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SPATIAL AND TEMPORAL VARIATIONS OF MAJOR ACIDIC SPECIES IN $PM_{2.5}$ PARTICLE FRACTION IN ZAGREB AIR

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ABSTRACT

This paper presents the spatial and temporal mass concentration variations of major acidic species (chlorides, nitrates and sulphates) in high risk particle fraction $PM_{2..5}$ in Zagreb air. The sampling was carried out at four measuring sites during the summer of 2002 (June – July) and winter 2002-2003 (November – January).

The results show no significant differences in pollutant concentration levels between the measuring sites in the winter, while significant differences were found for nitrates and sulphates in the summer. Higher mass concentrations of all pollutants were measured in the winter. The mass concentrations of investigated anions showed significant seasonal differences, except for chlorides at two sampling sites. The most abundant species contributing to the $PM_{2.5}$ mass were: sulphates > nitrates > chlorides.

Key Words: Chlorides, Nitrates, Sulphates, Sampling sites, Ion chromatography

1. INTRODUCTION

Acid aerosols in the air are formed primarily from the oxidation of sulphur oxides, nitrogen oxides, and hydrocarbons, mainly originating from combustion sources. In the atmosphere the primary pollutant sulphur dioxide is oxidised by both homogenous and heterogeneous reactions forming a sulphuric acid aerosol, which can react with other components present in the air mainly with gaseous ammonia, leading to various molecular forms of sulphates (Khoder 2002, Brook et al. 1997). Nitrogen dioxide (mainly the secondary pollutant) is readily oxidised to nitrates (Khoder 2002). Nitrates may be present in the gaseous phase as nitric acid vapour, while the sulphates are mainly found in the aerosol phase (Wyers and Duyzer 1997). Aerosol acidity and concentrations of each species are seasonally dependable, varying with the time of the day and location. Strong acids are more frequently present in fine (high-risk) particle fraction. Chemical analysis of aerosol particles has gained increasing importance because of the effects of these particles on the environment (Lippmann and Thurston, 1996, Harisson et al., 1997). Epidemiological studies have shown that the exposure to urban particles is associated with an increase in mortality and morbidity, mainly of cardiopulmonary origin (Levy et al., 1999). Particle size and chemical composition play a major role in defining the relative toxicity of particles (Lippmann and Thurston, 1996, Magari et al., 2002).

This paper presents the spatial and temporal mass concentration variations of major acidic species (chlorides, nitrates and sulphates) in high risk particle fraction $PM_{2,5}$ in Zagreb air measured at four sampling sites during the summer and winter period.

2. MATERIALS AND METHODS

The sampling of high-risk particle fraction was carried out at four measuring sites in Zagreb during the summer of 2002 (June – July) and winter 2002-2003 (November – January). The measuring sites are designated here as NR (northern residential part of the city with moderate traffic density and numerous green areas), CC (city centre with high traffic density and individual heating), RW (residential-industrial area in western part of the city with high traffic density) and RE (residential-industrial area in eastern part of the city).

Twenty-four hour samples of high-risk particle fraction were collected by means on quartz filters. The coarse particle fraction was removed from air stream using inertial impactor. Filters were dried to constant humidity in a desiccator for 24-hours before and after sampling. Particle mass concentration was determined using the gravimetric method. Samples were extracted from the filter media with an ultrasonic bath. Dionex DX-120 ion chromatograph equipped with suppressed conductivity detection, Dionex AS14: 4mm analytical column + AG14: 4mm guard column was used to measure anion content.

3. RESULTS AND DISCUSSION

Table 1 summarises the descriptive statistics, including the number of samples (N), average values ($\bar{\gamma}$), minimum (γ_{min}), and maximum (γ_{max}) of chloride mass concentrations in $PM_{2..5}$ particle fraction measured at four sampling sites in summer and winter, as well as the ratio between the mass concentration measured in winter and summer ($\bar{\gamma}_w$ / $\bar{\gamma}_s$). The same parameters for nitrate mass concentrations are shown in Table 2, and for sulphates in Table 3.

