectories show that contrary to Factors 4 and 5, which are thought to be from long range transport, trajectories of highest factor score days of Factor 7 advect to the surface as they come closer to the station site. Consequently, this factor is identified as local pollution factor. Although, other anthropogenic factors have higher contributions during summer time, the factor scores of Factor 7 do not show such a variation, which confirms the possible source region of this factor.

PMF analysis showed that Eastern Mediterranean atmosphere composed of 7 aerosol sources. Three of them originate from natural sources (2 crustal and one sea salt) and the rest of them are composed of

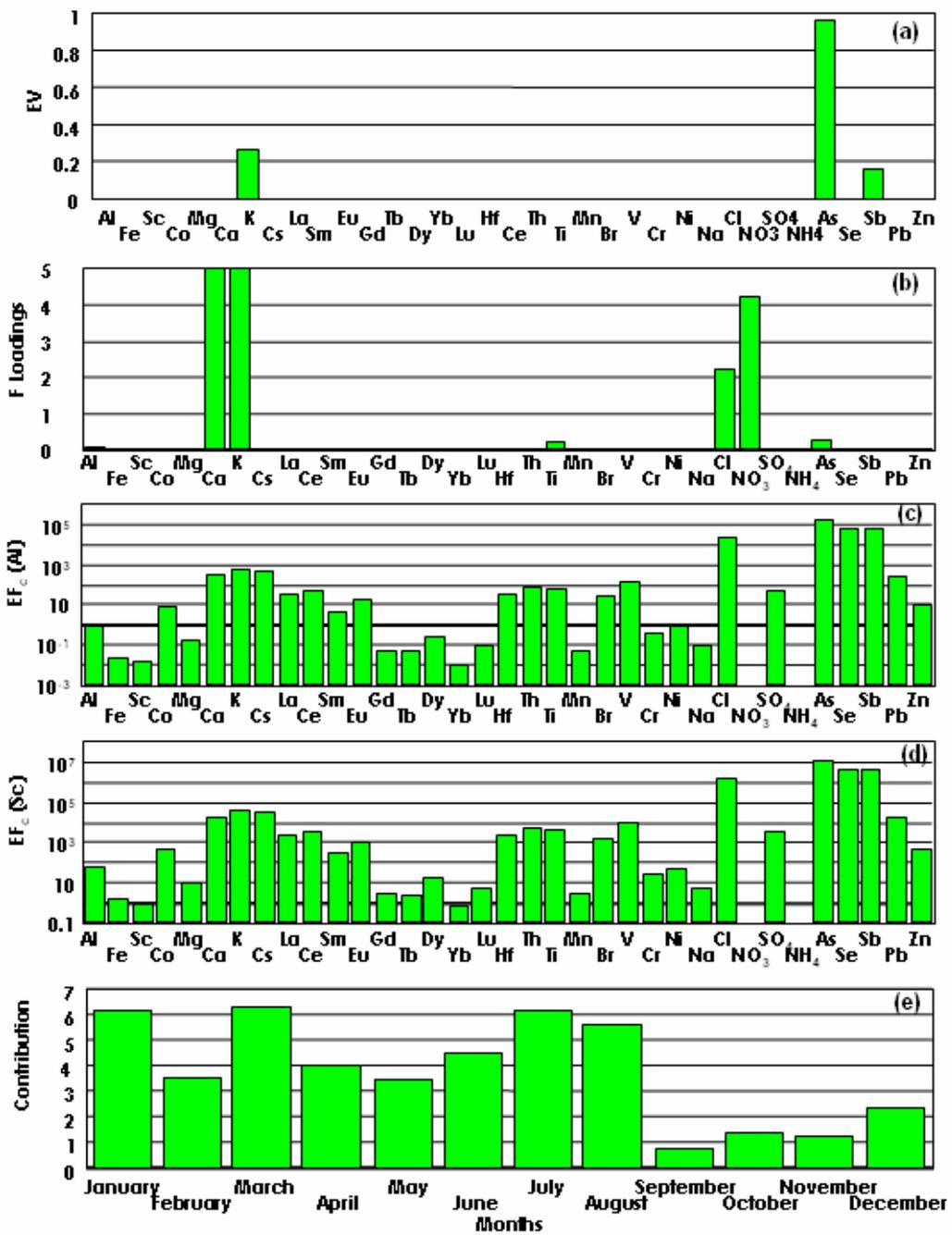
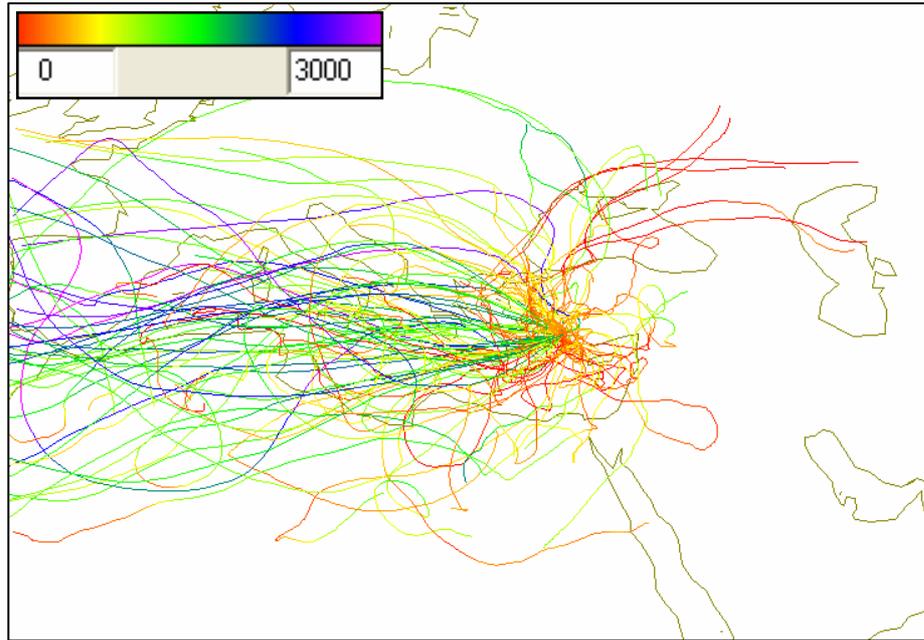
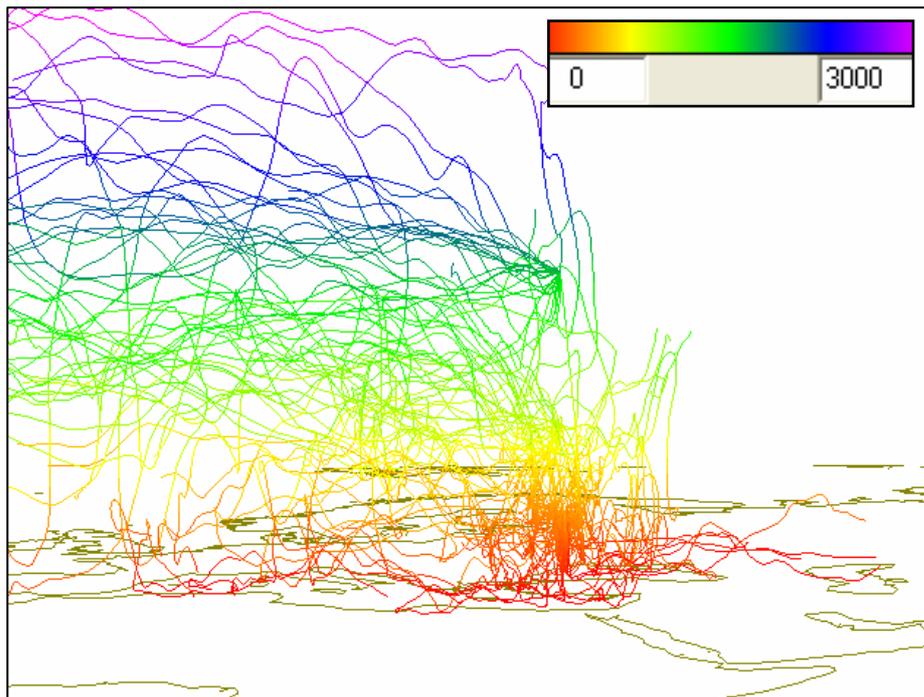


Figure 3.35. Explained Variation (a), Floading (b), Calculated Enrichment Factor with reference element Al(c) and Sc (d) and Monthly Variation in Factor Scores (e) of Antalya Factor 7



(a)



(b)

Figure 3.36. Top (a) and side view (b) of backtrajectories corresponding to highest 20% of the factor scores of Factor 7 of Antalya

anthropogenic emissions. Contribution of factors to total aerosol mass is important to assess true composition of aerosol. Since, the total particle mass is not measured in this study; the correct extraction of this information is not possible. However, with some assumptions, the contribution of each factor to the total aerosol mass can be calculated in to have an idea about the contributions of different components. For this calculation, it is assumed that each factor has soil, sea salt, SO_4^{2-} , NO_3^- , NH_4^+ and metal components. Each of these components has different concentrations in different factors. For example metals have high concentration in metal factor (Factor 5), but their concentrations are low in other factors. Sulfate has the highest concentration in long range transport factor (Factor 4) and relatively low concentrations in others. Crustal dust has high concentrations in Factors 3 and 6, but its concentration is low in the other factors. The concentration of each of these components should be calculated in every factor. Then, summing their concentrations in all factors, contribution of that component on total aerosol mass can be approximated.

For the calculation of crustal component concentrations of Al and Sc are used and the composition of crust is assumed to be same as the composition given by Mason (1966). For the concentration of sea salt component, Na in each factor is assumed originate from sea salt and the composition of sea water is assumed to be similar to that reported by Goldberg (1963). The concentrations of SO_4^{2-} , NO_3^- and NH_4^+ ions are used directly and the metals are assumed to be in the form of oxides in the atmosphere. Abundances of components were calculated for each factor and contribution of factors to total particle mass was determined by summing of each component over the factors. The results are shown in Figure 3.37. As can be seen from the figure, 89% of the aerosol mass in the Eastern Mediterranean atmosphere is composed of sea salt aerosol. This is not surprising in a station that is located just on the coast. Since

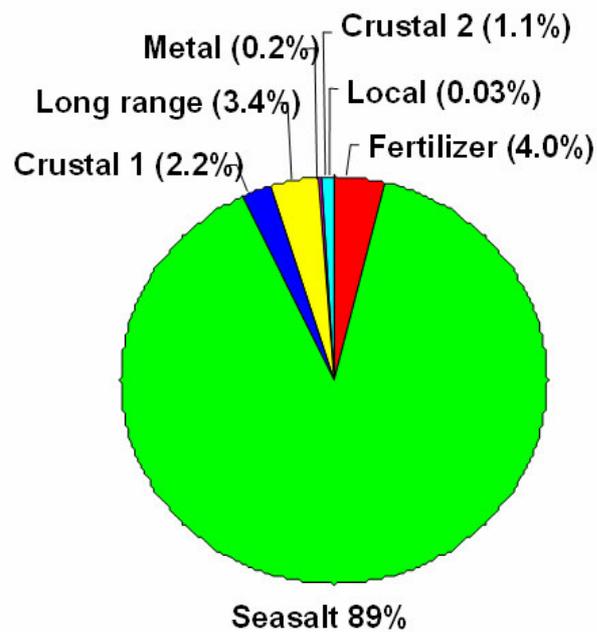


Figure 3.37. Contribution of each of the factor component to the aerosol mass in Eastern Mediterranean region.

the sea salt is not an important component for pollution and such high amounts of sea salt makes difficult to distinguish contributions of other factors. Contributions of components were also calculated excluding sea salt component. The results are given in Figure 3.38. Long range transport and fertilizer factors are two main non-sea salt factors in the Eastern Mediterranean aerosols. Contributions of each of these two factors to the total particle concentration are around 30%. These factors are followed by first and second crustal factors by 20% and 10%, respectively. Contributions of metals and local anthropogenic factors to the total particle mass are less than 2%.

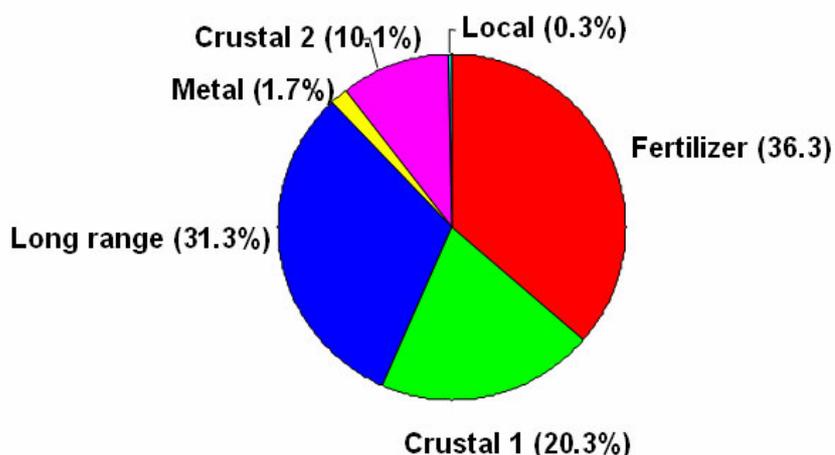
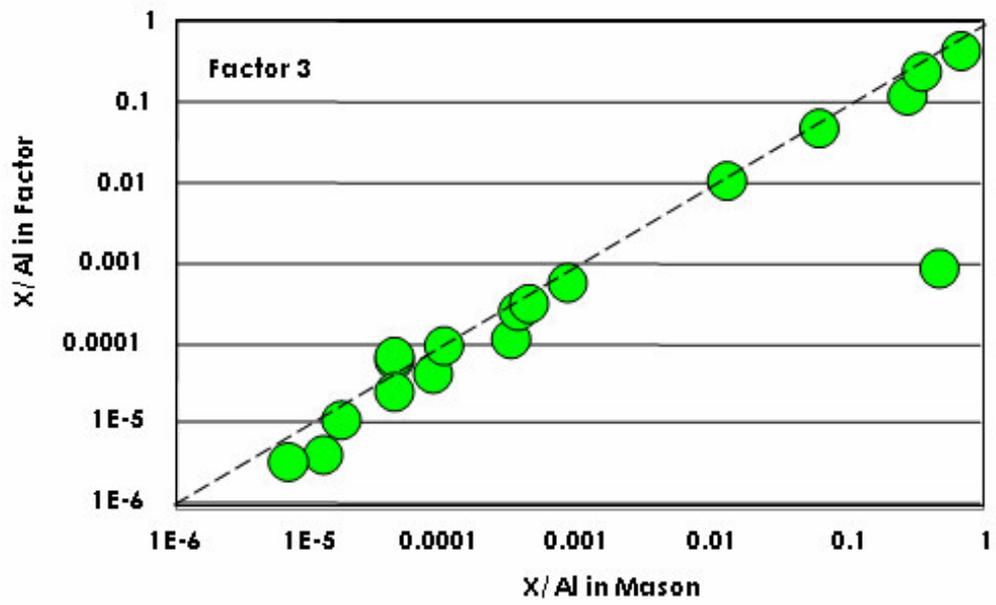
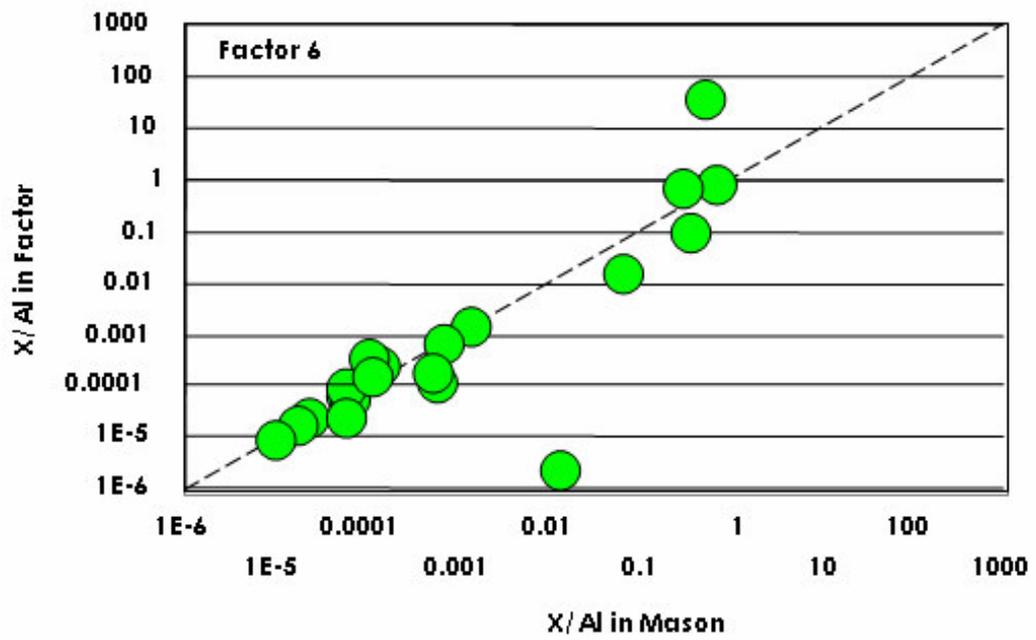


Figure 3.38. Contribution of each of the factor component to the aerosol mass in Eastern Mediterranean region, excluding sea salt.

The PMF exercise using data generated at Antalya station revealed two separate crustal components. The presence of two different crustal components in the Mediterranean region is expected. One of the crustal components should be composed of local soil particles generated in the proximity of station and the other one composed of particles transported from North Africa. Previous studies showed that differentiation of these compounds based on their chemical composition is not possible, because their compositions are fairly similar. But the North African dust is shown to have different mineralogical composition. However, mineral composition of the samples was not measured in this study. With this background, we suspected that one of these factors should represent the local soil and the other one Saharan dust, but which is which is not known. The element-to-Al ratios in factor profiles are compared with corresponding ratio in Mason's (1966) global average soil are given in Figure 3.39. Both, factor 3 and factor 6 profiles, except for few elements, have similar composition with global average soil. Consequently, their



(a)



(b)

Figure 3.39. Correlation of calculated X/Al ratios for Factor 3 (a) and Factor 6 (b) in the Antalya region with the X/Al ratio for Mason (1966).

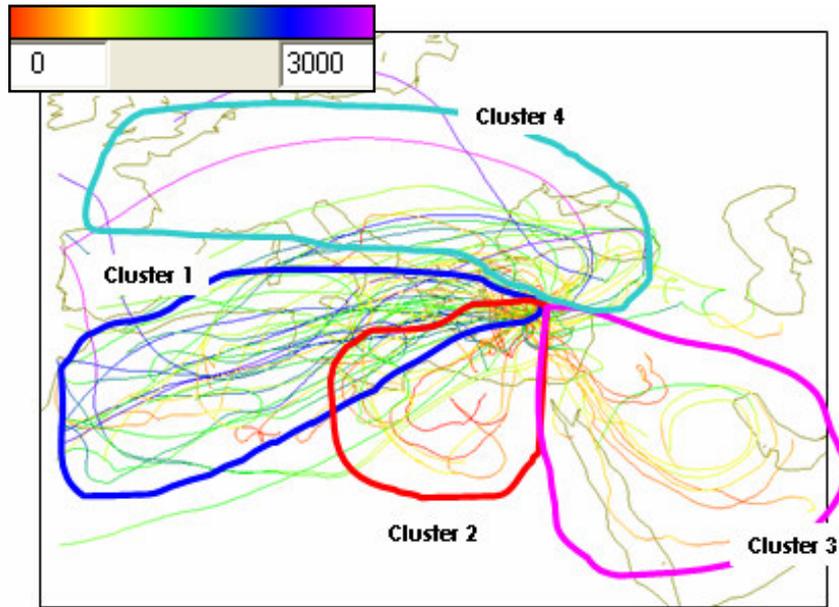
compositions can not be used to identify which of these factors represent the local soil and which one represents the dust transported from North Africa.

The trajectories that correspond to highest 20% of factor 3 and factor 6 scores are depicted in Figures 3.40 and 3.41. Interestingly, the flow that corresponds to the highest contributions of the factors are not dramatically different from each other. The trajectories given in both Figure 3.40a and 3.40b can be clustered into four groups. These clusters are shown in Figure 3.40a. The first cluster includes trajectories that originate over Morocco, Tunisia and Algeria. The second cluster includes trajectories that originate over southern parts of Libya. The third one includes trajectories that originate over Arabic peninsula and the last cluster includes trajectories that spend most of their time outside the North Africa. It should be noted that although trajectories in cluster 4 spent most of their time over Europe or Asia, at one time in their 5.5 day duration they spent some time over North Africa.

