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INVESTIGATION OF THE RELATIONSHIP BETWEEN AEROSOL AND RAINWATER COMPOSITIONS AT DIFFERENT LOCATIONS IN TURKEY

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ABSTRACT

Chemical compositions of particles and rainwater collected at four different locations in Turkey were compared to investigate relationship between aerosol and rainwater compositions. Results showed that aerosol composition can be closely reflected in composition of rainwater if below cloud processes dominate over the incloud processes. This is clearly observed for crustal elements in all stations and for most of the elements in urban station. However, in rural stations there were differences in rain and aerosol that is attributed to significant contribution from incloud processes. Scavenging ratios is found to be a suitable tool to construct rainwater composition using aerosol data. Differences observed in the data of different stations and between different elements or element groups, however, showed that composition of rainwater constructed from aerosol data can only be a crude one.

Key Words: Aerosol, Rainwater, Temporal variations, Scavenging ratio.

1. INTRODUCTION

Precipitation plays an important role in finding out the fluxes of many elements and species at atmosphere-ecosystem interfaces (Slinn, 1983; Galloway et al., 1982). However, field studies show that concentrations in wet depositions are highly variable, which makes it difficult to quantify these fluxes without long-term campaigns (Tuncer et al., 2001; Al-Momani et al., 1998). Most of the elements found in rainwater come from the aerosol and gas phase, either incorporated directly in the clouds (in-cloud scavenging) or washed-out by the precipitation itself (below-cloud scavenging). A better understanding of the rainfall phenomena therefore can only be achieved by studying the relationship between aerosol and rainwater media (Jaffrezo and Colin, 1988).

Atmospheric aerosol and rainwater both provide media to understand state of air pollution at a receptor and potential impacts on ecosystem. Mass and chemical composition of atmospheric particles had been extensively used to understand health effects of particles and pollutants associated with them, to understand mechanisms of transport from source to receptor, to understand reasons for visibility degradation (Hauck et al., 2004; Samura et al., 2003). Chemical composition of rainwater, on the other hand, is being used to understand transport of pollutants, acidity, persistent

organic compounds and heavy metals, from atmosphere to terrestrial and marine ecosystems and to assess the effect of such transport in worsening of various ecosystem components (Deboudt et al., 2004; Thalmann et al., 2002).
As can be easily recognized, these two areas of research are complementary to each other; in other words, questions addressed by analyzing atmospheric particles and rainwater are not the same, but complement each other. But unfortunately, sampling and analysis of rainwater is much more difficult compared to sampling and analysis of atmospheric aerosol. Because of this, data on chemical composition of rainwater are not as plentiful as data on chemical composition of particles, not only in Turkey, but also in everywhere in the world. If such a relationship, which allows constructing rainwater composition from aerosol data can be established, then questions about deposition fluxes of pollutants, acidification of environment, forest worsening etc. can be answered without undertaking difficult task of sampling and analysis of low levels of pollutants in rainwater.
Part of the concentration variations in rain can be associated with that in the aerosol due, in particular, to the effect of the source zones traversed by the cloud system. By classifying the precipitation collected at a given site according to the back-trajectories of the associated air-masses it is possible to distinguish more homogeneous groups than the entire initial sample (Slanina et al., 1983). But this type of classification is not enough to account for the diversity of the concentrations observed. It does not describe the magnitude of the exchanges between the two phases, rain and aerosol, the variations of which also contribute to this diversity. To a first estimation, this characteristic depends on the meteorological conditions (cloud type, phase contact time, precipitation intensity, etc.) and on the microphysical conditions (size and hygroscopy of the particles, number of condensation nuclei, etc.) (Slinn, 1983). The effects of some of these factors have been studied theoretically, but in practice, the coupling is expressed by the "scavenging ratio" (Engelmann, 1970; Chamberlain, 1960). They have been applied subsequently to estimate wet deposition fluxes for many other atmospheric species (Varhelyi and Gravenhorst, 1983) However, beside its role in the study of precipitation and aerosol relationship, the scavenging ratio potentially forms a tool for evaluating the wet deposition of species if the concentrations in the aerosol are known (Jaffrezo et al., 1990; Arimoto et al., 1985).
The main objective of this study is to find out a relationship, if exists any, between chemical compositions of aerosol and rainwater, using data sets generated in different parts of Turkey, so that difficult rainwater sampling and analysis can be avoided in the future.