Table 1. Mass concentration of chlorides ($\mu g\ m^{-3}$) in $PM_{2..5}$ particle fraction

Statistical parameters	**CC**		**NR**		**RE**		**RW**	
	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter
N	21	37	35	48	22	25	24	32
$\bar{\gamma}$	0,61	0,55	0,21	1,01	0,87	0,86	0,28	1,00
γ_{min}	0,02	0,00	0,00	0,00	0,00	0,07	0,00	0,03
γ_{max}	6,83	1,99	1,94	8,58	16,22	2,58	2,78	10,72
$\bar{\gamma}_w$ / $\bar{\gamma}_s$	0,90		4,81		0,99		3,57	

Table 2. Mass concentration of nitrates (μg m^{-3}) in $PM_{2..5}$ particle fraction

Statistical parameters	**CC**		**NR**		**RE**		**RW**	
	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter
N	21	37	35	48	22	25	24	32
$\bar{\gamma}$	0,97	6,76	0,79	6,28	0,72	11,25	0,90	7,11
γ_{min}	0,22	1,33	0,11	0,63	0,09	1,75	0,17	0,41
γ_{max}	1,45	18,63	1,68	18,61	1,48	34,10	1,73	19,73
$\bar{\gamma}_w$ / $\bar{\gamma}_s$	6,97		8,61		15,63		7,9	

Table 3. Mass concentration of sulphates (μg m^{-3}) in $PM_{2..5}$ particle fraction

Statistical parameters	**CC**		**NR**		**RE**		**RW**	
	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter
N	21	37	35	48	22	25	24	32
$\bar{\gamma}$	6,54	9,65	6,53	9,59	5,52	15,86	6,77	10,60
γ_{min}	1,28	1,67	0,41	0,72	0,98	2,07	0,61	0,99
γ_{max}	16,63	22,97	17,24	26,24	17,20	34,51	14,24	25,44
$\bar{\gamma}_w$ / $\bar{\gamma}_s$	1,48		1,47		2,87		1,57	

The measurements of acidic components (chlorides, nitrates, and sulphates) in high-risk particle fraction $PM_{2..5}$ at four sampling sites show no significant difference ($P>0.05$, ANOVA, one way analyses of variance) in pollutant concentration levels between the measuring sites in the winter, while significant differences ($P<0.05$) were found for nitrates and sulphates in the summer.

Higher mass concentrations of all pollutants were measured in the winter which may be due to high emissions of pollutants and their precursors from anthropogenic sources, combustion of fossil fuels and motor vehicle exhaust. The mass concentrations of investigated anions showed significant seasonal differences (one-tailed *t*-test), except for chlorides at sampling sites CC and RE. More pronounced differences were found for nitrates at all sampling sites, sulphates at sampling site RE, and chlorides at sampling site RN.

Chloride, nitrate, and sulphate content (%) in $PM_{2.5}$ particle fraction measured in the summer 2002 and the winter 2002/3 at the sampling site NR are shown in Figure 1. The same parameters measured at sampling site CC are shown in Figure 2, for sampling site RW in Figure 3, and for sampling site RE in Figure 4.

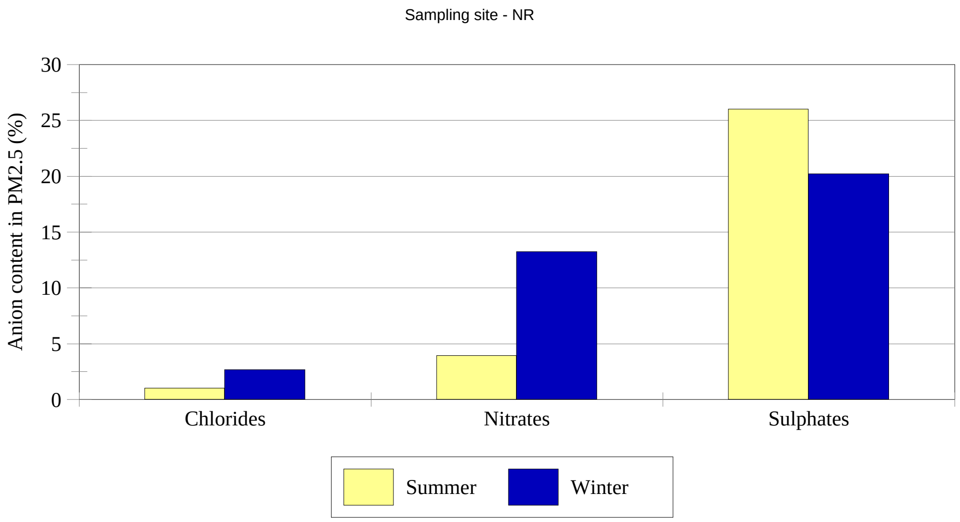

Figure 1. Anion mass content (%) in $PM_{2..5}$ particle fraction measured at sampling site NR in the summer 2002 and winter 2002/3