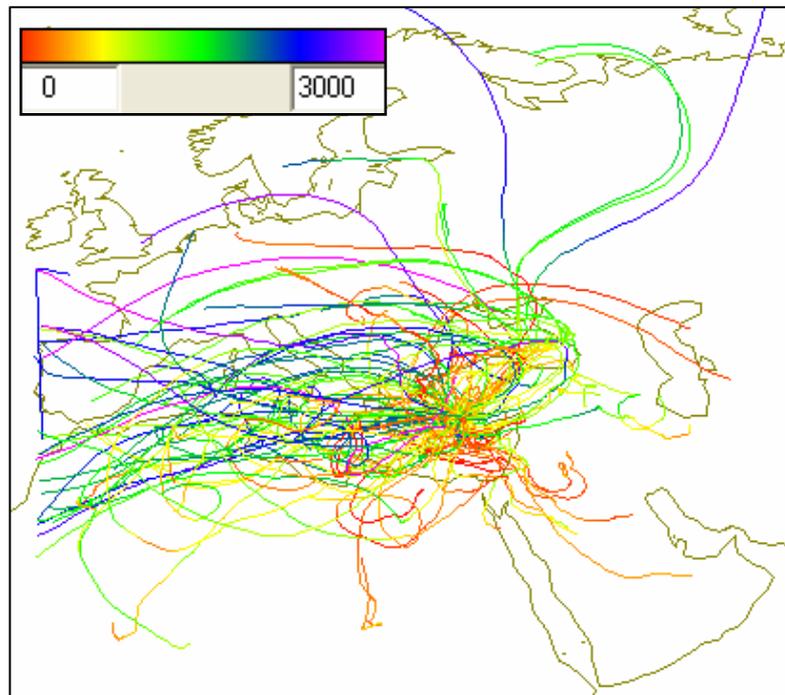
3.6.2. Amasra PMF Results

The final PMF result for Amasra station was calculated with 34 elements and ions by considering the scaled residual distributions of all the species in the analysis. The PMF result showed that Black Sea aerosols have 8 components. Theoretical Q value for 8-factor PMF is 12350 and the actual Q value is 20550.

Factor profile, variance explained, enrichment factors and monthly average factor scores of Factor 1 are given in Figure 3.42. Most of the variances of lithophilic elements are explained in this factor. None of the elements are enriched in a significant amount. This is a typical crustal factor. Since the soil is dry during summer season and soil particles can

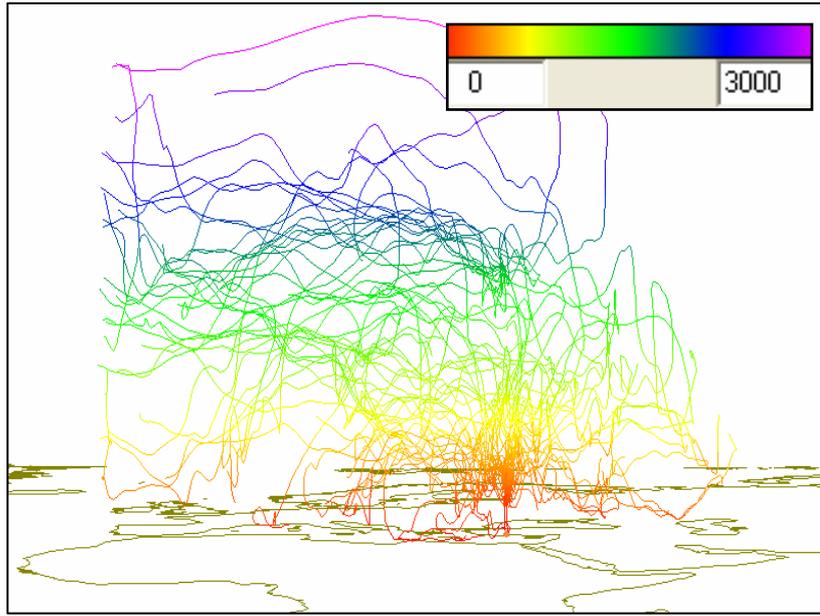


(a)

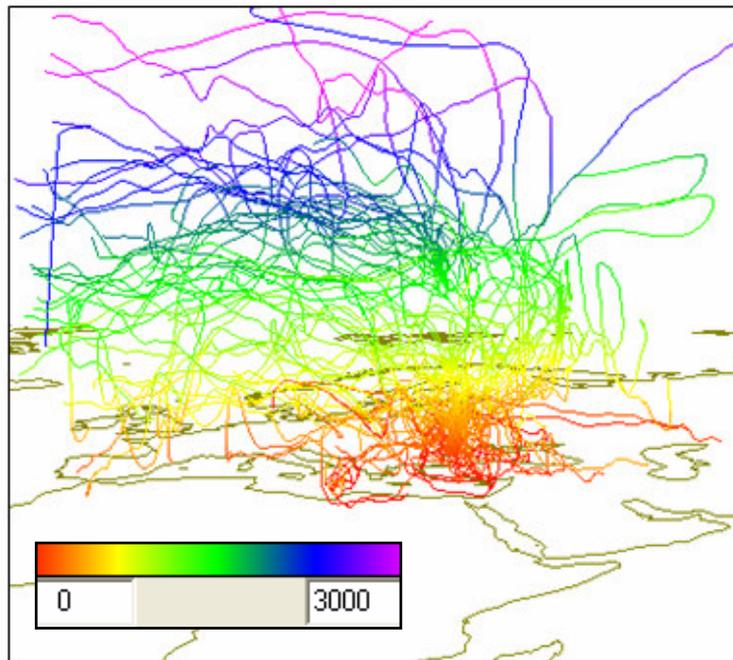


(b)

Figure 3.40. The top profiles of backtrajectories of the highest 20% contributing days for Factor 3 (a) and Factor 6 (b).



(a)



(b)

Figure 3.41. The vertical profiles of backtrajectories of the highest 20% contributing days for Factor 3 (a) and Factor 6 (b).

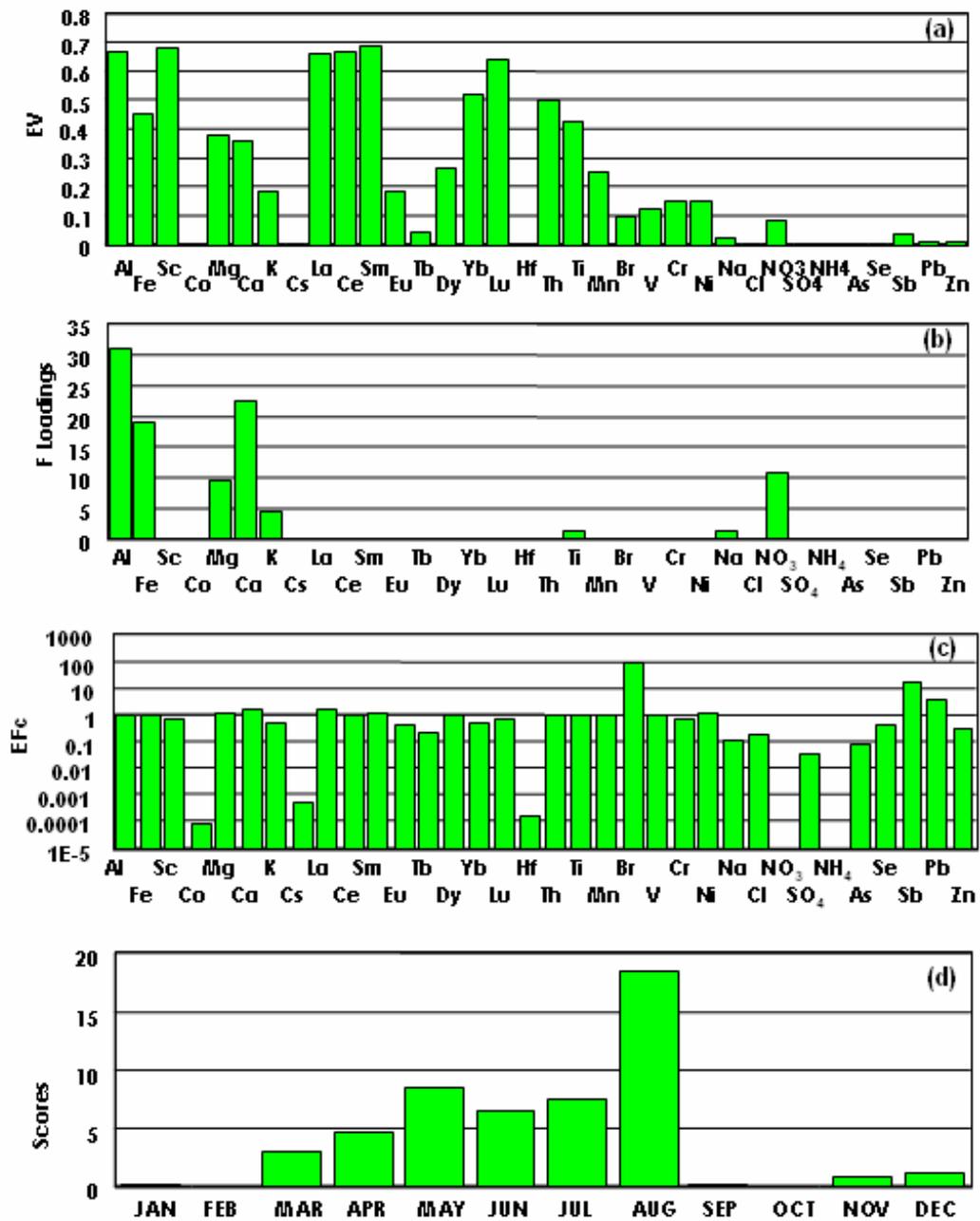


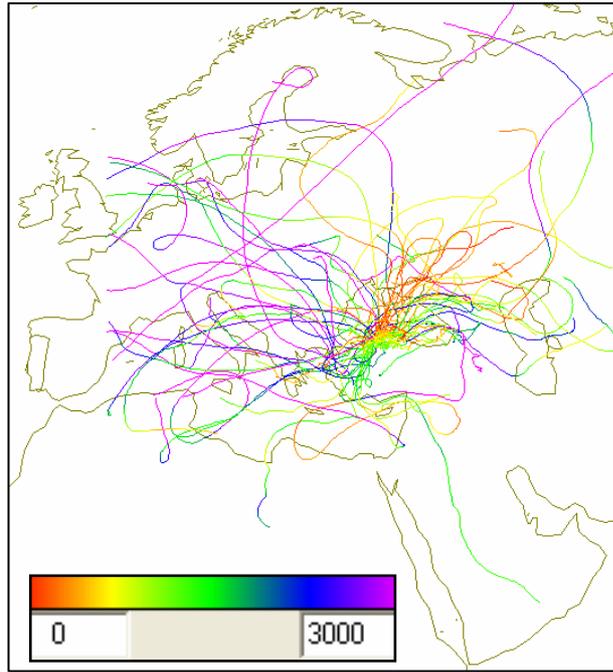
Figure 3.42. Explained Variation (a), Flooding (b), Calculated Enrichment Factor with reference element Al(c) and Monthly Variation in Factor Scores (d) of Amasra Factor 1

easily re-suspend, factor scores are higher during summer months. The concentration of all crustal elements particles in Factor 1 is 380 ng/m^3 whereas total concentration of all other components (SO_4^{2-} , NO_3^- , NH_4^+ , sea salt and anthropogenic elements) is 11 ng/m^3 .

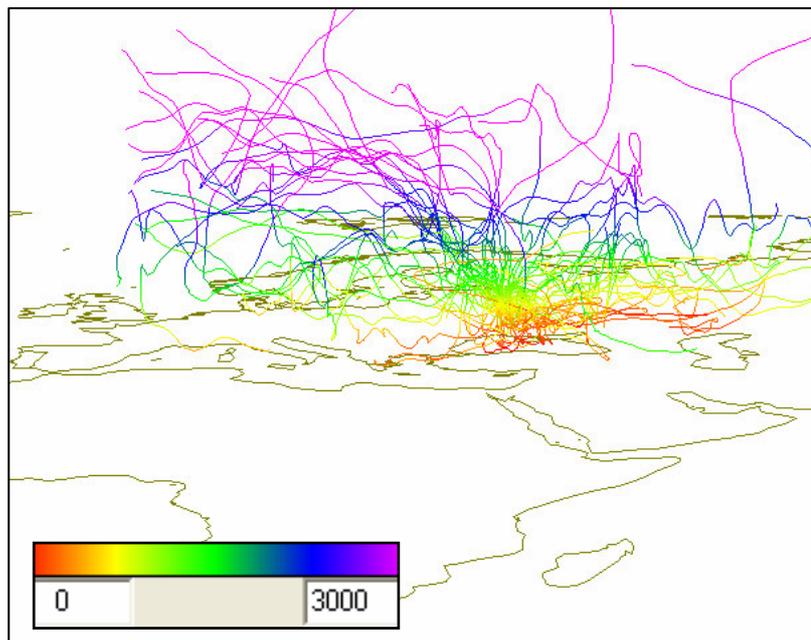
The backtrajectories corresponding to highest 20% of factor scores days are presented in Figure 3.43. The top view shows that trajectories are distributed to different wind sectors. Approximately similar distributions of trajectories are observed in other factors also. Such distribution is related to flow climatology of the region, no relation between the top views of the trajectories that corresponds to highest 20% of factors scores and sources and source regions of pollutants are observed. This is a clear indication that only low-lying trajectories carries information about factors, not the trajectories at all levels. The vertical profiles of the same trajectories shows that the trajectories do not advect to surface regions close to the Amasra station suggesting that local crust is not an important source of crustal aerosol component in the Black Sea atmosphere.

The comparison between element to Al ratios in the Factor 1 profile with the same ratio in the Mason composition is given in Figure 3.44. As can be seen from the figure, the soil composition of West Black Sea aerosols is found to be same as the reference soil composition.

Factor profile, variance explained, enrichment factors and monthly average factor scores for the second factor are given in Figure 3.45. This factor explains in low amounts variances of both the crustal and the anthropogenic elements. The highest concentrations in the factor profile are for SO_4^{2-} , NO_3^- and NH_4^+ ions. Figure 3.45c show that SO_4^{2-} , Br, Sb and Pb are highly enriched relative to soil. Since how much of the nitrogen concentration given in global compilations are in the form of NO_3^- and how much in the form of NH_4^+ is not known, enrichment factor



(a)



(b)

Figure 3.43. Top (a) and side view (b) of backtrajectories corresponding to highest 20% of the factor scores of Factor 1 of Amasra

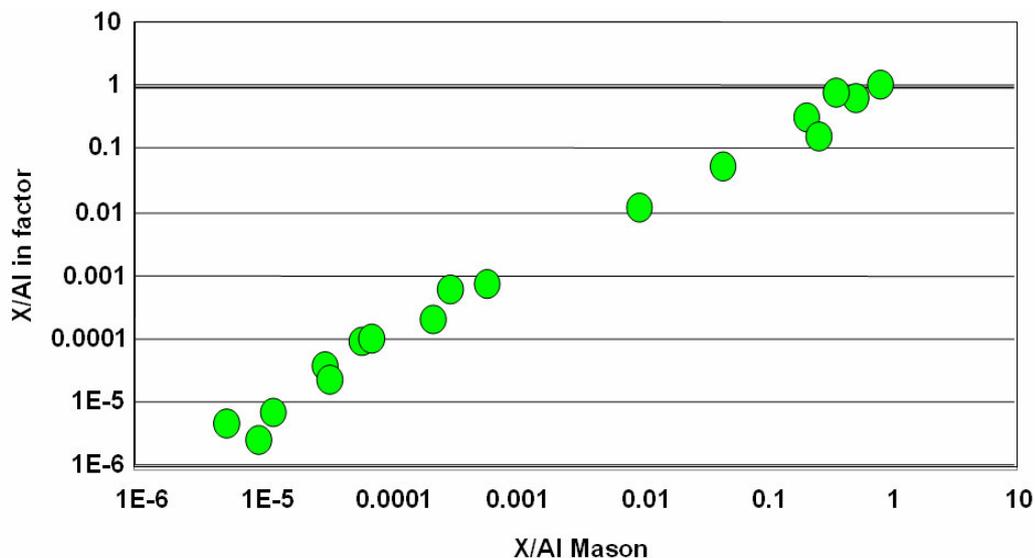


Figure 3.44. The comparison of X/Al ratios of lithophilic elements in Factor 1 with the same ratio in the Mason.

values of NO_3^- and NH_4^+ in atmospheric particles can not be calculated. However, since both NO_3^- and NH_4^+ are major components in Factor 2, they are also expected to be enriched in the factor profile.

Elements with mixed sources such as Mn, V, Cr and Ni are slightly enriched in Factor 2. It is believed that Cs is also enriched in this factor; however, this enrichment is considered to be an artifact due to the calculations performed in the program. This factor is an anthropogenic factor which has mainly metal components.

The backtrajectories corresponding to highest 20% contribution days to this factor are presented in Figure 3.46. From the top view, this factor looks like similar to the other anthropogenic factors where the trajectories mainly originated from west, north and northwest sectors. The important point is that the trajectories that reach to the receptor site from these sectors can contain almost all types of pollutants.

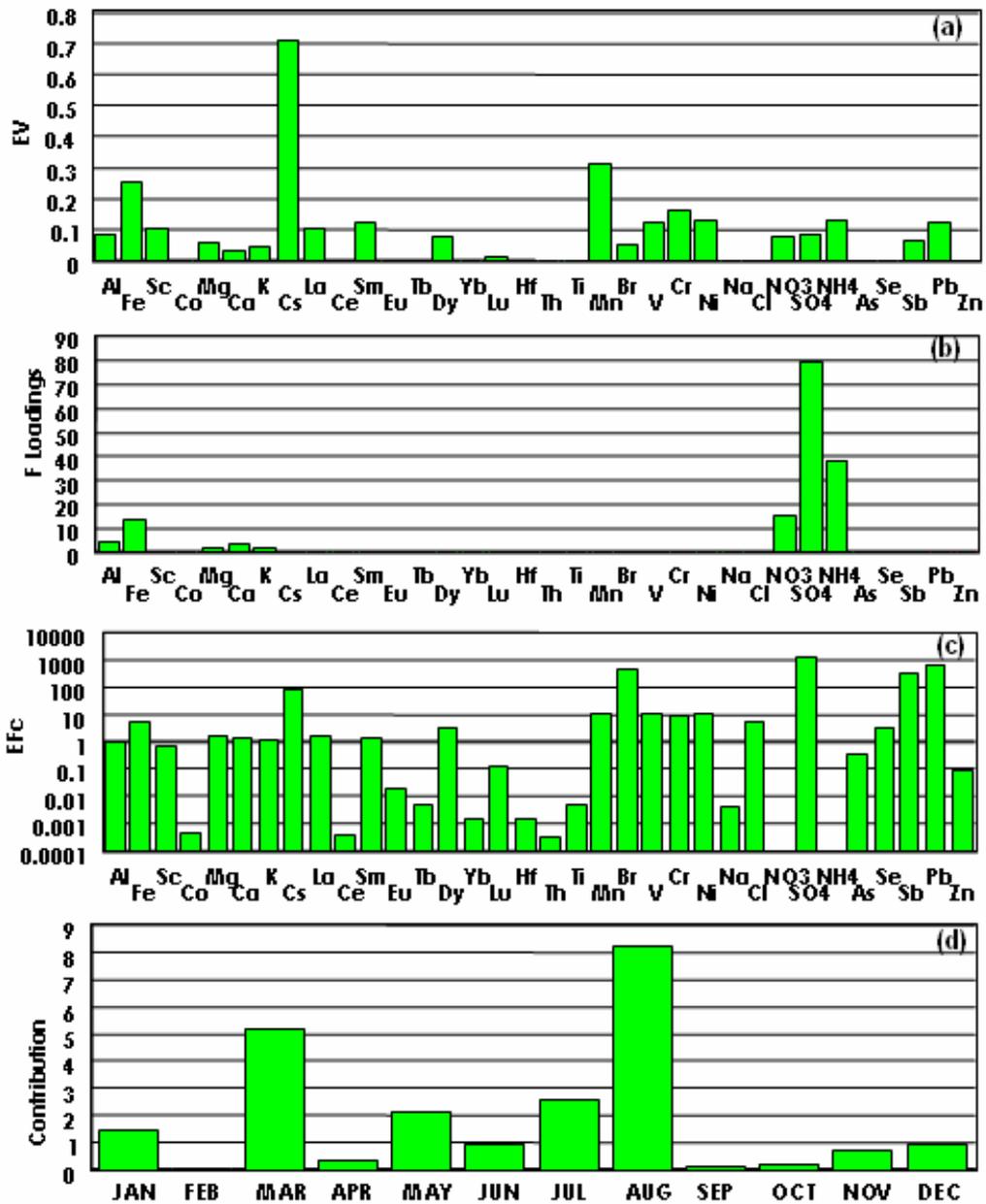
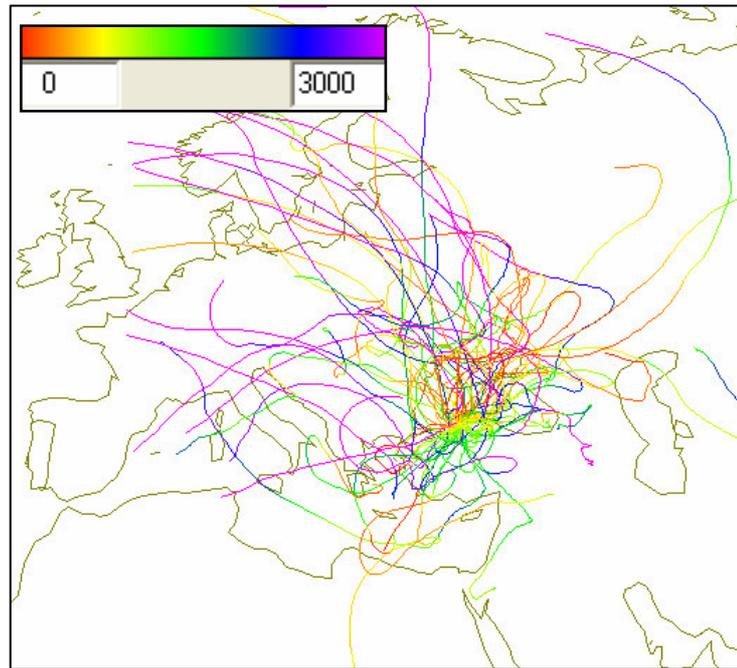
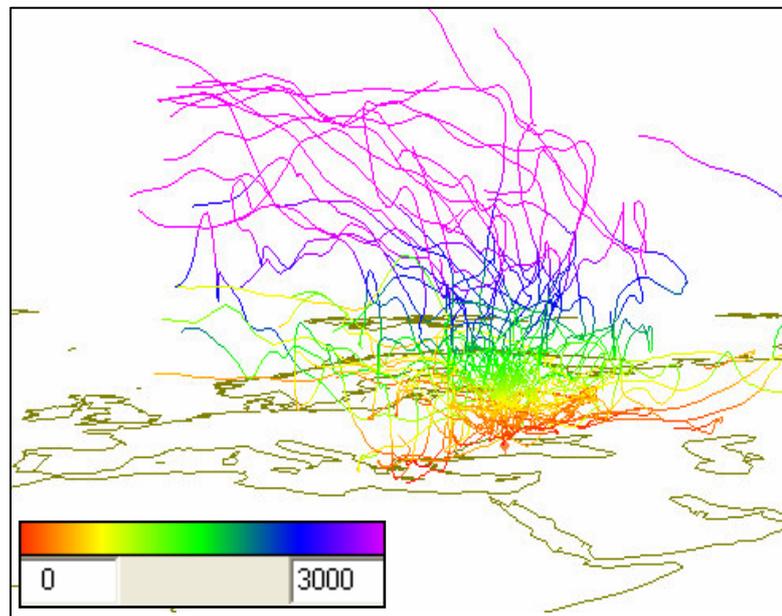