2. MATERIALS AND METHODS

In this study, aerosol and rainwater data generated in previous studies were used. The data include aerosol (Güllü, 1996) and rainwater (Al-Momani, 1995) compositions at Antalya Station, aerosol data at Amasra Station (Karakaş, 1999), aerosol and rainwater data at Çubuk Station that is generated by the Ministry of Health, through EMEP program, and aerosol (Yatın, 1994) and rainwater (Kaya, 1997) data at Ankara Station, and at the locations of the sampling stations are depicted in Figure 1.

Antalya Station was set up nearly 20 km away from the city of Antalya, in a land owned by the Ministry of Forestry. A Hi-Vol sampler, a Hi-Vol impactor, a wet and dry deposition sampler and a wet only precipitation sampler were attached to the base of the platform. The station was set up in December 1991. In this study, the aerosol data (597 samples) collected between 1992 and 1993 (Güllü, 1996) and precipitation data (115 samples) collected between 1992 and 1993 (Al-Momani, 1995) are used.

Amasra station was set up about 20 km east of Amasra town and 3.5 km far from the Black Sea. The station was set up in February 1993. In this study, the aerosol data (345 samples) collected between 1995 and 1997 (Karakaş, 1999) and precipitation data (177 samples) collected between 1995 and 1999 (El-Agha, 2000) are used.

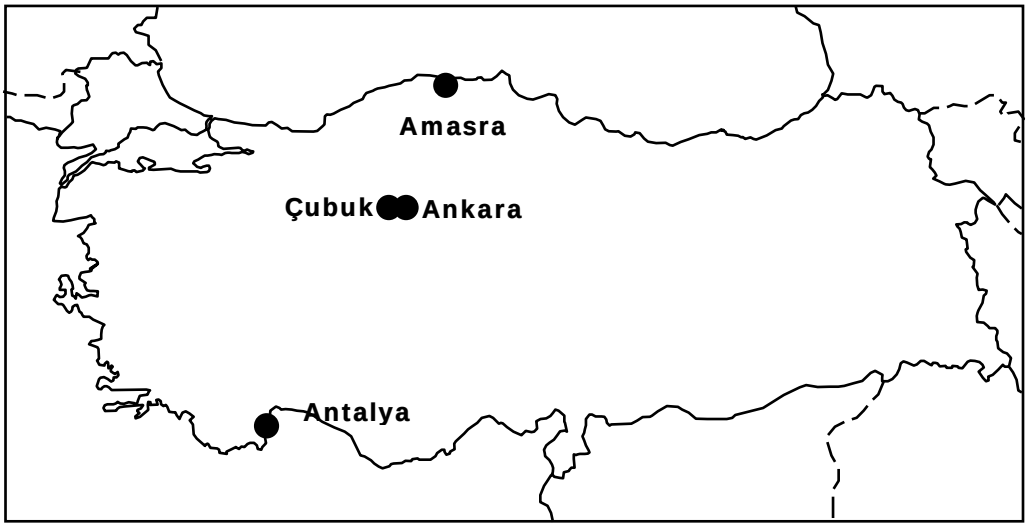

Figure 1. Locations of Sampling Stations

Çubuk Station was set up around 50 km away from the city of Ankara and 12 km away from Çubuk town. The station was set up in 1992 and it has been collecting air and precipitation samples since then. Çubuk Station is the only certified EMEP station in Turkey. The station is managed by the Ministry of Health using strict sampling and analytical protocols common to all EMEP network. Precipitation data generated in the station is evaluated by Tuncer (2000) and aerosol data by Yörük (2004).

Ankara Station was set up in the Middle East Technical University, which is located at a suburban area that is placed 10 km to the heavily populated districts in the city. There were a dichotomous sampler and two cascade filtration samplers in the station for parallel sampling. Samplers were installed on the roof of Department of Environmental Engineering in METU and operated for 24 hours to compare the size fractionation efficiency of the three samplers used in this study. The station was set up in February 1993. In this study, the aerosol data (108 samples) collected at 1993 (Yatın, 1994) and precipitation data (71 samples) collected between 1993 and 1994 (Kaya, 1997) are used.