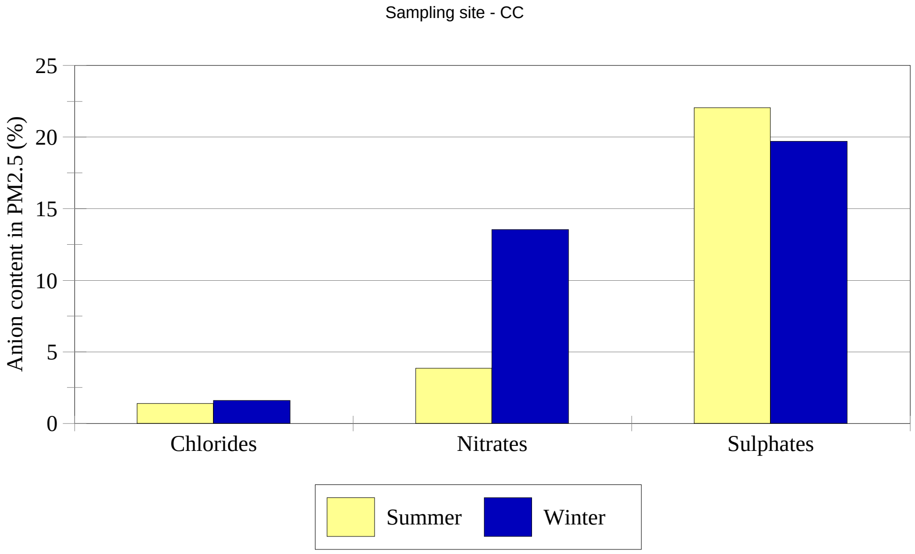

Figure 2. Anion mass content (%) in $PM_{2..5}$ particle fraction measured at sampling site CC in the summer 2002 and winter 2002/3

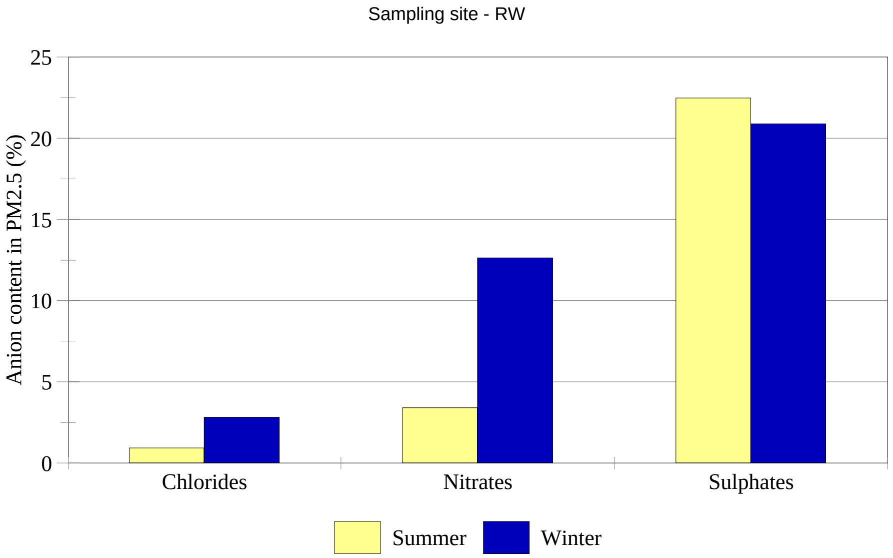

Figure 3. Anion mass content (%) in $PM_{2..5}$ particle fraction measured at sampling site RW in the summer 2002 and winter 2002/3

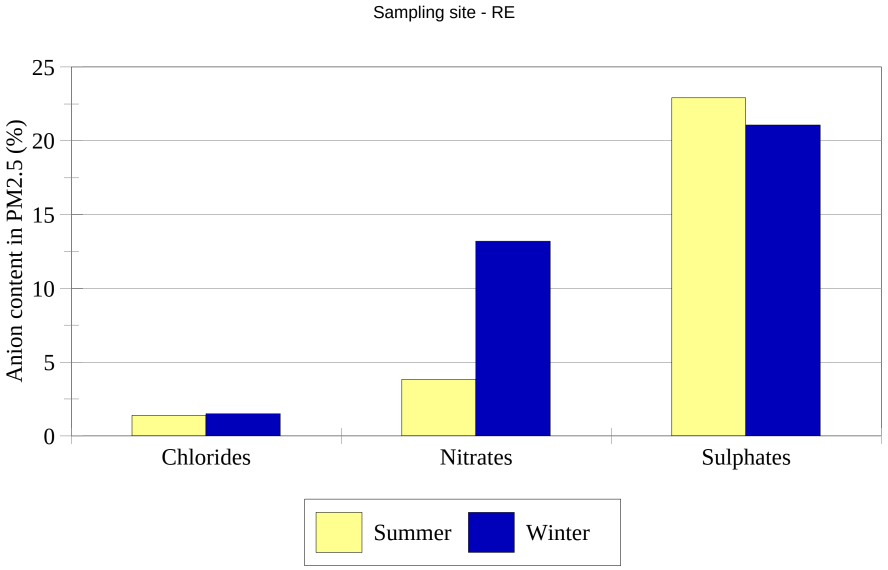

Figure 4. Anion mass content (%) in $PM_{2..5}$ particle fraction measured at sampling site RE in the summer 2002 and winter 2002/3