Figure 3.45. Explained Variation (a), Flooding (b), Calculated Enrichment Factor with reference element Al(c) and Monthly Variation in Factor Scores (d) of Amasra Factor 2



(a)



(b)

Figure 3.46. Top (a) and side view (b) of backtrajectories corresponding to highest 20% of the factor scores of Factor 2 of Amasra

Vertical profiles of the same factors show that trajectories that lay near the surface follow two different paths. The first path transports pollutants from north and the second path carries pollutants from the Middle East. Generally, trajectories coming from Europe do not move under than 1000 m. Thus, the source regions that affect this factor must be within these two sectors.

Source regions crudely suggested by backtrajectories profiles was tested by calculating PSCF distributions. The highest 40% of Factor 2 scores were used as polluted data set. Statistically significant PSCF values are shown in Figure 3.47. Central parts of Russia and the Middle East region, especially Israel, are the two important source regions for this factor which agrees with the transport paths of low-level trajectories. It is documented in the literature that there are important emission sources in the central parts of Russia (Kakareka et al, 2004). Thus transport of metal bearing particles from this region is not surprising. It can be said that Israel also contributes to the same factor. In Israel, metal industry is not so dense but there are 6 power plants located along the coast which are the most important emission sources in that region.

Factor profile, variance explained, enrichment factors results and monthly average factor scores of Factor 3 are given in Figure 3.48. This factor explains most of the variances of Na and Cl. As well as smaller fraction of variances of NO_3^- ion and crustal elements variances are also explained in this factor. In this factor Na and Cl have the highest concentrations which are followed by NO_3^- , NH_4^+ and some crustal elements.

Calculated EF_c values, demonstrates that Na, Cl, Br, Sb and Pb are enriched. To these elements, NO_3^- and NH_4^+ ions can be added. Concentration of sea salt component found by using Goldberg's (1963) sea water composition is 4600 ng/m^3 . Concentrations of other

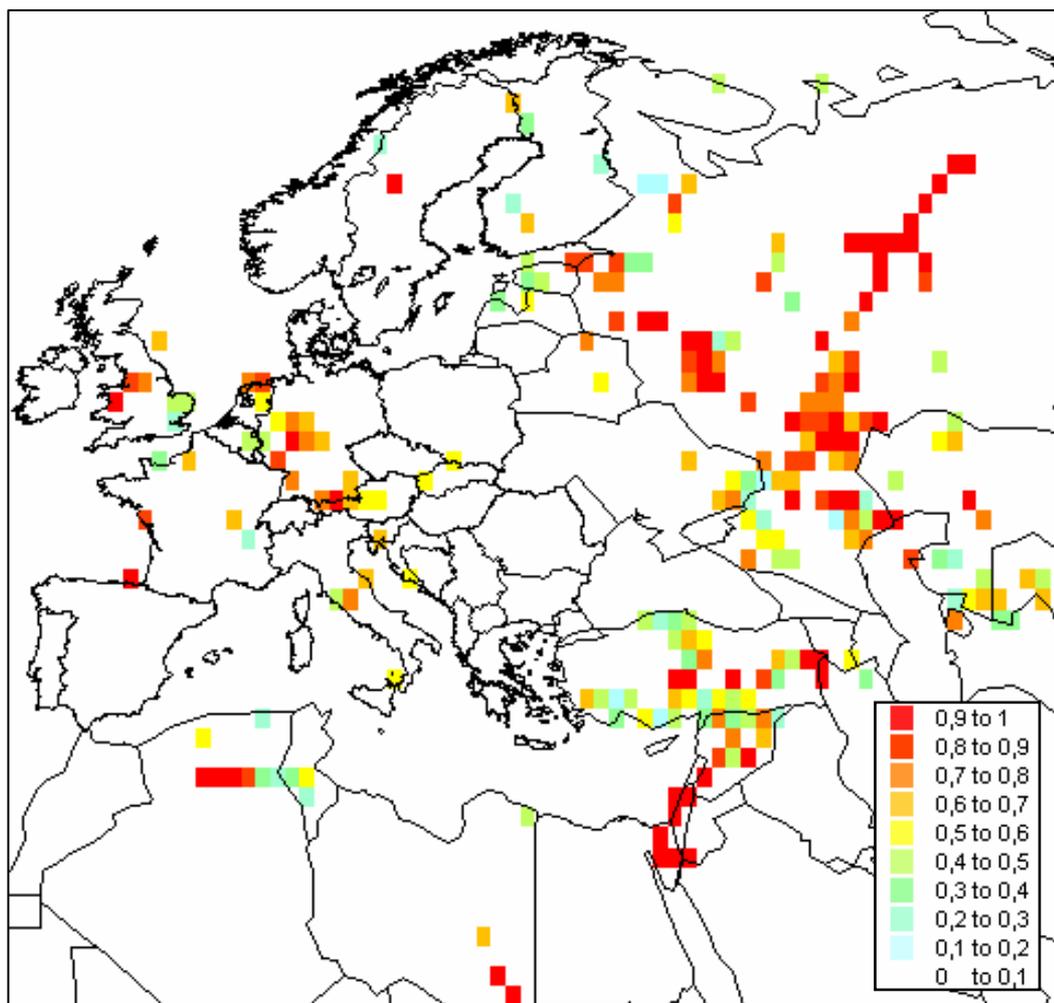


Figure 3.47. Calculated PSCF values for highest 40% factor scores of Factor 2 of Amasra

components in Factor 3 are small with some anthropogenic emissions. Therefore Factor 3 is considered as sea salt factor.

The factor scores do not show net seasonal variation. The trajectories corresponding to the highest 20% contributing days are given in Figure 3.49. The top view of this factor is not so different from the top view images of other factors. However, in vertical profiles of the trajectories, the advection of the trajectories over the Black Sea is noticeable.

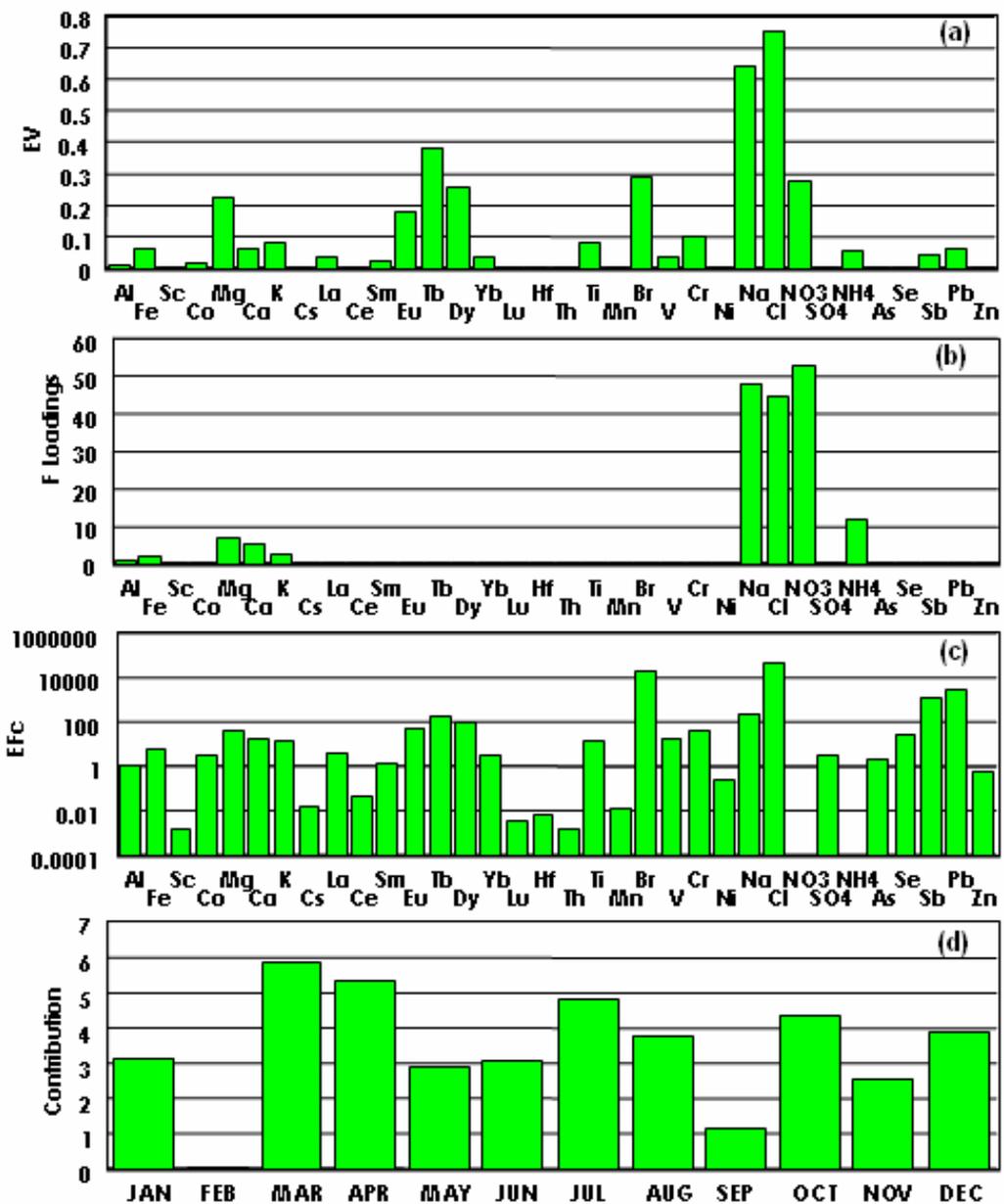
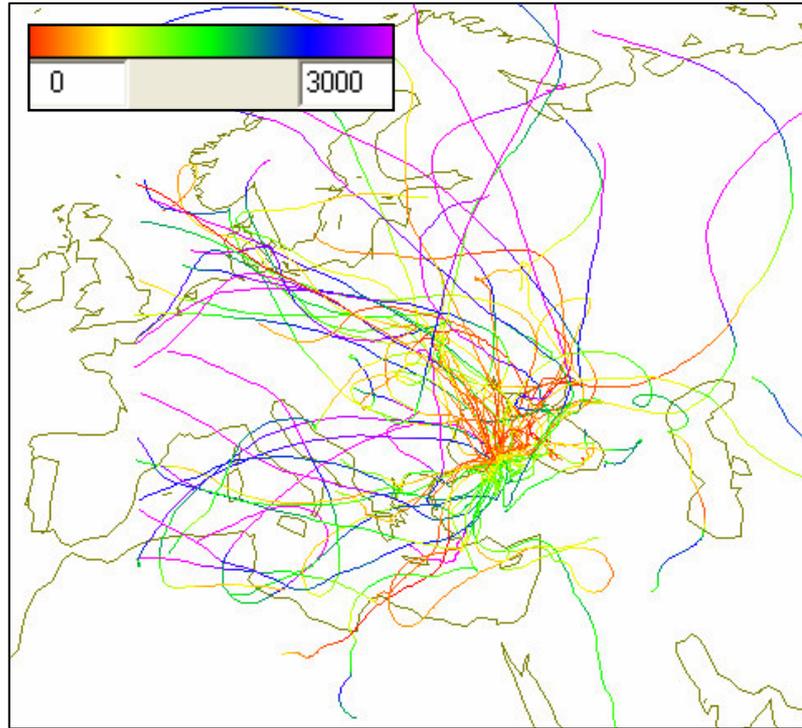
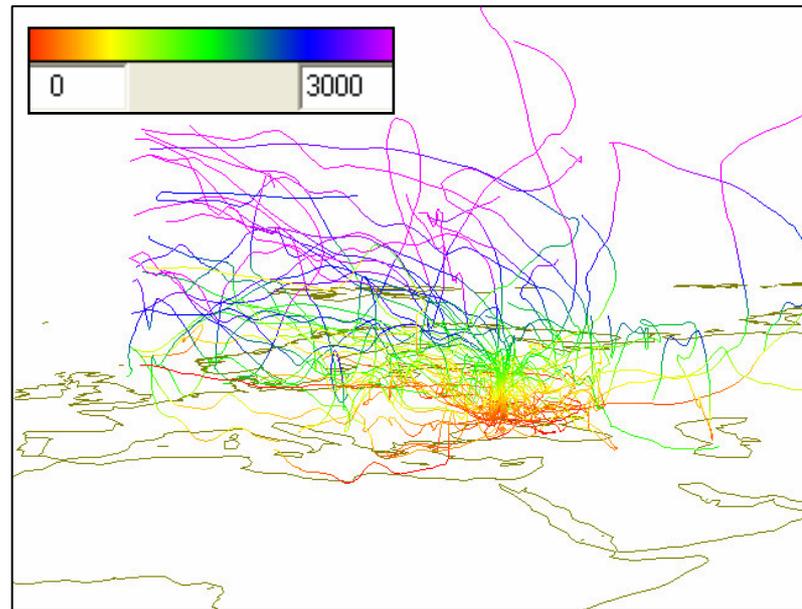


Figure 3.48. Explained Variation (a), Flooding (b), Calculated Enrichment Factor with reference element Al(c) and Monthly Variation in Factor Scores (d) of Amasra Factor 3



(a)



(b)

Figure 3.49. Top (a) and side view (b) of backtrajectories corresponding to highest 20% of the factor scores of Factor 3 of Amasra

However, the composition of this factor is different than the sea salt composition of Antalya station. In sea salt factor of Amasra station intrusion of some anthropogenic species to the factor are also observed.

Factor profile, variance explained, enrichment factors results and monthly average factor scores for the fourth factor are given in Figure 3.50. This factor explains most of the variance in As concentrations. The factor also explains variances of some crustal and anthropogenic elements. The highest concentrations observed in Factor 4 are for SO_4^{2-} and NO_3^- ions.

In this factor there is also a crustal component. However, Al is under predicted. Therefore, Sc is taken as the reference for the EF_c calculations. In Factor 4, SO_4^{2-} , As, Se, Sb, Pb and Br are highly enriched and V and Cr also have EF_c values greater than 10.

Factor scores are higher during winter months, suggesting a local contribution of the composition of Factor 4. The backtrajectories corresponding to highest 20% contribution days to Factor 4 scores are given in Figure 3.51. The top view is same with the previous factor. However, vertical profile shows that trajectories which move below 1000 m are under influenced by the local sources.

This factor is identified as anthropogenic originated and As factor. To distinguish the source regions, PSCF is applied and statistical significance of the PSCF values are tested by bootstrapping technique. The distribution of PSCF values are shown in Figure 3.52. The regions that effect the composition of this factor are identified as eastern part of Turkey, Middle East, especially Israel, and Balkans.

Factor profile, variance explained, enrichment factors results and monthly average factor scores of Factor 5 are given in Figure 3.53. In this factor,