As it is mentioned in the previous paragraphs, samples of aerosol and rainwater collected at Antalya, Amasra, Çubuk and Ankara stations were analyzed for trace elements and ions. Since the objective of sampling in these stations was not to find

out a relation between rain and particle composition, different elements and ions were measured at each station. Ions were generally measured in both aerosol and rainwater samples at all stations. Additionally, Ca, K, Mg and Cr were measured at all stations except Çubuk Station. These elements were measured in rainwater samples but not in particle samples at Çubuk Station. Trace elements were analyzed by AAS and INAA. Trace elements were measured at Antalya, Amasra and Ankara stations but not measured at Çubuk Station.

3. RESULTS AND DISCUSSION

Similarities in spatial patterns of elements and ions (i.e., SO_4^{2-}, NO_3^-, NH_4^+, Cl^-, Na, K, Mg, Ca, Al, Fe, Cr, Ni, V, Pb, Cd and Zn) measured in rainwater and aerosol samples collected at Antalya, Amasra, Ankara and Çubuk stations might provide information the common sources affecting composition of both particles and precipitation.

Concentrations of Cl, Na, Fe, Pb, Mg and K show similar spatial variation in both aerosol and rainwater samples, pointing out a single source affecting both particle and rainwater composition. Sodium and chlorine are elements associated with sea salt, in both aerosol and rain. Their concentrations at different stations depend on relative distance to coast. This is valid for both matrices. Iron, magnesium and potassium are crustal and their concentrations in both aerosol and rain are controlled by plenty of re-suspended soil particles in the atmosphere. All of these elements (Cl, Na, Fe, Mg and K) are known to associate with coarse particles, which are scavenged nearly three times more efficiently than fine particles bearing anthropogenic elements (Güllü, 1996; Galloway et al., 1992). Coarse particles are effectively removed by below cloud scavenging (washout) which is a local process. Thus, coarse particles incorporated in rain represent local aerosol collected at the receptor, suggesting good agreement between aerosol and rain concentrations.

Concentrations of anthropogenic elements and ions such as Cr, Ni, Zn, NH_4^+ and SO_4^{2-}, which are associated with fine atmospheric aerosols, have different spatial patterns in aerosol and rainwater. For these elements, wet deposition with incloud processes might be important. These elements might be incorporated into cloud droplets in any source region, and then are transported to other locations within the cloud. (El-Agha, 2000; Al-Momani, 1995). Composition of rainwater in this sense is not expected to be the same with composition of the aerosols sampled. The only exception for this scenario is Pb. Lead is also an anthropogenic element associated with fine particles and it is expected to show similar spatial pattern with other anthropogenic elements. The unexpected observation for Pb is due to its local contributions from roads around stations and decrease in Pb concentrations in European atmosphere in recent years that increased the relative contributions of local sources on Pb concentrations at receptors such as Amasra and Antalya. Because of these reasons Pb shows similar pattern as the local elements.

Aluminum and calcium are crustal elements and expected to depict similar spatial pattern with other crustal elements (i.e., Fe, K, Mg), but spatial variation in Al and Ca concentrations in rain and aerosol are significantly different. The reason for this distinct pattern could not be explained.

3.1. Temporal Variation in Concentrations of Rainwater and Aerosol

Temporal variations in ion concentrations are generally studied for different time-scales. Short-term variations are the episodic changes in concentrations, while long-term variations are the average changes in the time scales of seasons or years.

3.1.1. Short-Term Variations

Concentrations of ions show large variations from one day to another because of daily changes in emission strengths, local meteorology and transport patterns. Episodic changes might be pronounced for both soil and anthropogenic elements for different reasons. Investigation of short-term variations provides useful information on point sources, source regions and transport patterns and specific meteorological patterns that cause elevated levels of elements and ions (Tuncer, 2000). Daily variations in concentrations of selected species in rain and aerosol samples collected at Çubuk Station are given in Figure 2. Similar behavior is also observed for all species in other stations. Maximum concentration values in rainwater samples correspond to minimum in aerosol data for all species depicted in Figure 2 at most of the time. This pattern indicates a relation between compositions of aerosol and rainwater. However, the relation is complex as not every dip in aerosol concentrations correspond to a rain event. This situation is observed clearly from aerosol and rainwater concentrations measured at Çubuk and Antalya stations. There is not a statistically significant correlation between SO_4^{2-}concentrations of aerosol and rainwater samples with 95% confidence. Poor correlation is also observed for rest of the elements.

Some relation between short-term variations in aerosol composition can be obtained if data on variability is averaged over long periods of time. Concentrations of elements and ions in atmospheric particles are scavenged out by rain hence a decrease in concentrations is observed during rain events. Atmosphere is expected to be reloaded gradually with particles after rain.

3.1.2. Long-Term Variations

Long-term variations in concentrations of ions might provide information on factors affecting ion compositions at receptor site. Such variations were shown to be because of factors such as seasonal and systematic variations in the source strengths, seasonal changes in transport patterns and seasonal changes in particle scavenging in the atmosphere (Güllü et al., 1998). For example, more frequent transport of anthropogenic ions such as SO_4^{2-} and NO_3^- from a specific wind sector covering a polluted region during a particular season may well lead to an increase in the concentrations at the sampling site at that period. As another example, more extensive dust generation in the dry season causes the concentrations of crustal ions to increase (Tuncer, 2000).

As pointed out in the previous section, daily variations in aerosol composition after rain events are detected when the data is averaged over a long period of time. This is probably due to high variability of the processes in a single event. This also suggests that any relationship between aerosol and rain composition might be better explained using long-term averaged data.

Monthly variation in concentrations of anthropogenic elements in rainwater and particles in Antalya, Çubuk and Amasra stations shows a similar pattern for most of

the elements indicating a relation in monthly time scale. As a general trend, concentrations of anthropogenic elements are higher in summer than in winter due to more extensive scavenging of these pollutants during winter. Their seasonality can only be explained by long-range transport as these elements are transported to the site within clouds. Similar variations in aerosol and rainwater concentrations are also observed for crustal and marine elements on monthly basis. Therefore, monthly average concentrations of most of the elements in rainwater and aerosol are related to each other.

3.2. Scavenging Ratio

Scavenging ratio (SR) is a mean of calculating concentrations of species in rainwater if there is aerosol data. Three different calculation procedures are used in this study. In the first calculation method, overall averages of wet precipitation concentrations are divided by the overall averages in aerosol samples. In the second procedure, only paired samples that are sampling days with valid airborne and precipitation data, are considered. In the third procedure, monthly averages of SR values are calculated. However, only annual average SR values are presented in this paper.

Annual average SR values are calculated from volume weighted average (VWA) concentration of elements and ions in all precipitation samples collected during one year period and the average concentration of all aerosol samples collected during the same period at Antalya, Ankara, Amasya and Çubuk stations. Annual SR values are given in Table 1. Scavenging ratios are in general agreement with values reported in the literature. There are significant differences for some elements at different stations.

For the samples collected at Antalya station, even though annual SR values show significant variations from one constituent to another, the order of SR values might be generalized as sea salt elements, anthropogenic elements and crustal elements in descending order. The order of SR values is determined by particle size in the atmosphere that determines their scavenging efficiencies. Sea salt particles are the largest ones with mass median diameter (MMD) between 4.5-5 μm (Kuloğlu, 1997). These particles are scavenged out most effectively resulting in the highest SR values. Crustal particles are known to be in the coarse mode but their MMD are smaller than that of marine particles (3-3.5 μm) (Kuloğlu, 1997). Therefore, SR values for crustal elements are smaller than SR values for marine elements. Atmospheric particles are the smallest with MMD varying between 0.5-1.5μm and their SR values are the smallest. Although Mg and K are marine elements, their SR values are lower than the major sea salt elements that are Na and Cl. This is due to the contribution of crustal material in addition to sea salt. Scavenging ratios for anthropogenic elements show significant variations. For instance, SR values for Pb and Zn vary from 443 to 12643. When all anthropogenic elements are originated from distant sources, particles in air mass would be an aged, internally mixed aerosol during long transport times. High variability observed in calculated SR values for anthropogenic elements is due to wide range of MMDs of these elements. Scavenging ratios of NO_3^- are larger than other elements and sulphate. This is due to the incorporation of gaseous HNO_3^- and coarse particle NO_3^- formation on sea salt particles (Wolff, 1987).