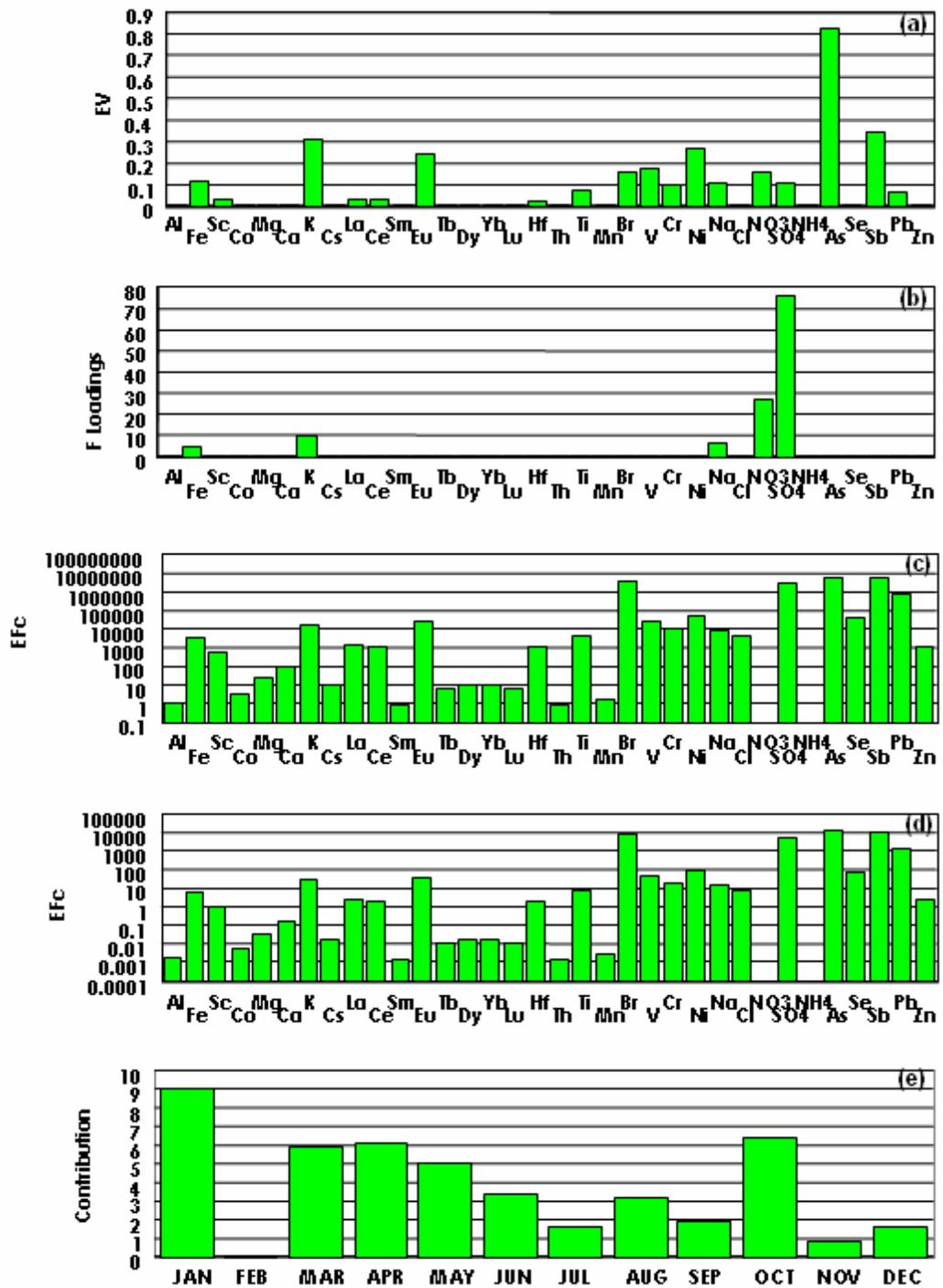
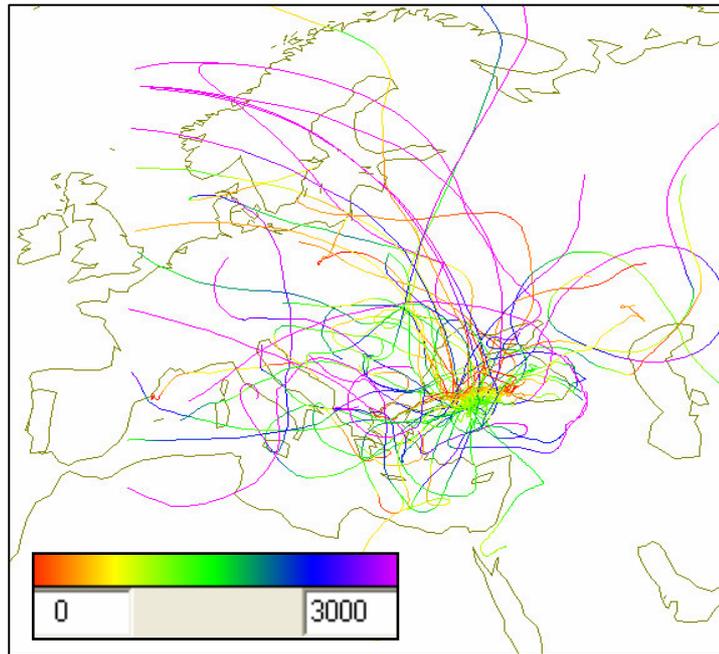
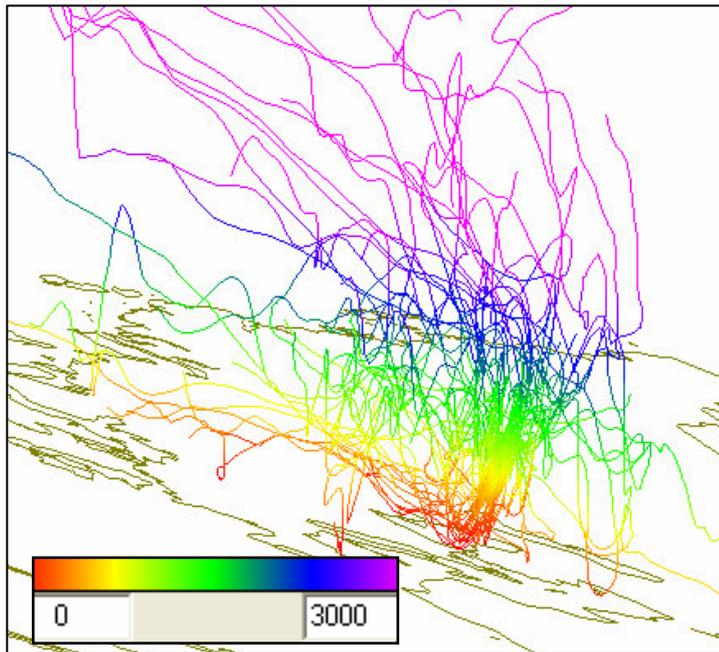


Figure 3.50. Explained Variation (a), Floading (b), Calculated Enrichment Factor with reference element Al(c) and Sc (d) and Monthly Variation in Factor Scores (e) of Amasa Factor 4



(a)



(b)

Figure 3.51. Top (a) and side view (b) of backtrajectories corresponding to highest 20% of the factor scores of Factor 4 of Amasra

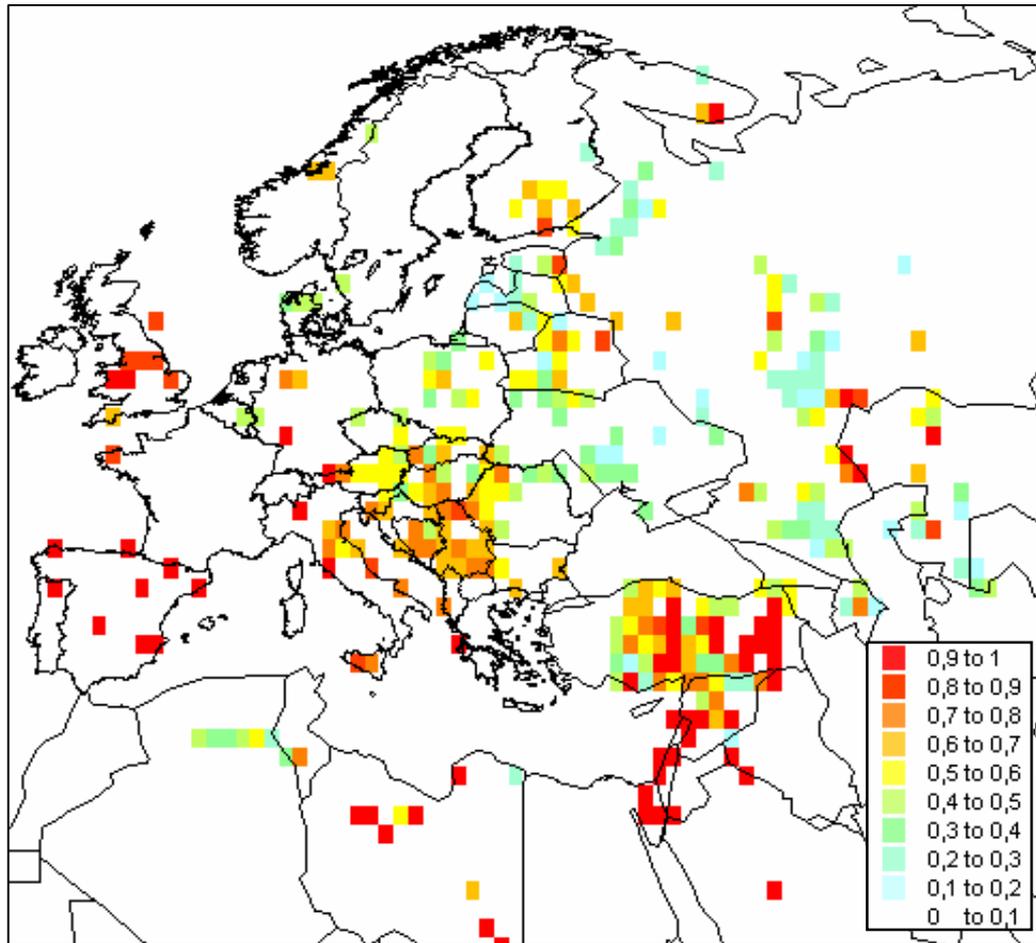


Figure 3.52. Calculated PSCF values for highest 40% factor scores of Factor 4 of Amasra

NH_4^+ has highest concentration; besides NO_3^- , Cl and some crustal elements are also in high concentrations. A significant portion of variances of some of the crustal elements, NH_4^+ , As and Sb are explained in this factor. A significant fraction of variance in Co concentrations are explained by Factor 5. Cobalt, Br, Cl, As, Se, Sb and Zn are enriched in this factor. The factor scores are higher in summer months especially during August, September and October months.

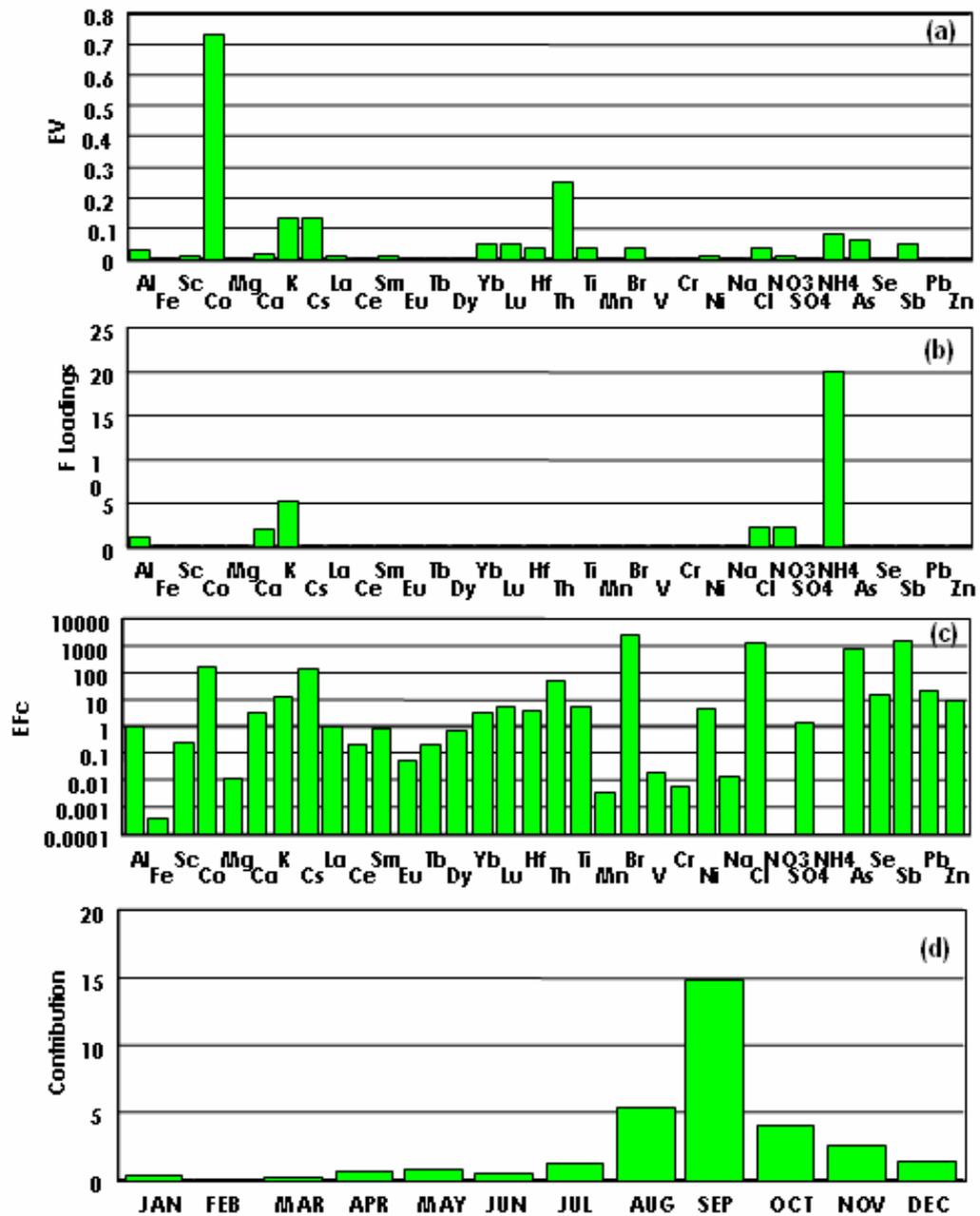


Figure 3.53. Explained Variation (a), Flooding (b), Calculated Enrichment Factor with reference element Al(c) and Monthly Variation in Factor Scores (d) of Amasra Factor 5

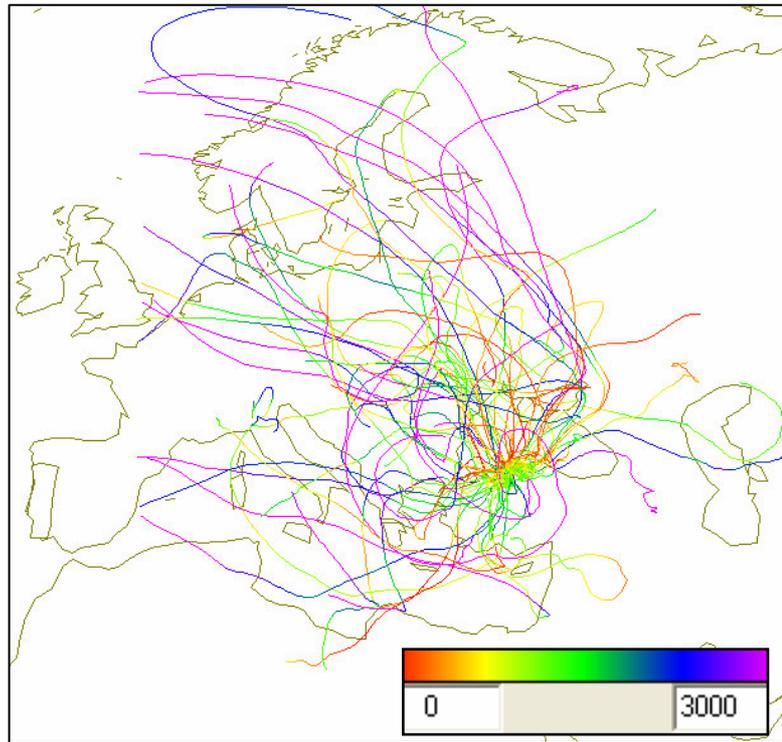
The backtrajectories of highest contribution 20% days to Factor 5 are presented in Figure 3.54. The top view of backtrajectories is again similar figures reported for other anthropogenic factors. The air masses are mainly from north, northwest and west sectors. From the vertical profile, it is observed that the trajectories that pass over Europe are not moving lower than 1500 m; but, the trajectories that are arriving from the north sector are low –level.

The PSCF values are calculated for the factor scores and the distribution is given in Figure 3.55. The source regions are in the western parts of Turkey, Italy and Germany. Besides, there are some source regions identified in the northern part of Caspian Sea and western parts of Ukraine.

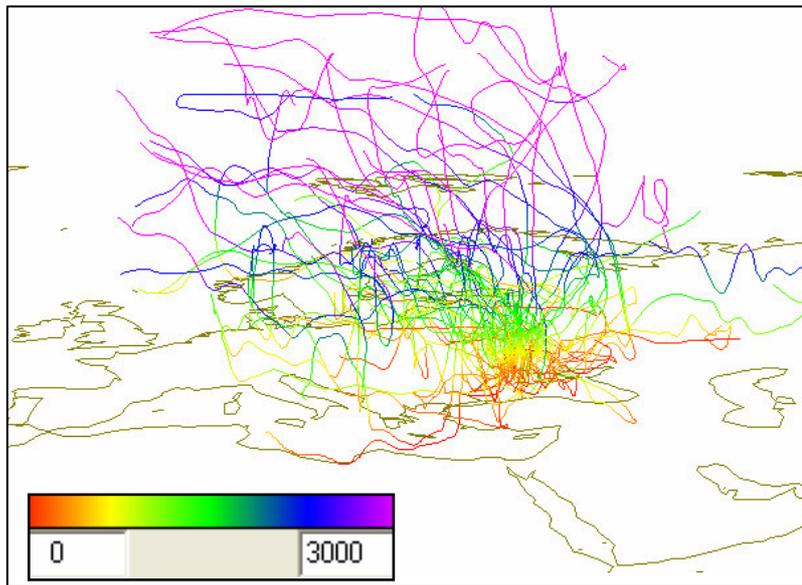
Factor 5 is an anthropogenic factor with highly enriched with metals, but exact identification of this factor could not be possible.

Factor profile, variance explained, enrichment factors results and monthly average factor scores for the sixth factor are given in Figure 3.56. This factor is a clear SO_4^{2-} factor. The significant part of the variances of SO_4^{2-} and NH_4^+ are explained by this factor. Also this factor also explains the variances of Sb, Pb and some crustal elements.

The SO_4^{2-} and NH_4^+ have the highest concentrations the factor profile. Chloride, SO_4^{2-} , As, Se, Sb and Zn are enriched and NO_3^- and NH_4^+ are expected to be enriched. An important point to note in this factor is that species SO_4^{2-} , NO_3^- , NH_4^+ , As and Se are well documented thermal power plant marker species. Since all power plant marker species are enriched in Factor 6, this factor represents a component derived from power plant emissions.



(a)



(b)

Figure 3.54. Top (a) and side view (b) of backtrajectories corresponding to highest 20% of the factor scores of Factor 5 of Amasra

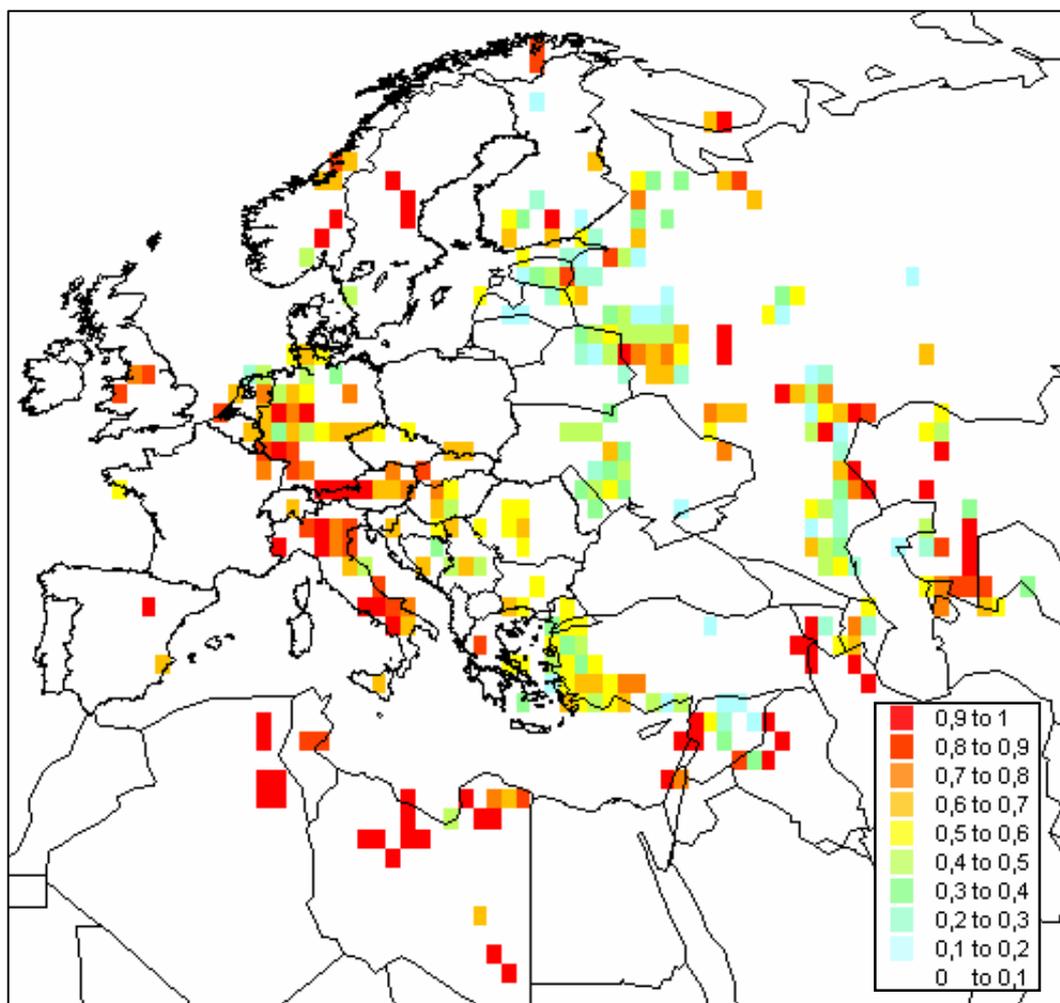


Figure 3.55. Calculated PSCF values for highest 40% factor scores of Factor 5 of Amasra

Factor scores do not show significant seasonal variation. It is possible that this factor is affected from mixture of both the emissions from distant sources and relatively closer sources. This factor is named as SO_4^{2-} factor.