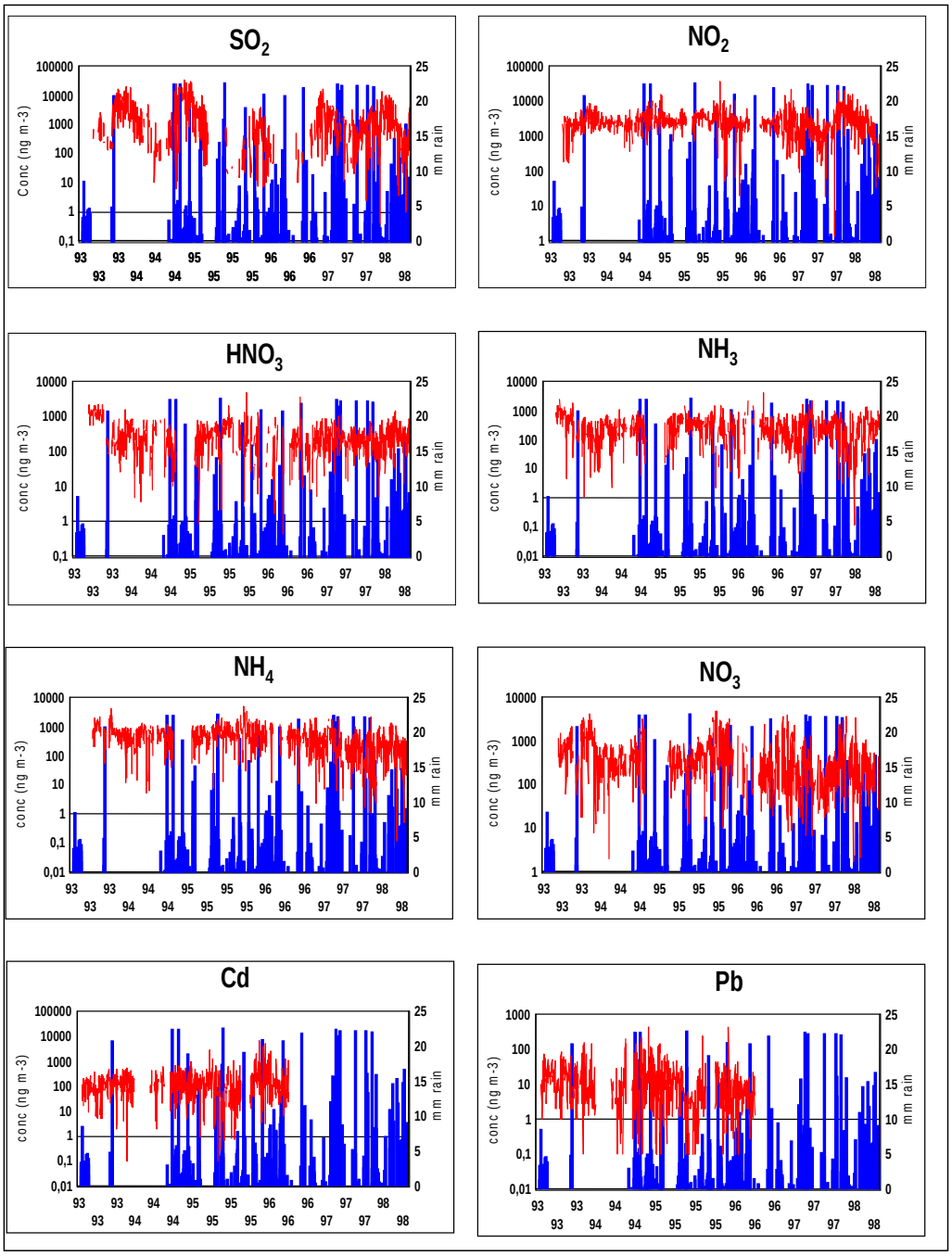

Figure 2. Daily variation in concentrations of selected species in rain and aerosol samples collected at Çubuk Station.

For the samples collected at Amasra Station, the SR values generally follows an order of crustal elements, seasalt elements and anthropogenic elements in descending order. All crustal elements have higher SR values in Amasra than in Antalya. However, marine elements have higher SR values in Antalya than in Amasra. This could be due to the location of Antalya Station, that is close to sea that contributes to

marine elements. Acidity forming species, which are NO_3^- and SO_4^{2-}, have lower SR values in Amasra than in Antalya. These species are associated with fine fraction of aerosol and hence they have low scavenging ratio (El-Agha, 2000).
For the samples collected at Ankara Station, the general pattern for SR values follows an order of seasalt elements, crustal elements and anthropogenic elements in descending order. Anthropogenic elements have low SR values compared to marine and crustal elements. The reason could be the local contribution such as industry and transport.
It can be concluded that, SR values calculated for the stations agree well with SR values provided in the literature. There exist differences in SR values calculated for different stations resulted from different integration times. The most useful SR values are the ones that based on average aerosol and VWA precipitation data. Annual average SR values are more reliable than paired SR values as variability of SR values increase when paired SR values are used.

Table 1. Scavenging ratios calculated for annual average concentrations.

	Amasra	Ankara	Antalya	Cubuk
Ca	6971.78	26927.50	1256.67	2723.46
Al	35757.81	5513.22	1141.99	
Fe	30760.01	4024.41	1635.57	
Ni	14133.70	1212.62	10279.50	
Cl	5282.74	62488.40	12695.68	
Na	10724.88	6830.29	11974.64	
K	26764.02	888.87	3120.25	1223.58
Mg	16178.86	2644.69	6024.63	792.32
V	3742.60	454.55		
Pb	889.09	209.69	443.07	
Cd	22233.62	67659.86		
SO_4	664.97	470.97	1279.07	1725.27
NO_3	2310.88	1145.02	4337.63	3909.85
NH_4	821.08		870.73	2497.21
Zn	21199.58	1.65	11643.69	
Cr	11631.36	424.22	2144.45	

4. CONCLUSIONS

In this study, relationship between chemical composition of atmospheric aerosol and rainwater is investigated using the data collected at Antalya, Amasra, Ankara and Cubuk stations. Data generated in these stations are suitable to establish such a relationship, because in all four stations chemical composition of particles and rainwater were simultaneously determined for fairly long periods of time.

Spatial variations of elemental concentrations (variation of concentrations from one station to another) show similarities for crustal elements pointing out that crustal elements measured in rainwater represent the aerosol population at the receptor. However, such similarities are not observed for marine and anthropogenic elements, suggesting that composition of rain for these groups of elements is also affected from transport of these species from distant source regions within cloud droplets.
Short-term variations in rain amount influence chemical composition of particles. But there is no one-to-one relationship between concentrations of elements in aerosol and concentrations in rainwater. Effect of rain on aerosol composition can be seen clearly if concentrations are averaged over a reasonably long periods of time.
Comparison of seasonal variations in concentrations of elements in rain and particles at four stations shows that seasonal variation in concentrations of elements and ions in rainwater closely reflects seasonal pattern in aerosols, suggesting that if there is seasonal variation data in aerosol, this can be used to construct seasonal variations of elements in rainwater.

REFERENCES

Al-Momani, I.F., Aygun, S., Tuncel, G., 1998. Wet deposition of major ions and trace elements in the Eastern Mediterranean basin. Journal of Geophysical Research 103, 8287-8299.
Al-Momani, I. F., 1995. Long-Range Atmospheric Transport of Pollutants to the Eastern Mediterranean Basin, Ph.D. Thesis, Department of Chemistry, METU, Ankara, Turkey.
Arimoto, R., Duce, R. A., Ray, B. J., Unni, C. K., 1985. Atmospheric trace elements at Enewetakatoll- 2. Transport to the ocean by wet and dry deposition. Journal of Geophysical Research 90, 2391-2408.
Chamberlain, A. C., 1960. Aspects of the deposition of radioactive and other gasses and particles. International Journal Air Pollution 3, 63-88.
Deboudt, K., Flament, P., Bertho, M-L., 2004. Cd, Cu, Pb, and Zn concentrations in atmospheric wet deposition at a coastal station in western Europe. Water, Air, and Soil Pollution 151, 335-359.
El-Agha, O., 2000. Chemical Composition of Precipitation in Black Sea Region, Ph.D. Thesis, METU, Ankara, Turkey.
Engelmann, R. J., 1970. Scavenging prediction using ratios of concentrations in air and pecipitation. In: Precipitation Scavenging (1970). AEC Symp., Springfield, IL., Ser. 22, 475-485.
Galloway, J. N., Savoie, D. L., Keene, W. C., Prosperot, J. M., 1992. The temporal and spatial variability of scavenging ratios for NSS sulfate, nitrate, methanesulfonate and sodium in the atmosphere over the North Atlantic Ocean. Atmospheric Environment 27A, 235-250.
Galloway, J. N., Thornton, J. N,., Norton, S. A., Volchok, H. L., McLean, R.A., 1982. Trace metals in atmospheric deposition: a review and assessment. Atmospheric Environment 16, 1677-1700.
Güllü, G. H., 1996. Long Range Transport of Aerosols, Ph.D. Thesis, Environmental Engineering Department, METU, Ankara, Turkey.