The backtrajectories corresponding to highest 20% contribution days to Factor 6 are presented in Figure 3.57. The top view of the trajectories is same as the trajectory profile of other anthropogenic factors. The vertical

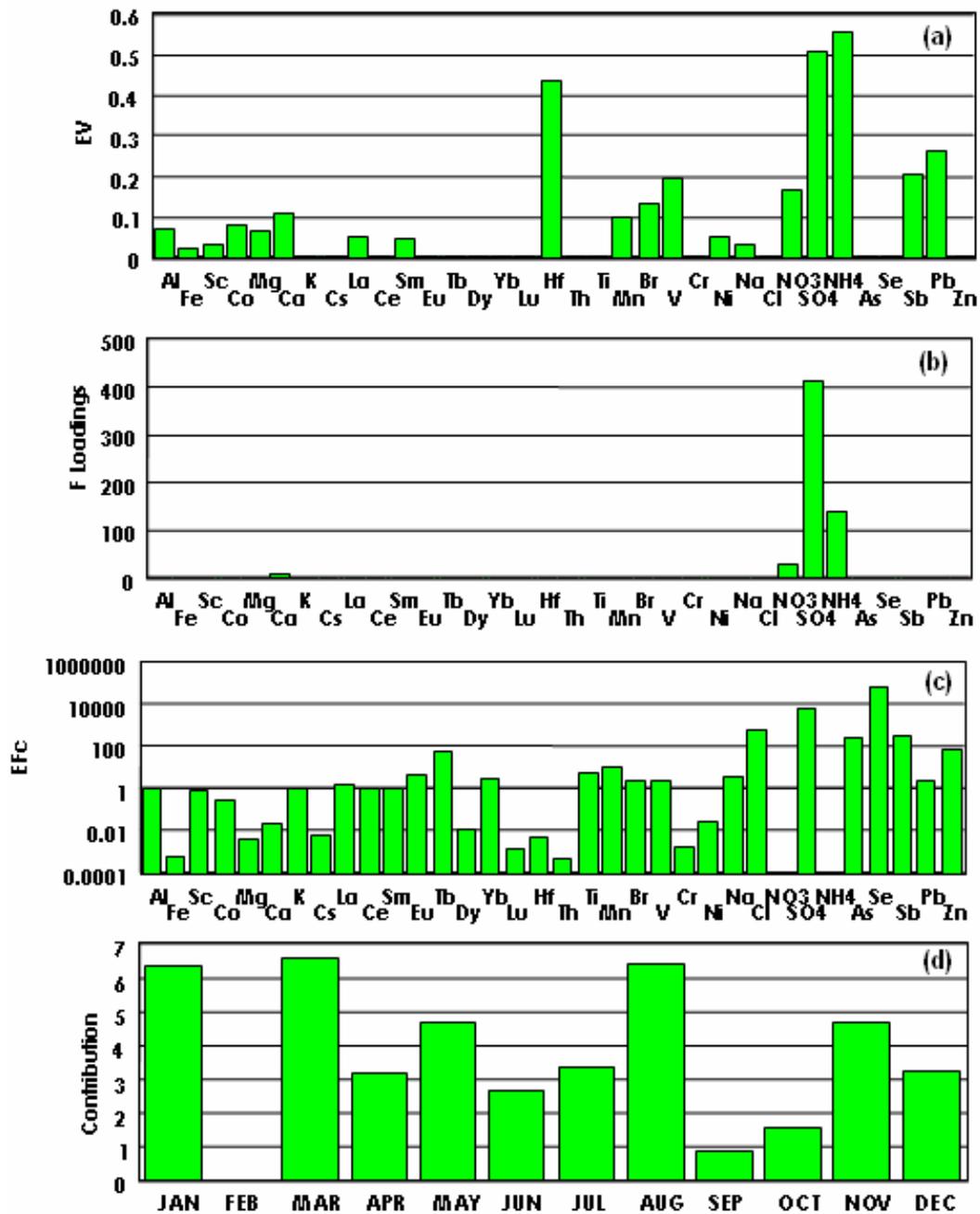
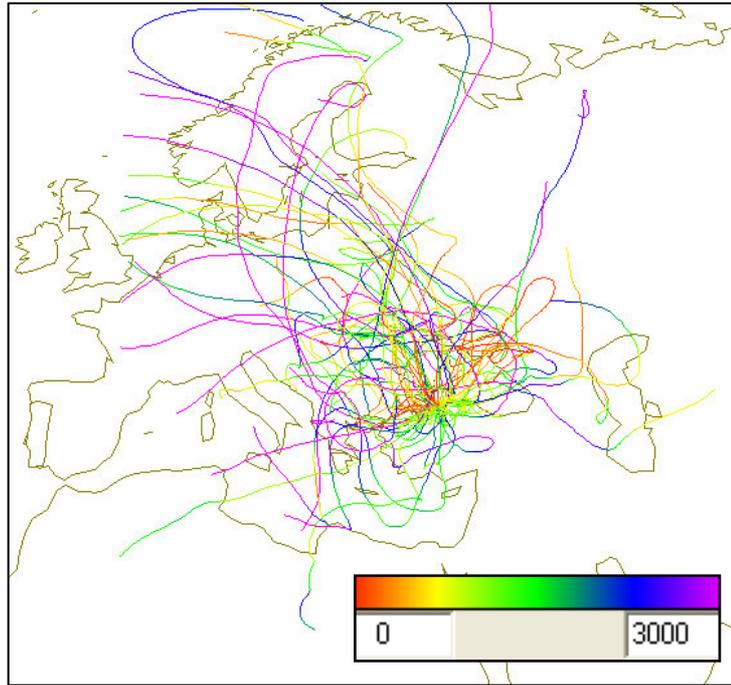
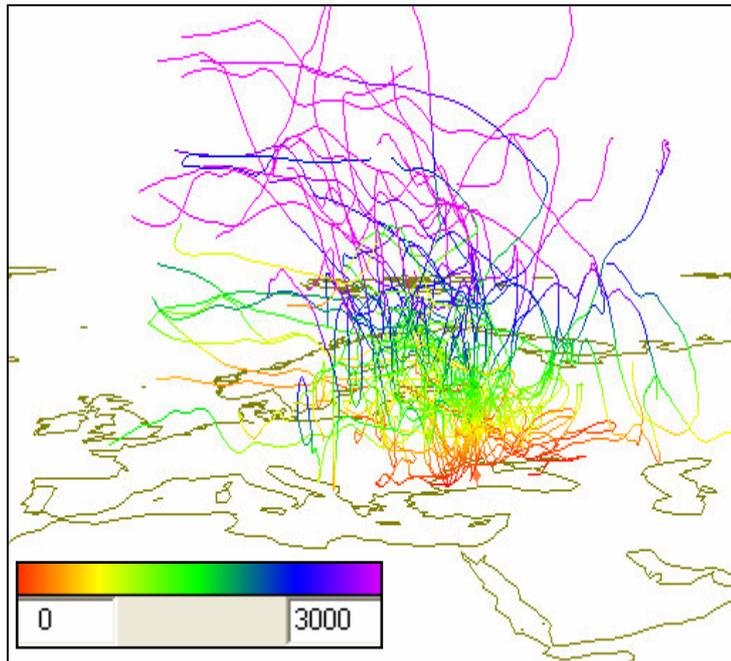


Figure 3.56. Explained Variation (a), Flooding (b), Calculated Enrichment Factor with reference element Al (c) and Monthly Variation in Factor Scores (d) of Amasra Factor 6



(a)



(b)

Figure 3.57. Top (a) and side view (b) of backtrajectories corresponding to highest 20% of the factor scores of Factor 6 of Amasra

profile of the trajectories showed that the air masses that originate from Europe move at high altitudes, whereas trajectories from the northern part are moving at lower altitudes. This shows that the contributing sources to this factor may be located in the northern sector.

The exact locations of source regions are calculated using PSCF analysis. Distributions of statistically significant PSCF values to Factor 6 are given in Figure 3.58. This figure illustrates that the main sources of this factor are located in the central part of Russia and in the Balkan countries.

Factor profile, variance explained, enrichment factors results and monthly average factor scores of Factor 7 are given in Figure 3.59. This factor explains almost all of the variance in Se concentrations. Besides, smaller fractions of variances of other anthropogenic and crustal elements are also explained by Factor 7. When the concentrations of the species are considered, the most significant specie is SO_4^{2-} ion. SO_4^{2-} , Cl, As, Se, Sb and Zn are enriched species in this factor. The composition of this factor is very similar to the composition of Factor 6. Factor scores are higher during summer season.

This factor is a combustion factor with high Se and SO_4^{2-} in it. The trajectories of highest 20% contribution days to Factor 7 are presented in Figure 3.60. The top view is similar to those of other anthropogenic factors. From the vertical profile, it is observed that the trajectories arriving from Europe pass through the Europe at high altitudes. The low-lying trajectories generally originate from northeast sector. Trajectories do not advect to surface near to the station. This shows that the local sources do not effect the composition of the factor.

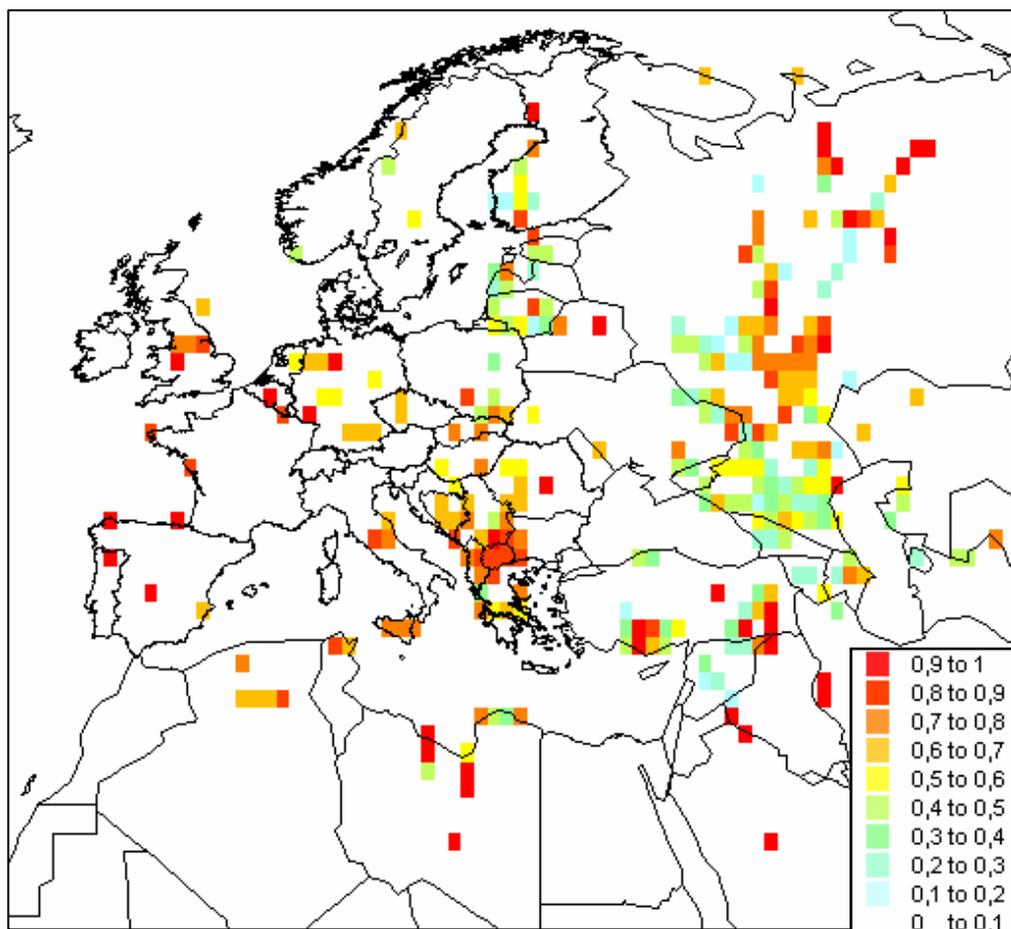


Figure 3.58. Calculated PSCF values for highest 40% factor scores of Factor 6 of Amasra

In order to assess the exact location of the sources, PSCF is applied to factor scores and the distribution of PSCF values are shown in Figure 3.61. The major source points are found as surrounding of Caspian Sea and central regions of Russia. Besides, even in smaller values, western Turkey and Belarus are the secondary important source regions for this factor.

Factor profile, variance explained, enrichment factors results and monthly average factor scores of Factor 8 are given in Figure 3.62. This factor

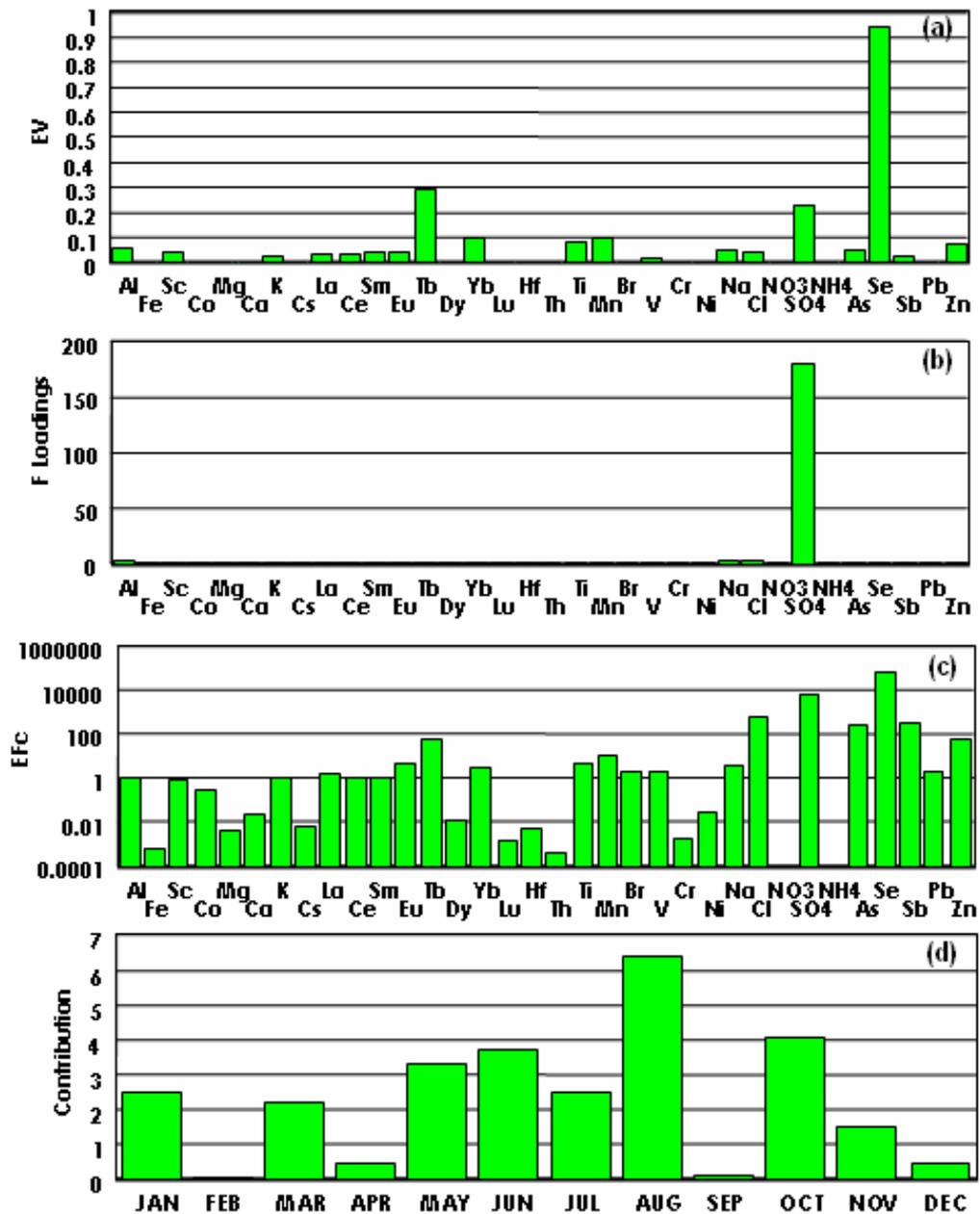
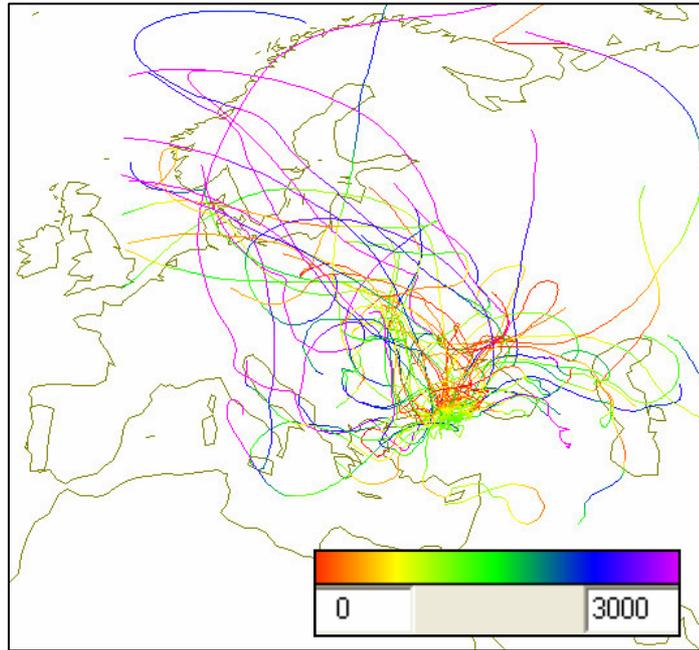
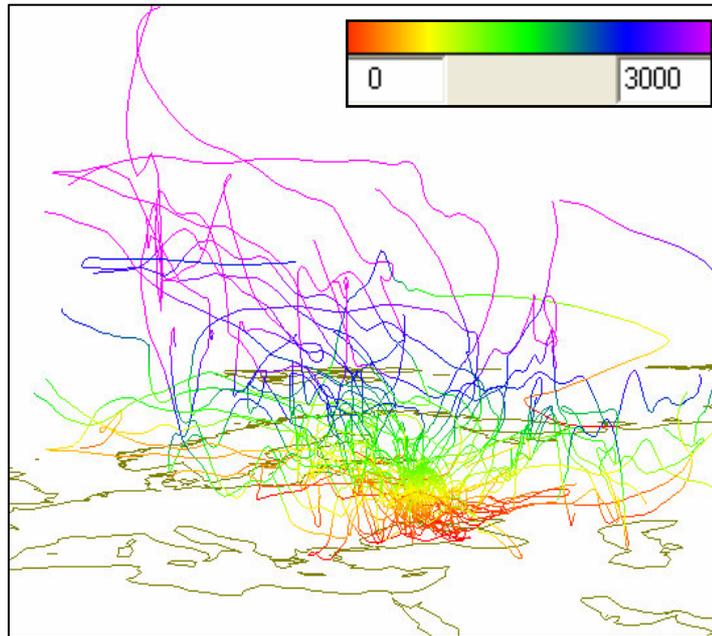


Figure 3.59. Explained Variation (a), Flooding (b), Calculated Enrichment Factor with reference element Al(c) and Monthly Variation in Factor Scores (d) of Amasra Factor 7



(a)



(b)

Figure 3.60. Top (a) and side view (b) of backtrajectories corresponding to highest 20% of the factor scores of Factor 7 of Amasra

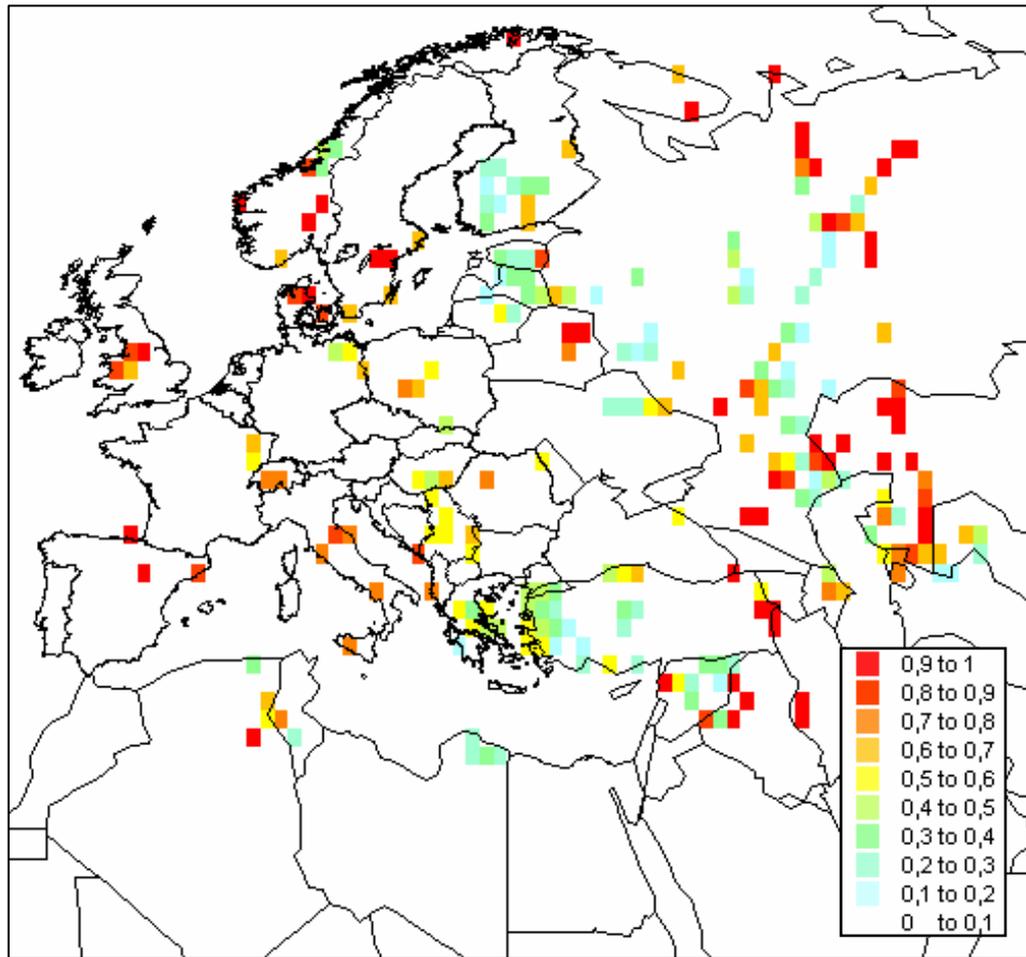


Figure 3.61. Calculated PSCF values for highest 40% factor scores of Factor 7 of Amasra

explains almost all variance in Zn concentrations. Therefore this factor is named as Zn factor. Aside from this element, this factor also explains some of the variances of NO_3^- , NH_4^+ , Sb, Pb as well as crustal elements.

Selenium, Sb, Br, Pb, Zn, some of the crustal elements and elements with mixed sources such as Mn, V, Cr and Ni are enriched. This factor is an anthropogenic factor with high enriched with metals. Factor scores do not show specific seasonal variation. This shows that this factor is

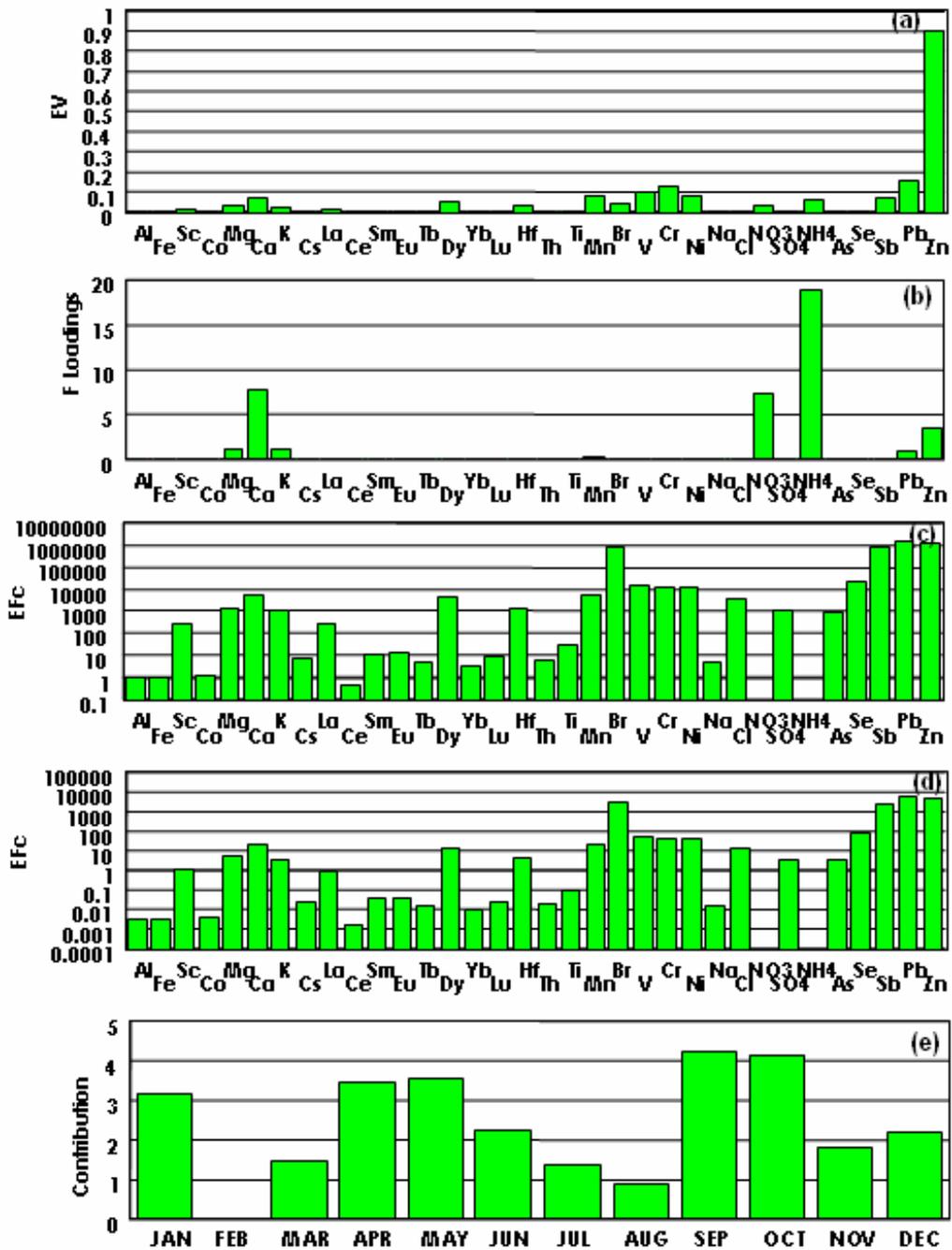


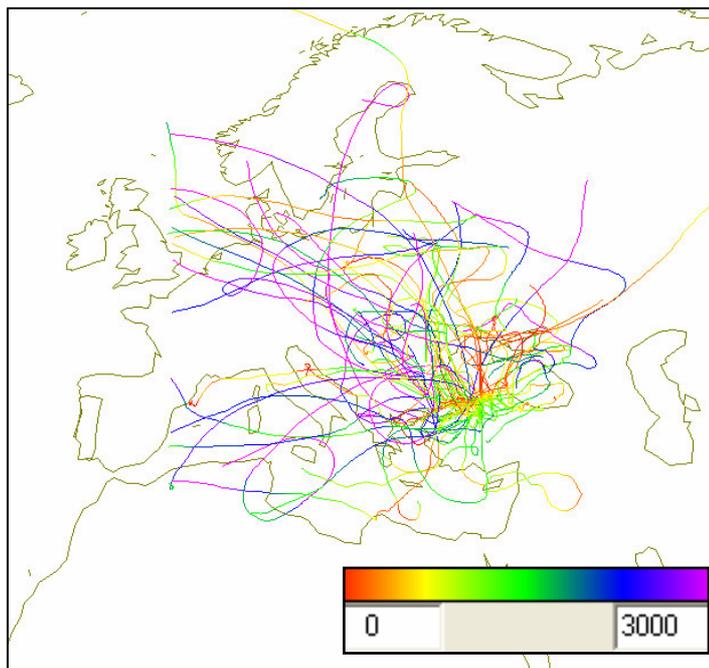
Figure 3.62. Explained Variation (a), Flooding (b), Calculated Enrichment Factor with reference element Al(c) and Sc (d) and Monthly Variation in Factor Scores (e) of Amasa Factor 8

affected both from distant sources and sources that are closer to the station site.

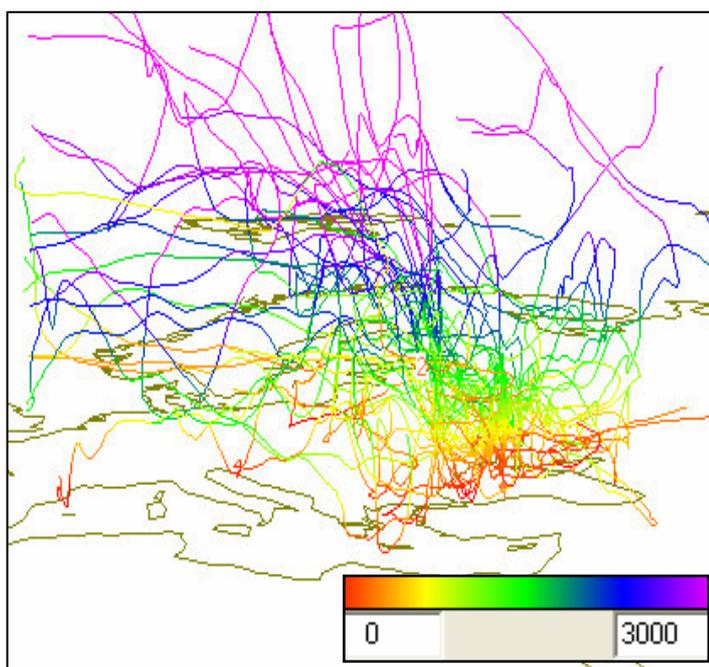
The trajectories corresponding to highest 20% of Factor 8 scores are presented in Figure 3.63. The top view is similar to those of previously discussed anthropogenic factors. The vertical profile of the trajectories showed that air masses arriving to the station from north, northeast and south east sectors descent under 1000 m. The PSCF results that are applied the factor scores represented in Figure 3.64. As observed from the figure, different regions in different sectors are signed as source regions. The important regions are especially, in northern part of Caspian Sea, region in between Russia and Belarus, Middle East region, particularly Israel, Trakya region of Turkey, Balkan countries like Bulgaria, Romania and Serbia, and Germany.

The total 8 components have identified with PMF in the Black Sea aerosols. Two of them are natural (one crustal and one sea salt) and six of them are anthropogenic components.

The contribution of each factor to total particle load and contribution of different source types to total particle load are shown in Figures 3.65a and 3.65b, respectively. As can be seen from the figures, contribution of third factor, namely sea salt factor, to the total particle mass is too high (65.5%). Observing such a high loading of sea salt to the particle loading is not so surprising. The contribution of sea salt factor to Black Sea aerosols is not as high as the contribution of sea salt factor to Mediterranean aerosols. As discussed previously, Black Sea station is located 3 km away from the sea and Mediterranean station is located just on the sea side. Since the marine aerosols are coarse particles, they removed from the atmosphere quickly as they move away from the sea. Thus, their contributions to total aerosol load decreases. Therefore, in



(a)



(b)

Figure 3.63. Top (a) and side view (b) of backtrajectories corresponding to highest 20% of the factor scores of Factor 8 of Amasra

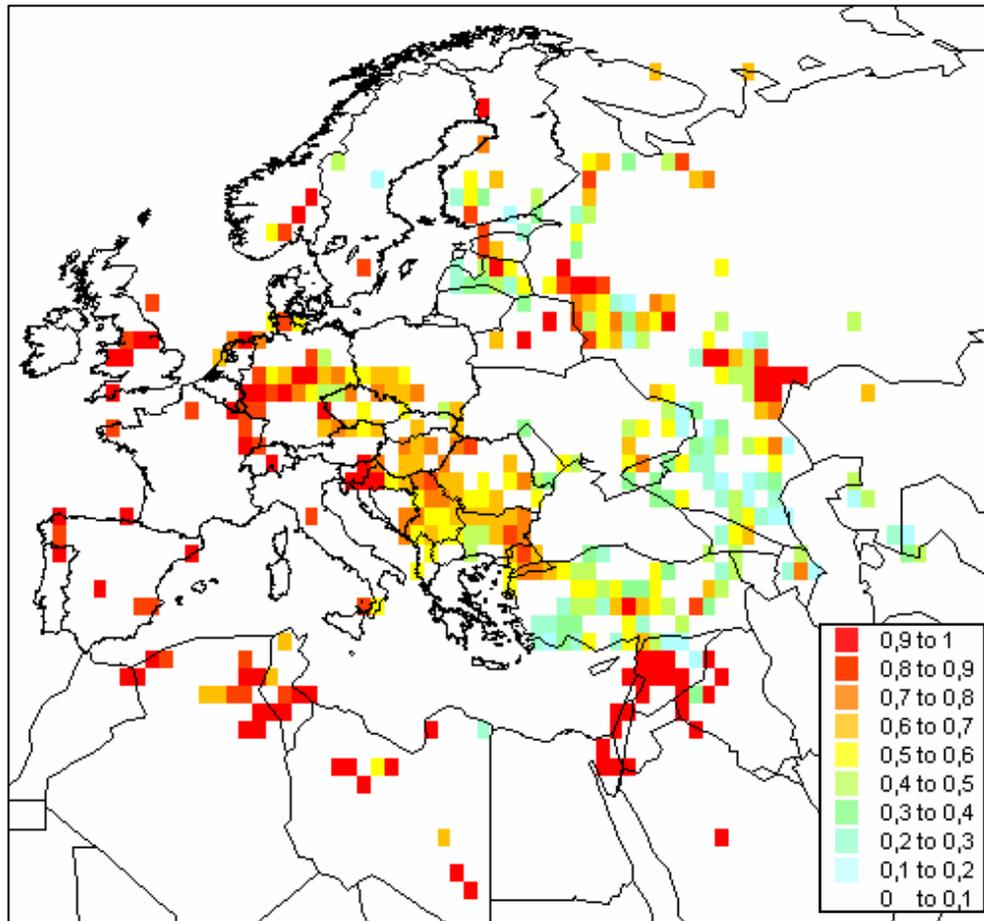


Figure 3.64. Calculated PSCF values for highest 40% factor scores of Factor 8 of Amasra

Antalya station, the contribution of sea salt to aerosol load is 90 % whereas in Amasra station, this input decreases down to 60%.

The two most important factors that contribute to the particle load are As factor (Factor 4), and SO_4^{2-} factor (Factor 6). Generally, high contribution of SO_4^{2-} is expected to contribute in high amounts to the aerosol load. However, high contribution of As factor to aerosol burden is unusual. Factor 4 is composed of 12 ng/m^3 of crustal material, 600 ng/m^3 of sea salt, 76 ng/m^3 of SO_4^{2-} , 27 ng/m^3 of NO_3^- , 0.01 ng/m^3 of NH_4^+ and 0.8

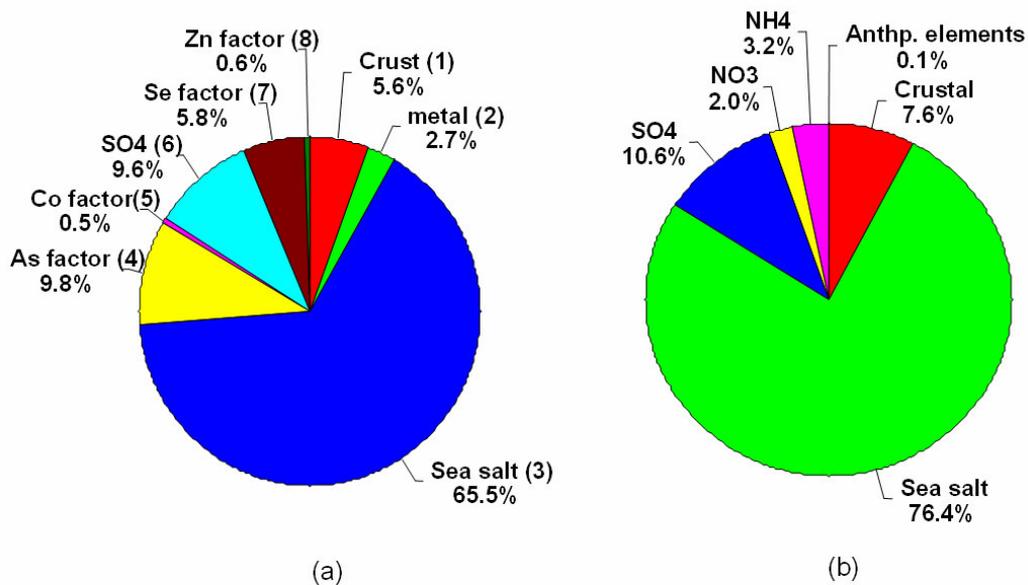


Figure 3.65. Contribution of factors to total mass(a) and percent contribution of components to the total mass (b) obtained in Amasra

ng/m³ of metal oxides. Therefore, high contribution of this factor to particle load is due to high sea salt component. The air masses corresponding to this factor picks up the pollutants from sources and while carrying them to the sampling point, they also pick up sea salt aerosol as they pass over the Black Sea. When the air mass reaches to the sampling point, it includes both anthropogenic and sea salt component.

The contribution of seventh factor which is Se factor, and first factor, crustal factor are 5.5 % each. The contribution of crustal component to total aerosol load is expected to be high. The high contribution of Se factor is due to the high input of NO₃⁻ ion to this factor. Contribution of NO₃⁻ to this factor is approximately 180 ng/m³.

Metal factors namely, Factor 2 and Factor 8, have less than 3% contribution to total aerosol mass. The sea salt has the highest contribution (76%) to the total particle load. One of the reasons for using high contribution of sea salt is that it occurs in more than one factor. Most of the air masses, no matter from where they originate, has to cross the Black Sea to reach the sampling point. This mechanism adds a sea salt component to factors, particularly the ones that source regions on the north. Contributions of crustal material and SO_4^{2-} aerosols to total particle load are between 7 to 10%. These two components are the two highest contributors after sea salt.

3.6.4. Comparison of PMF Results

In previous sections, it was discussed that the source regions of anthropogenic elements and ions affecting Antalya and Amasra stations are different. Some differences and similarities are detected in the aerosol components according to the PMF analysis of these two regions.

If the Mediterranean and Black Sea stations factor compositions, which show aerosol components, have one-to-one similarities, even though the source regions of these factors are different, then it can be said that both stations are influenced from same source types. For instance, this situation is observed for the crustal and marine components of Black Sea and Mediterranean regions. The third factor of Antalya station and the first factor of Amasra station represent the crustal components. The similarity in the crustal components is given in Figure 3.66. In Figure 3.67, the top and vertical profiles of the crustal components of the highest 20 % contributing days are given. As detected from the figure, the transportation patterns of crustal components to the station sites are different from each other. The top views shows that Antalya station is affected significantly from Northern Africa whereas the air masses that transport crustal component to Amasra station come from in every

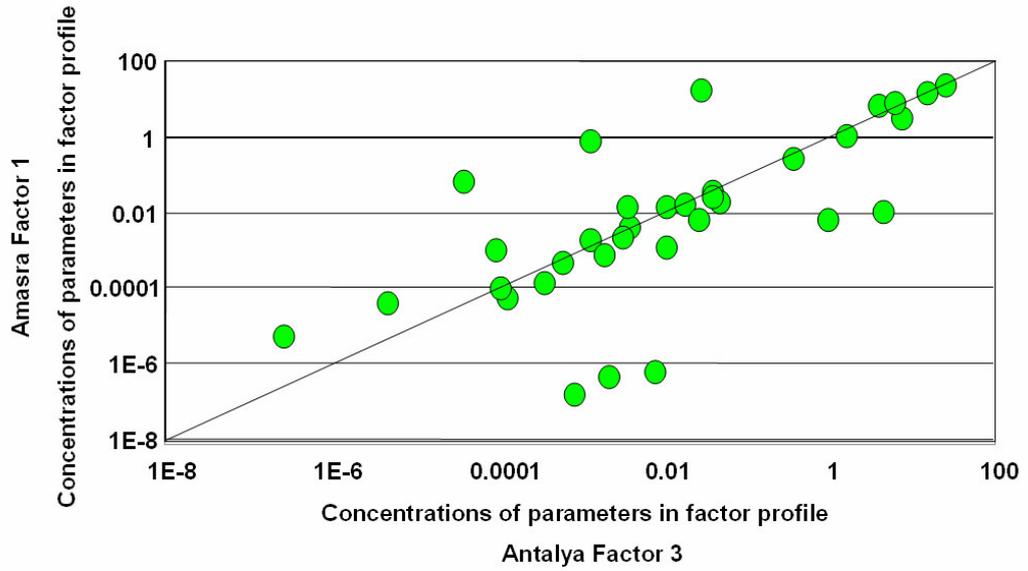


Figure 3.66. Correlation of crustal components in Factor 3 of Antalya station and Factor 1 of Amasra station.