Güllü, G. H., Ölmez, İ., Aygün, S., Tuncel, G., 1998. Atmospheric trace element concentrations over the eastern Mediterranean Sea: Factors affecting temporal variability. Journal of Geophysical Research 103, 21943-21954.
Hauck, H., Berner, A., Frischer, T., Gomiscek, B., Kundi, M., Neuberger, M, Puxbaum, H., Preining, O, AUPHEP-Team., 2004.AUPHEP-Austrian project on health effects of particulates-general overview. Atmospheric Environment 38, 3905-3915.
Jaffrezo, J. L., Colin, J. L., 1988. Rain-aerosol coupling in urban area: scavenging ratio measurement and identification of some transfer processes. Atmospheric Environment 22, 929-935.
Jaffrezo, J. L., Colin, J. L., Gros, J. M., 1990. Some physical factors influencing scavenging ratios. Atmospheric Environment 24A, 3073-3083.
Karakas, D., 1999. Determination of the European Contribution on the Aerosol Composition in the Black Sea Basin and Investigation of Transport Mechanisms, PhD Thesis, Department of Chemistry, METU, Ankara, Turkey.
Kaya, G., 1997. Chemical Composition and Fluxes of Pollutants in Wet and Dry Deposition, MSc. Thesis, Department of Chemistry, METU, Ankara, Turkey.
Kuloğlu, E., 1997. Size Separation and Dry Deposition Fluxes of Particles in The Easter Mediterranean Basin, MSc. Thesis, METU, Ankara, Turkey.
Samura, A., Al-Agha, O., Tuncel, S.G., 2003. Study of trace and heavy metals in rural and urban aerosols of Uludag and Bursa (Turkey). Water, Air and Soil Pollution:Focus 3, 109-126.
Slanina, J., Baard, J.H., Zijp, W.L. and Asman, W.A.H. 1983. Tracing the sources of the chemical composition of precipitation by cluster analysis. Water Air and Soil Pollution 20, 41-45.
Slinn, W. G. N., 1983. In Air-Sea Exchange of Gasses and Particles (edited by Liss P.N. and Slinn W.G.N.) 299-405, Reidal, Dordrecht.
Thalmann, E., Burkard, R., Wrzesinsky, T., Eugster, W., Klemm, O., 2002. Ion fluxes from fog and rain to an agricultural and a forest ecosystem in Europe. Atmospheric Research 64, 147-158.
Tuncer, B., Bayar, B., Yesilyurt, C., Tuncel, G., 2001.Ionic composition of precipitation at the Central Anatolia .Atmospheric Environment 35, 5989-6002.
Tuncer, B., 2000. Chemical Composition in Central Anatolia, MSc. Thesis, Environmental Engineering Department., METU, Ankara, Turkey.
Varhelyi, G., Gravenhorst, G., 1983. Production rate of airborne seasalt sulfur deduced from chemical analysis of marine aerosols and precipitation. Journal of Geophysical Research 88, 6737-6751.
Wolf, G. T., 1987. Characteristics and consequences of soot in the atmosphere. Environmental International 11, 259-269.
Yatın, M., 1994. Source Apportionment of Urban Aerosols Using Receptor Modeling Approach: An Application to Ankara, Ph.D. Thesis, Department of Chemistry, METU, Ankara, Turkey.
Yörük, E., 2004. Composition of Atmosphere at the Central Anatolia, MSc. Thesis, Environmental Engineering Department., METU, Ankara, Turkey.