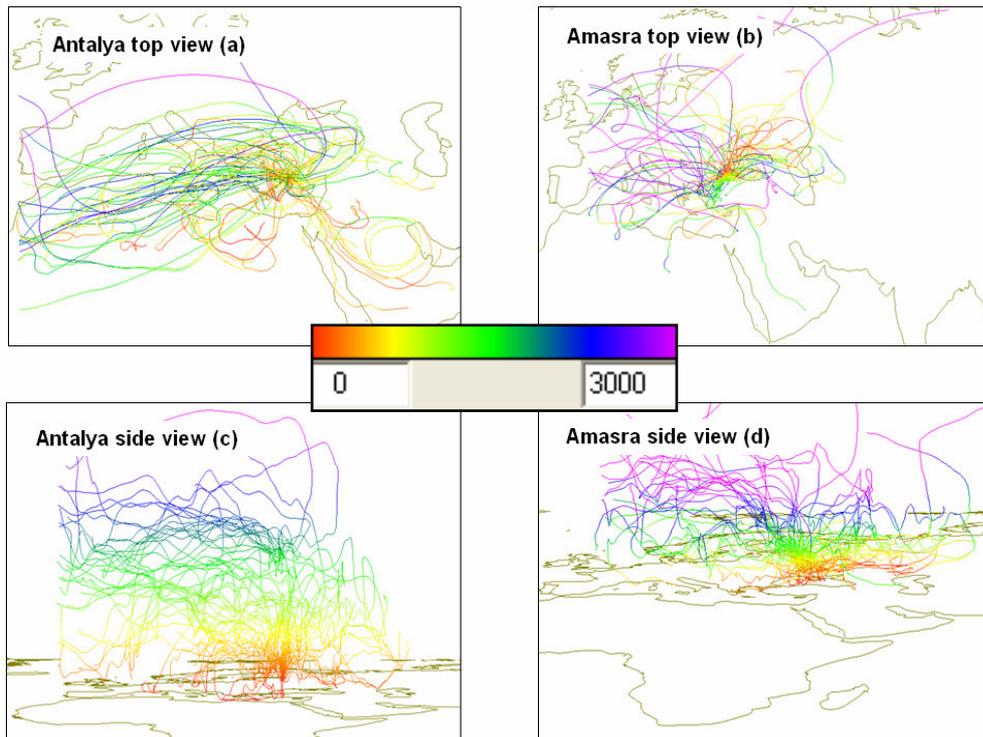


Figure 3.67. Top and vertical profiles of highest 20 % contributing days to the crustal factors of Antalya and Amasra stations.

direction. Consequently, although the crustal compositions in these two stations are same, the source regions are completely different.

In order to identify a similar relation between the anthropogenic components in the Mediterranean and Black Sea atmospheres as in the case of crustal factors, correlations between the factor profiles are analyzed. During this analyses soil originated elements are not taken into consideration, only the elements like Mn, Cr and V which are known to be high anthropogenic contribution elements are included. The factors are said to be correlated if the relationship between the parameters is within 95% confidence interval, otherwise, it is assumed that there is no correlation between the factors. According to the correlation results, it is detected that Factor 5 and Factor 6 of Amasra station are correlated with Factor 1 and Factor 4 of Antalya station, respectively. Also in both of the coastal stations, even the compositions are different, a common arsenic factor is determined.

The relation between Black Sea Factor 6 and Mediterranean Factor 4 is shown in Figure 3. As viewed from the figure, even though there is a statistical relation between these two factors, compositions of these factors are not same at all. Sb, Br and NH_4^+ in Black Sea, Se and Zn in Mediterranean are enriched more. The important point here is that these factors are made up of mixture of emissions from different sources. When the factor analysis is applied to the measurements in the city centers, each factor can represent a single source since the sampling is done near by the sources. However, the pollutants observed in the rural area studies are emitted from sources which are hundreds of kilometers away from the study area and the air masses reaching to station site collect the pollutants from different regions. Consequently, identifying similar factor from two stations has a low probability; even so having same compositions in these two factors has a very low chance.

Factor 4 in Antalya station and Factor 6 in Amasra station has high SO_4^{2-} contributions. The comparison elements in the SO_4^{2-} components in Antalya and Amasra stations are given in Figure 3.68. In rural studies, the contribution of thermal power plants to SO_4^{2-} load is dominating since more than 80% of total SO_2 emissions are from this sector. But this does not mean that the contributions of other pollutant to SO_4^{2-} factor are not occurred. Having similar element concentrations in the SO_4^{2-} factors showed that the SO_4^{2-} component has similar components in the Black Sea and Mediterranean aerosols and that those similar sources do effect the formation of this composition. However, observing some elements in different concentrations may be due to both the different contributions to the factor and also some more effective physical and chemical processes in one side than the other side. For instance, Br in Black Sea is higher in SO_4^{2-} factor. This can be due to the temperature difference between Antalya and Amasra regions. However, such a conclusion is just a

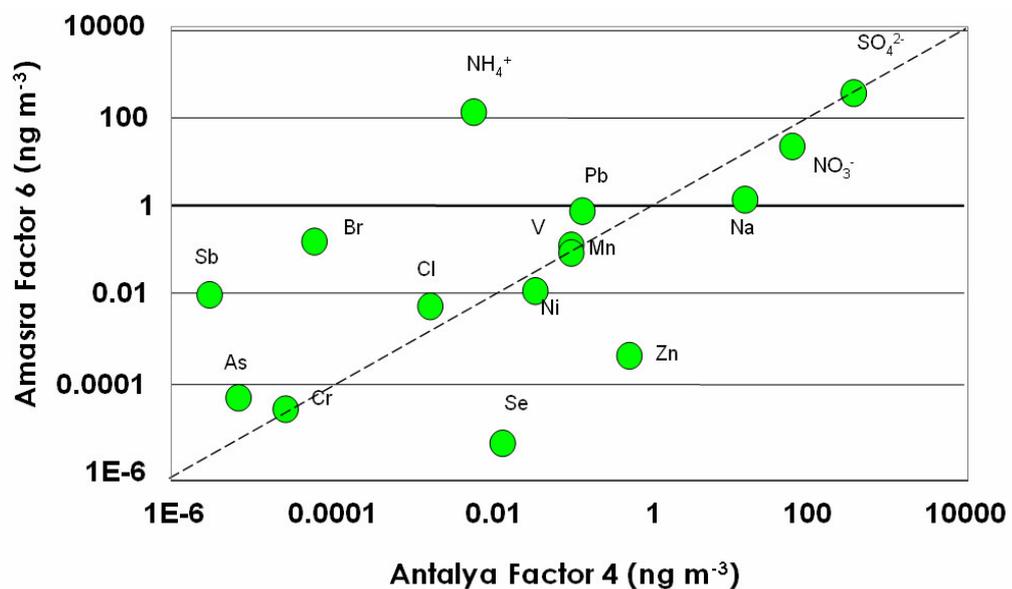


Figure 3.68. Comparison of compositions of elements and ions in the SO_4^{2-} components of the Antalya and Amasra aerosols.

speculation at the moment. Whatever the reason is SO_4^{2-} factor in Black Sea and Mediterranean aerosols are similar to each other and formed from similar source mixtures. But it should be mentioned that source regions of these two stations are not the same.

As remembered from the previous discussions, Factor 5 in Amasra is highly enriched with metal elements and has high concentrations of NH_4^+ ion. Factor 1 in Antalya also has high NH_4^+ concentration and it was showed that this factor was due to oxidation of NH_3 particles in the atmosphere. The similarity in the compositions of fertilizer factors of Mediterranean and Black Sea regions is presented in Figure 3.69.

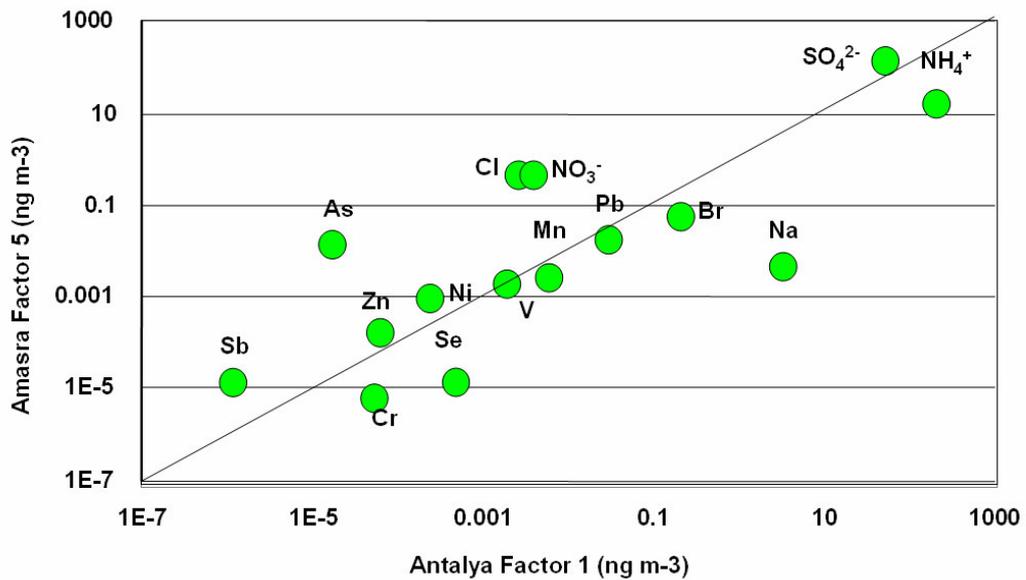


Figure 3.69. Comparison of compositions of elements and ions in the fertilizer components of the Antalya and Amasra aerosols.

Since the PMF study for the Çubuk station was performed previously (Yörük, 2004), in this study PMF is not applied to Çubuk data set. Instead, the result of the PMF calculated by Yörük (2004) is used for the comparison of the factor results. In Central Anatolia region aerosols are composed of 6 components. One of them is crustal factor, one other contains mainly SO_4^{2-} and due to the transportation of particles from distant sources, two of them are due to local sources and the remaining two of them could not be identified at all. Since the number of parameters measured in the Çubuk station is very low and since, especially in this kind of studies, the tracers for different sources are not measured, identification of all sources could not be possible. For the same reasons, it is not possible to conduct any conclusion between the compositions of SO_4^{2-} factor in three stations.

The evaluations up to now showed that the measurements that were held in three stations have two similar factors. First one is crustal component which is composed of lithophilic elements and the second one is the anthropogenic component, which is mainly composed of SO_4^{2-} and transported to each station site by means of long range transport. The PMF analyses in the Mediterranean and Black Sea regions showed that aside from these two factors, sea salt and particles due to the use of fertilizer are other common components. However, since the marker elements for the characterization of factors did not measured in Çubuk station, it is impossible to judge on the existence of similar aerosol components in the Central Anatolia region. The other factors identified in each of the regions are realized to be distinct to each station site.

CHAPTER 4

CONCLUSION

In this study, samples collected at Antalya, Amasra, Uludağ and Çubuk are analyzed together with the aim of to compare the aerosol compositions, sources and source regions of pollutants.

The number of measured parameters in Uludağ and Çubuk station were around 10 whereas samples collected in Antalya and Amasra stations were analyzed for 40 elements and ions. The comparison of Antalya and Amasra stations between each other are done in detail.

Concentration differences of elements and ions for Antalya and Amasra stations are considerably smaller than differences observed between these stations and Çubuk and Uludağ stations. In addition to that concentrations of all measured anthropogenic parameters in Çubuk and Uludağ stations are significantly smaller than concentrations determined in Antalya and Amasra stations. This comparison indicates that both of the coastal regions are under similar influence of pollution load.

For most of the crustal elements, the concentrations observed in the two coastal stations are similar. Since Antalya station is by the sea side whereas Amasra and Uludağ stations are located some distance away from the coast, marine elements observed in higher concentrations in Antalya station than Amasra and Uludağ stations. Concentrations of

marine elements observed in Amasra and Uludağ stations are statistically similar.

In all of the stations, crustal elements have higher concentrations during summer season. Concentrations of marine elements are expected to be higher during winter months and lower in summer months. However, the expected trend is only observed in Antalya station. In Amasra and Uludağ, seasonal variations for marine elements are not so clear.

The seasonal variation of anthropogenic elements and ions are not as clear as crustal elements. Sulfate showed a seasonal pattern with higher concentrations in summer only at Antalya station. In all other stations there is not such a significant seasonal variation in SO_4^{2-} concentration. For NO_3^- ion, both in Antalya and Uludağ stations, higher concentrations are observed during summer season whereas in Çubuk station, a SO_4^{2-} maximum was observed in winter period. On the other hand, there is not any seasonal variation for the Black Sea station for NO_3^- . For NH_4^+ , none of the stations shows any seasonal variation.

For major crustal elements, the baseline concentrations of elements and ions are comparable to each other for Amasra and Antalya stations. This shows that the soil input for these two coastal stations are not so different from each other. The highest background concentrations for marine elements are observed in Antalya station. Obviously regional uniformity is not valid for the elements that are very strongly affected from local sources.

Almost all anthropogenic elements and ions have similar baseline concentrations at Antalya and Amasra stations. For Çubuk and Uludağ stations, the baseline concentrations of anthropogenic elements and ions observed to be much lower than Amasra and Antalya stations. Most of

baseline calculations show that expected regional uniformity of regional baseline concentrations is not observed throughout Turkey.

For Uludağ and Çubuk stations, in general, the contributions of episodes to elemental concentrations are around 80 to 90%. For the coastal stations, the contribution of episodes is around 70%. The observed results showed that Çubuk and Uludağ stations are under stronger influence of local sources more than Amasra and Antalya stations. The higher average to background ratio observed at two high altitude stations can be an indication of higher contribution of relatively local sources on observed concentrations of elements at the Anatolian Plateau.

Binary correlations between anthropogenic elements depicted different patterns in different stations. They indicated a local and a long-range transported components in the Mediterranean at Antalya aerosol population, correlations in Black Sea data set, on the other hand, indicated one unique anthropogenic component.

In Antalya, Amasra and Çubuk stations, most frequent, flows are from W, WNW, NW and NNW sectors. These four sectors are more influential in determining composition of particles in the Mediterranean, Black Sea and Central Anatolia regions.

The seasonal variations in the calculated flow frequencies may also contribute to the observed seasonal variation of the concentrations of elements and ions. For this reason, seasonal variation of the flow climatology of each region should be evaluated. For Amasra and Çubuk stations, transport from SW, W, W and WNW sectors are considerably higher in winter than in summer. On the contrary, air mass flow frequency from NW, NNW, N, NNE, NE and ENE sectors are higher in summer season. For Mediterranean region, although the difference is not as high, when compared with other two stations, transport from W, WNW and NW

sectors are higher in winter months. Eastern European emissions or the local emissions within Turkey have higher influence in the aerosol compositions observed in the stations than emissions in the Western European countries.

Source regions effecting Mediterranean, Black Sea and Central Anatolia regions have some similarities. Especially emissions to the atmosphere in some regions in the Russia have effects on three station site. Similarly, releases of pollutants in some Balkan countries are also affecting all of three stations. However, the differences in the source regions of the station sites are more than the similarities. The source regions calculated for Central Anatolia and Black Sea resemble each other more than Mediterranean station. The major part of the pollutants measured in Mediterranean region is due to Aegean coast, whereas Central Anatolia and Black Sea stations are not affected from the same region as much as the Antalya station does. Even though more than 75% of the air masses spend their times in the northwest sector, eastern parts of the Turkey and Middle East region seems to be important source regions for central Anatolia. However, it is clearly detected that the source regions effecting Mediterranean, Black Sea and Central Anatolia are not the same at all.

Source apportionment studies showed that Çubuk, Antalya and Amasra regions are under effect of 6, 7 and 8 source types, two of which are in similar source category. First one is crustal component which is composed of lithophilic elements and the second one is the anthropogenic component, which is mainly composed of SO_4^{2-} and transported to each station site by means of long range transport. The PMF analyses in the Mediterranean and Black Sea regions showed that aside from these two factors, arsenic, sea salt and particles due to the use of fertilizer are other common components. The second crustal and metal factors are distinct sources identified in the Antalya region. The specific sources of Amasra

region are four metal factors, namely manganese, cobalt and zinc factors. The specific factors at the Çubuk region are identified as motor vehicle source, mixed urban factor, NO_3^- factor and Cd factor.

4.1. Recommendations for future studies

In this study, a detailed comparison between Antalya and Amasra stations are made due to high number of trace elements which are indicators for various sources. However, such a detailed comparison could not be held for Uludağ and Çubuk regions. For a detailed and much more effective research, the data sets can be completed with new trace element measurements. Besides, the measurement period in the Uludağ region is very low for many statistical computations.

Also, persistent organic pollutants (POPs) are stable for long period of time in the atmosphere. Due to their stability, they can be transported over long distances. These organic compounds are not being measured in any of these four stations. The data set can be further be detailed for these compounds.

Although, bootstrap method identifies the source regions of pollutants, incorporating the height of the trajectory segment to the PSCF analysis can surely give more certain source analysis.

The data set can be further extended with the measurements in the Southeastern Black Sea region and Eastern Anatolia regions to be able to compare the source differences of pollutants over the Anatolian Plateau.

REFERENCES

- Adachi, K and Tainosho, Y., 2004. Characterization of heavy metal particles embedded in tire dust. **Environment International** **30**, 1009-1017.
- Al-Agha, Ö. And Tuncel G., 2003. Evaluation of air quality over Black Sea major ionic composition of rainwater. **Water, Air and Soil Pollution** **1**, 1-10.
- Al-Momani, I.F., Tuncel, S.G., Eler, Ü., Örtel, E., Şirin, G. and Tuncel, G., 1995. Major ion composition of wet and dry deposition in the eastern Mediterranean basin. **Science of the Total Environment** **164**, 75-85.
- Andreae, M.O., Raemdonck, H., 1983. Dimethyl sulfide in the surface ocean and the marine atmosphere - a global view. **Science** **221**, 744-747.
- Anttila, P., Paatero P., Tapper, U. and Jarvinen, O., 1995. Source identification of bulk wet deposition in Finland by positive matrix factorization. **Atmospheric Environment** **29**, 1705-1718.
- Arimoto, R., 2001. Eolian dust and climate: relationships to sources, tropospheric chemistry, transport and deposition. **Earth-Science Reviews**, **54**, 29-42.
- Ashbaugh, L.L., 1983. A statistical trajectory technique for determining air pollution source regions. **Journal of the Air Pollution Control Association** **33**, 1096-1098.
- Berdowski, J.J.M., Mulder, W., Veldt, C., Visschedijk, A.J.H. and Zandveld, P.Y.J., 1998. Particulate emissions (PM10-PM2.5-PM0.1) in Europe in 1990 and 1993. **Bilthoven, RIVM**.
- Blanchard, D.C., 1963. The electrification of the atmosphere by particles from bubbles in the sea. **Prog. Oceanogr.** **1**, 71–202.

Blanchard, D.C., Woodcock, A.H., 1980. The production, concentration, and vertical distribution of the sea-salt aerosol. In: **Kneip, T.J., Liou, P.J. (Eds.), Aerosols: Anthropogenic and Natural Sources and Transport. Annals of the New-York Academy of Sciences 338**, 330–347.

Chabas, A. and Lefevre, R.A., 2000. Chemistry and microscopy of atmospheric particulates at Delos (Cyclades-Greece). **Atmospheric Environment 37**, 225-238.

Chester, R., Sharples, E.J. and Sanders, G.S., 1984. Saharan dust incursion over the Tyrrhenian Sea. **Atmospheric Environment 18**, 929-935.

Cheng, M.-D., Hopke, P.K., Zheng, Y., 1993. A receptor-oriented methodology for determining source regions of particulate sulfate at Dorset, Ontario. **Journal of Geophysical Research 98**, 16839-16849.

Christensen, W.F. and Gunst, R.F., 2004. Measurement error models in chemical mass balance analysis of air quality data. **Atmospheric Environment 38**, 733-744.

Christoffersen, T.S., Hjorth, J., Horie, O., Jensen, N.R., Kotzias, D., Molander, L.L., Neeb, P., Ruppert, L., Winterhalter, R., Virkkula, A., Wirtz, K. and Larsen, B., 1998. Cis-Pinic acid, a possible precursor for organic aerosol formation from ozonolysis of alfa-pinene. **Atmospheric Environment 32**, 1657-1661.

Cunningham, W.C. and Zoller, W.H., 1981. The chemical composition of remote area aerosols. **Journal of Aerosol Science 12**, 367-384.

Çetin, B., 2002. Elemental Tracers for Saharan Dust. **M.S. Thesis, Department of Environmental Engineering**, Middle East Technical University, Ankara.

Davidson, C.I. and Wu, Y.L., 1989. Control and fate of atmospheric trace metals. **Series C: Mathematical and physical sciences, Vol 268. Kluwer Academic Publishers**, 143-173.

Duce, R.A., Hoffman, G.L., Ray, B.J., Fletcher, I.S., Wallace, G.T., Fasching, J.L., Pietowicz, S.R., Walsch, P.R., Hoffman E.L., Miller, J.M. and Heffter, J.L., 1976. Trace metals in the marine atmosphere: sources and fluxes. In: Windom, H.L., Duce R.A. (Eds.), **H.a. Co. Marine Pollutant Transfer**, 77-119.

Duce, R.A., Liss, P.S., Merrill, J.T., Atlas, E.L., Buat-Menard, P., Hicks, B.B., Miller, J.M., Prospero, J.M., Arimoto, R., Church, T.M., Ellis, W., Galloway, J.N., Hansen, L., Jickells, T.D., Knap, A.H., Reinhardt, K.H., Schneider, B. Soudine, A., Tokos, J.J., Tsunogai, S., Wollast, R. and Zhou, M., 1991. The atmospheric input of trace species to the world ocean. **Global Biogeochemical Cycles** **5**, 193-259.

Eder, B.K., 1989. A principle component analysis of SO₂-, precipitation concentrations over the eastern United States. **Atmospheric Environment** **23**, 2739-2750.

Eliassen, A. and Saltbones, J., 1983. Modelling of long range transport of sulphur over Europe: a two year model run and some model experiments. **Atmospheric Environment** **17**, 1457-1473.

Elsom, D., 1987. Atmospheric pollution-causes, effects and control policies, **Basil Blackwell Inc.**

EMEP-WMO, 1997. Workshop on Strategies for Monitoring of Regional Air Pollution in relation to the need within EMEP, GAW and other international bodies. Aspenäs Herrgård, Lerum, Sweden June 2-4, 1997. Kjeller (EMEP/CCCReport 10/97).

EPA, 1996a. Air quality criteria for particulate matter. North Carolina, **U.S. Environmental Protection Agency** (EPA/600/P-95/001).

EPA, 1996b. Exposure Factors Handbook. Technical Report. North Carolina, **U.S. Environmental Protection Agency** (EPA/600/P-95/002Ba).

Erduran, M.S and Tuncel, S.G., 2001. Gaseous and particulate air pollutants in the Northeastern Mediterranean Coast. **The Science of the Total Environment** **281**, 205-215.

Feczko, T., Molnár, A., Mészáros E. and Major, G., 2002. Regional climate forcing of aerosol estimated by a box model for a rural site in Central Europe during summer. **Atmospheric Environment** **36**, 4125-4131.

Freidlander, W.F. 1973. Chemical Element Balances and Identifications of Air Pollution Sources. **Environment Science Technology** **7(3)**, 235-240.

Fuelberg, H.E., Loring, R.O., Watson, M.V., Sinha, M.C., Pickering, K.E., Thompson, A.M., Satche, G.W., Blake, D.R. and Schoelberl, M.R., 1996. TRACE A trajectory intercomparison: 2. Isentropic and kinematic methods. **Journal of Geophysical Research** **101**, 23927-23939.

Gaffney, J.S., Marley, N.A., Cunningham, M.M., Martello, D.V. and Anderson, N.J., 2002. Using natural Pb and its daughters (^{210}Bi and ^{210}Po) to estimate aerosol residence times. **Proceedings of the NETL Conference, Pittsburgh.**

Gangiotti, G., Milan, M.M., Salvador, R., Mantilla, E., 2001. Long range transport and re-circulation of pollutants in the Western Mediterranean during the project: Regional cycles of air pollution in the West-Central Mediterranean area. **Atmospheric Environment** **32**, 6267-6276.

Goldberg, E.D., 1963. The Oceans as a Chemical System, in the Sea. Hill, M.N. (Ed.), Vol. 2, Ch. 1, **Interscience**: New York.

Gordon, G.E., 1980. Receptor models. **Environmental Science and Technology** **14**, 972.

Güllü, G., 1996. Long range transport of aerosols. **Ph. D. Thesis, Department of Environmental Engineering**, Middle East Technical University, Ankara.

Güllü, G., Ölmez, İ., Aygün, S. and Tuncel, G., 1998. Atmospheric trace element concentrations over the Eastern Mediterranean Sea: Factors effecting temporal variability. **Journal of Geophysical Research** **103**, 21943-21954.

Hacısalihoğlu, G., Eliyakut, F., Ölmez, İ., Balkaş T.I. and Tuncel, G., 1992. Composition of particle in the Black Sea atmosphere. **Atmospheric Environment** **26A**, 3207-3218.

Harris, J.M. and Kahl, J.D.W., 1994. Analysis of 10-day isentropic flow patterns for Barrow, Alaska: 1985-1992. **Journal of Geophysical Research** **99**, 25845-25855.

Harrison, R.M., Yin, J., Mark, D., Stedman, J., Appleby, R.S., Booker, J. and Moorcroft, S., 2001. Studies of the coarse particle ($2.5\text{-}10\mu\text{m}$) component in UK urban atmospheres. **Atmospheric Environment** **35**, 3667-3679.

Hellén, H., Hakola, H. and Laurila, T., 2003. Determination of source contributions of NMHCs in Helsinki (60°N , 25°E) using chemical mass balance and the Unmix multivariate receptor models. **Atmospheric Environment** **37**, 1413-1424.

Henry, R.C., 1987. Current factor analysis receptor models are ill-posed. **Atmospheric Environment** **21**, 1815-1820.

Henry, R., 1997. History and fundamentals of multivariate air quality receptor models. **Chemometrics and Intelligent Laboratory Systems** **37**, 37-42.

Herut B., Krom, M.D., Pan, G. and Mortimer, R., 1999. Atmospheric input of nitrogen and phosphorus to the southeast Mediterranean: sources, fluxes and possible impact, **Limnology and Oceanography** **1**, 1683-1692.

Hillamo, R., Pacyna, J.M. and Bartonova, A., 1988. Characterization of aerosols during long-range transport episodes of air pollution to Norway. **Journal of Aerosol Science** **19**, 1257-1261.

Ho, K.F., Lee S.C. and Chiu, G.M.Y., 2002. Characterization of selected volatile organic compounds, polycyclic aromatic hydrocarbons and carbonyl compounds at a roadside monitoring station. **Atmospheric Environment** **36**, 57-65.

Hopke, P.K., Gladney, E.S., Gordon, G.E., Zoller, W.H. and Jones, A.G., 1976. The use of multivariate analysis to identify sources of selected elements in the Boston urban aerosol. **Atmospheric Environment** **10**, 1015-1025.

Hopke, P.K., 1985. Receptor modeling in Environmental Chemistry., **John Wiley**, New York, 155-197.

Hopke, P.K., Li, C.L., Ciszek, W. and Landsberger, S., 1995. The use of bootstrapping to estimate conditional probability fields for source locations of airborne pollutants. **Chemometrics and Intelligent Laboratory Systems** **30**, 69-79.

Hopke P.K., 2003. Recent developments in receptor modeling. **Chemometrics** **17 (5)**, 255-265.

Huang, S., Rahn, K.A. and Arimoto, R., 1999. Testing and optimizing two factor-analysis techniques on aerosol at Narragansett, Rhode Island. **Atmospheric Environment** **33**, 2169-2185.

Huang, S., Arimoto, R. and Rahn, K.A., 2001. Sources and source variations for aerosol at Mace Head, Ireland. **Atmospheric Environment** **35**, 1421-1437.

Israelevich PL, Levin Z, Joseph JH, Ganor E, 2001. Desert aerosol transport in the Mediterranean region as inferred from the TOMS aerosol index. **Journal of Geophysical Research-Atmospheres** **107 (D21): Art. No. 4572**.

Juntto, S., Paatero, P., 1994. Analysis of daily precipitation data by positive matrix factorization. **Environmetrics** **5**, 127-144.

Kakareka, S., Gromov, S., Pacyna, J. and Kukharchyk T., 2004. Estimation of heavy metal emission fluxes on the territory of NIS. **Atmospheric Environment** **38**, 7101-7109.

Karakaş, D., 1999. Determination of the European contribution on the aerosol composition in the Black Sea basin and investigation of transport mechanisms. **Ph.D. Thesis, Department of Chemistry**, Middle East Technical University, Ankara.

Karakaş (Yenisoy), S., 1995. Determination of major ions in Uludağ National Park. **M.S. Thesis, Department of Science Education**, Middle East Technical University, Ankara.

Katsoulis, B.D., 1999. The potential for long-range transport of air-pollutants into Greece: a climatological analysis. **The Science of The Total Environment** **231**, 101-113.

Kessler, C. Porter, T.H., Firth, D., Sager, T.W. and Hemphill, M.W., 1992. Factor analysis of trends in Texas acidic deposition. **Atmospheric Environment** **26A**, 1137-1146.

Khalil, M.A.K. and Rasmussen, R.A., 2003. Tracers of wood smoke. **Atmospheric Environment** **37**, 1211-1222.

Koch, S., Winterhalter, R., Uherek, E., Kolloff, A., Neeb, P. and Moortgat, G.K., 2000. Formation of new particles in the gas-phase ozonolysis of monoterpenes. **Atmospheric Environment** **34**, 4031-4042.

Kubilay, N. and Saydam A.C., 1995. Trace elements in atmospheric particulates over the Eastern Mediterranean: concentrations, sources and temporal variability. **Atmospheric Environment** **29**, 2283-2300.

Kuhlbusch, T.A.J., John, A.C., Fissan, H., Schmidt, K.-G., Schmidt, F., Preffer, H.-U. and Gladtko, D., 1998. Diurnal variations of particle number concentrations - influencing factors and possible implications for climate and epidemiological studies. **Journal of Aerosol Science** **29**, 213-214.

Kuloğlu, E., 1997. Size separation and dry deposition fluxes of particles in the Eastern Mediterranean basin. **M.S. Thesis, Department of Environmental Engineering**, Middle East Technical University, Ankara.

Luck, J.M. and Ben Othman, D., 2002. Trace element and Pb isotope variability during rainy events in the NW Mediterranean: constraints and anthropogenic and natural sources. **Chemical Geology** **182**, 443-460.

Lupu, A. and Meanhaut, W., 2002. Application and comparison of two statistical trajectory techniques for the identification of source regions of atmospheric aerosol species. **Atmospheric Environment** **36**, 5607-5618.

Martensson, E.M., Nilsson, E.D., de Leeuw, G., Cohen, L.H., Hansson, H.C., 2003. Laboratory simulations and parameterization of the primary marine aerosol production. **Journal of Geophysical Research-Atmosphere** **108**, art. no. 4297.

Mason, B., 1966. Principles of Geochemistry. **3rd Ed., John Wiley, New York.**

Millan, M.M., Artisano, B., Alonso, L., Navazo, M., Castro, M., 1991. The effect of meso-scale flows on regional and long range transport in the Western Mediterranean. **Atmospheric Environment** **25A**, 949-963.

Mishra, V.K., Kim, K.H., Kang, C.H. and Choi, K.H, 2004. Wintertime sources and distribution of airborne lead in Korea. **Atmospheric Environment** **38**, 2653-2664.

Paatero, P. and Tapper, U., 1993. Analysis of different modes of factor-analysis as least-squares fit problems. **Chemometrics and Intelligent Laboratory Systems** **18**, 183-194.

Paatero, P. and Tapper, U., 1994. Positive matrix factorization: a non-negative factor model with optimal utilization of error estimates of data values. **Environmetrics** **5**, 111-126.

Paatero, P., 1997. Least square formulation of robust non-negative factor analysis. **Chemometrics and Intelligent Laboratory Systems** **37**, 23-35.

Paatero, P., 2000. User's guide for positive matrix factorization programs PMF2 and PMF3, Part 1: tutorial.

Paatero, P., 2002. User's guide for positive matrix factorization programs PMF2 and PMF3, Part 2: Reference.

Pacyna, J.M., Larssen, S. and Semb, S., 1991. European survey for NO_x emissions with emphasis on Eastern Europe. **Atmospheric Environment** **25A**, 425-439.

Pacyna, J.M., 1998. Source inventories for atmospheric trace metal. In Atmospheric Particles. Harisson, R.M., Van Grieken, R.E. (Eds), **IUPAC Series on Analytical and Physical Chemistry of Environmental Systems** **5**, 387-423.

Pakkanen, T. A., 1996. Study of formation of coarse particle nitrate aerosol. **Atmospheric Environment** **30**, 2475-2482.

Piazzola, J. and Despiiau, S., 1997. Vertical distribution of aerosol particles near the air-sea interface in coastal zone. **Journal of Aerosol Science** **28**, 1579-1599.

Polissar, H., Hopke, P.K., Paatero, P., Malm, W.C. and Sisler, J.F., 1998. Atmospheric aerosol over Alaska: 2. Elemental composition and sources. **Journal of Geophysical Research** **103**, 19045-19057.

Polissar, A.V., Hopke, P.K. and Poirot, R.L., 2001. Atmospheric aerosol over Vermont: 1. Seasonal variability and sources. **Environmental Science and Technology** **35**, 4604-4621.

Poor, N., Pribble, R. and Greening, H., 2001. Direct wet and dry deposition of ammonia, nitric acid, ammonium and nitrate to the Tampa Bay Estuary, FL, USA. **Atmospheric Environment** **35**, 3947-3955.

Posfia, M. and Molnar, A., 2000. Aerosol particles in the atmosphere: a mineralogical introduction. **In Environmental Mineralogy**, 434.

Prendes, P., Andrade, J.M., Lopez-Mahia, P. and Prada, D., 1999. Source apportionment of inorganic ions in airborne urban particles from Coruna city (N.W. of Spain) using positive matrix factorization. *Talanta* **49**, 165-178.

Priece, C., Panner, J. and Prather, M., 1997. NO_x from lightning: 1. Global distribution based on lightning physics. **Journal of Geophysical Research** **102**, 5929-5241.

Prospero, J. M., Barrett, K., Church, T., Dentener, F., Duce, R.A., Galloway, J.N., Levy, H., Moody, J., Quinn, P., 1996. Atmospheric deposition of nutrients to the North Atlantic Basin. **Biogeochemistry** **35**, 27-73.

Prospero, J.M., 1999. Long term measurements of transport of African mineral dust to the southeast United States: Implications for the regional air quality. **Journal of Geophysical Research** **104**, 15917-15927.

Qin, Y., Oduyemi, K. and Chan, L. Y., 2002. Comparative testing of PMF and CFA models. **Chemometrics and Intelligent Laboratory Systems** **61**, 75-87.

Qin, Y. and Oduyemi, K., 2003. Chemical composition of atmospheric aerosol in Dundee, UK. **Atmospheric Environment** **37**, 93-104.

Quality of Urban Air Review Group, 1996. **Airborne particulate matter in the United Kingdom. UK.**

Ramadan, Z., Eickhout, B., Song, X.H., Buydens, L.M.C. and Hopke, P.K., 2003. Comparison of positive matrix factorization and multilinear engine for source apportionment of particulate pollutants. **Chemometrics and Intelligent Laboratory Systems** **66**, 15-28.

Ranmar, D.O., Matveev, V., Dayan U., Peleg, M., Kaplan, J., Gertler, A.W., Luria, M., Kallos, G., Katsafados, P. and Mehrer, Y., 2002. Impact of coastal transportation emissions on inland air pollution over Israel: Utilizing numerical simulations, airborne measurements, and synoptic analyses. **Journal of Geophysical Research** **107**, Art. No. 4331.

Raymond, H.A., Yi, S., Moumen, N., Han, Y.J. and Holsen, T.M., 2004. Quantifying the dry deposition of reactive nitrogen and sulfur containing species in remote areas using a surrogate surface analysis approach. **Atmospheric Environment** **38**, 2687-2697.

Roelle, P.A., Aneja, V.P., Gay, B., Geron, C. and Pierce, T., 2001. Biogenic nitric oxide emissions from cropland soils. **Atmospheric Environment** **35**, 115-124.

Ölmez, İ., Beal, J.W. and Villaume, J.F., 1994. A new approach to understanding multiple-source groundwater contamination: Factor analysis and chemical mass balances. **Water Research** **28**, 1095-1101.

Ölmez, İ., Güllü, G., Ames, M., Huang, X., Keskin, S.S., Che, J., Wakefield, A., Gone, J.K. and Beal, J., 1997. **Trace Metals. Upstate New York trace metals program, Volume 2, M.I.T. Report No. MITNRL-064.**

Seinfeld J.H and Pandis, S.N., 1998. Atmospheric chemistry and physics-From air pollution to climate change. **John Wiley and Sons Inc., Wiley Interscience.**

Slater, J.F., Dibb, J.E., Keim, B.D. and Talbot, R.W., 2002. Light extinction by fine atmospheric particles in the White Mountains region of New Hampshire and its relationship to air mass transport. **The Science of the Total Environment** **287**, 221-239.

Solomon, P. A., Salmon, L. G., Fall, T., and Cass, G. R., 1992. Spatial and temporal distribution of atmospheric nitric acid and particulate nitrate concentration in the Los Angeles Area. **Environmental Science and Technology** **26**, 1594-1601.

Sokolik, I. N., Winker, D. M., Bergametti, G., Gillette, D. A., Carmichael, G., Kaufman, Y. J., Gomes, L., Schuetz, L. and Penner, J. E., 2001. Introduction to special section: Outstanding problems in quantifying the radiative impacts of mineral dust. **Journal of Geophysical Research** **106**, 18015–18027.

Tarrason, L. and Tsyro, S., 1998. Long-range transport of fine secondary particles, as presently estimated by the EMEP Lagrangian model. **Oslo, DNMI (EMEP/MSC-W Note 2/98) (Research report/Norwegian Meteorological Institute no. 69)**.

Thunell R.C., 1998. Seasonal and annual variability in particle fluxes in the Gulf of California: A response to climate forcing. **Deep Sea Research Part I: Oceanographic Research Papers** **45**, 2059-2083.

Thurston, G.D. and Spengler, J.D., 1985. A qualitative assessment of source contributions to inhealable particulate matter pollution in Metropolitan Boston. **Atmospheric Environment** **19**, 9-25.

Treffeisen, R., Rinke, A., Fortmann, M., Dethloff, K., Herber A. and Yamanouchi, T., 2005. A case study of the radiative effects of Arctic aerosols in March 2000. **Atmospheric Environment** **39**, 899-911.

Tov, D.A., Peleg, M., Matveev, V., Mahrer, Y., Seter, I., Luria, M., 1997. Recirculation of polluted air masses over the East Mediterranean coast. **Atmospheric Environment** **31**, 1441-1448.

Tuncel, S.G., Baykal, A.H., Tuncel, G., Özer, U., 1994. Measurement of NO_x, SO₂, SPM and O₃, at a high altitude station in the northwestern Turkey. **Israel Journal of Chemistry** **34**, 403-409.

Tuncer, B., Bayar, B., Yeşilyurt, C. and Tuncel, G., 2001. Ionic composition of precipitation at the Central Anatolia. **Atmsopheric Envrionment** **35**, 5989-6002.

Uzun B. and Tuncel G., 2000. Investigation of biogenic sulfur in Eastern Mediterranean basin. **3rd Mediterranean Basin Conference on Analytical Chemistry, Book of Abstracts**, 93.

Vasconcelos, L.A.P., Kahl, J.D.W., Liu, D., Macias, E.S. and White, W.H., 1996. Spatial resolution of a transport inversion technique. **Journal of Geophysical Research** **101**, 19337-19342.

Wang, J.L., Ding W.H. and Chen T.Y., 2000. Source determination of light non-methane hydrocarbons by simultaneous multi-site sampling in a metropolitan area. **Chemosphere - Global Change Science** **2**, 11-22

- Warneck, P., 1987. Chemistry of the natural atmosphere. **International Geophysics Series 41**, Academy Press, 757.
- Watson, J.G. and Chow, J.C., 1994. Clear sky visibility as a challenge for Society. **Annual Rev. Energy Environment 19**, 241-266.
- Watson, J.G., Zhu, T., Chow, J.C., Engelbrecht, J., Fujita, E.M. and Wilson, W.E., 2002. Receptor modeling application framework for particle source apportionment. **Chemosphere 49**, 1093-1136.
- Wehrens, R., Putter, H., Buydens, L.M.C., 2000. The bootstrap: a tutorial. **Chemometrics and Intelligent Laboratory Systems 54**, 35-52.
- WHO, 1996. **Regional Office for Europe: Revised WHO Air Quality Guidelines**.
- Wolff, G. T., 1984. On the nature of nitrate in coarse continental aerosols. **Atmospheric Environment 18**, 977-981.
- Wolff, G.T. and Korsog, P.E., 1985. Estimates of the contributions of sources to inhalable particulate concentrations in Detroit. **Atmospheric Environment 19**, 1399-1409.
- Wu, P. M., and Okada, K., 1994. Nature of coarse nitrate particles in the atmosphere-a single particle approach. **Atmospheric Environment 28**, 2053-2060.
- Yeatman, S.G., Spokes, L.J. and Jickells, T.D., 2001. Comparison of coarse-mode aerosol nitrate and ammonium at two polluted coastal sites. **Atmospheric Environment 35**, 1321-1335.
- Yörük, E., 2004. Composition of the atmosphere at the Central Anatolia. **M.S. Thesis, Department of Environmental Engineering**, Middle East Technical University, Ankara.
- Yu, J., Griffin, R.J., Cocker, D.R., Flanagan, R.C., Seinfeld, J.H. and Blanchard, P., 1999. Observation of gaseous and particulate products of monoterpene oxidation in forest atmosphere. **Geophysical Research Letters 26**, 1145-1148.