The content of acidic components nitrates and sulphates in $PM_{2..5}$ particle fraction showed significant differences ($P<0.01$, ANOVA, one-way analysis of variance) between sampling sites in the summer and winter, while the chloride content showed no significant difference ($P>0.05$).

The nitrate content in $PM_{2.5}$ particle fraction showed significant seasonal difference (one-tailed *t*-test) at all sampling sites, while chloride and sulphate content in $PM_{2.5}$ particle fraction showed significant seasonal difference only at sampling sites NR. Higher contributions of nitrates and chlorides to particle mass were in winter period at all sampling sites, while the sulphates contribution in the summer.

The high level of nitrate content in the winter has been observed by Kaneyasu et al. (Kaneyasu et al., 1995). This phenomenon has been accounted for by the shifting of the NH_4NO_3 (s) ↔ HNO_3 (g) + NH_3 (g) equilibrium to the aerosol phase (Solomon et al., 1992). The high level of chloride content in winter could be attributed to the thermodynamic equilibrium of NH_4Cl (s) ↔ NH_3 (g) + HCl (g) reaction (Willson et al., 1985). The high sulphate content in the summer may be due to strong solar radiation in the summer, and photochemical gas-phase oxidation of gas precursor pollutant. During the winter period the aqueous-phase oxidation of gas precursor pollutant to secondary aerosols mainly take place. This process is slower than photochemical gas-phase oxidation (Van Der Zee et al., 1998).

The most abundant species contributing to the $PM_{2.5}$ mass were: sulphates > nitrates > chlorides.

4. CONCLUSION

Mass concentration of major acidic species (chlorides, nitrates and sulphates) in high-risk particle fraction $PM_{2,5}$ in Zagreb air show no significant differences in pollutant concentration levels between the measuring sites in the winter, while significant differences were found for nitrates and sulphates in the summer.

The mass concentrations of investigated anions showed significant seasonal differences, except for chlorides at two sampling sites. Higher mass concentrations of all pollutants were measured in the winter.

The most abundant species contributing to the $PM_{2.5}$ mass were: sulphates > nitrates > chlorides.

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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.

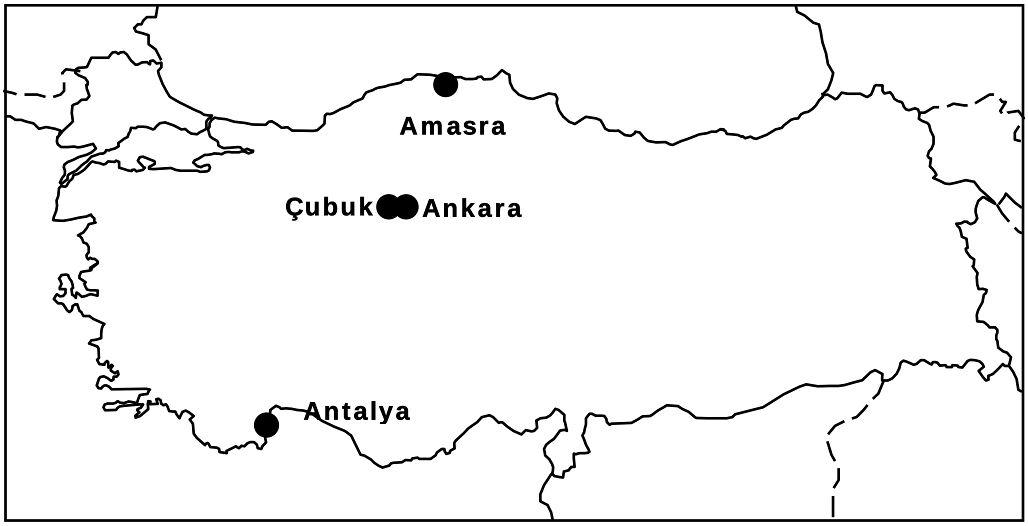

Figure 1. Locations of Sampling Stations

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).

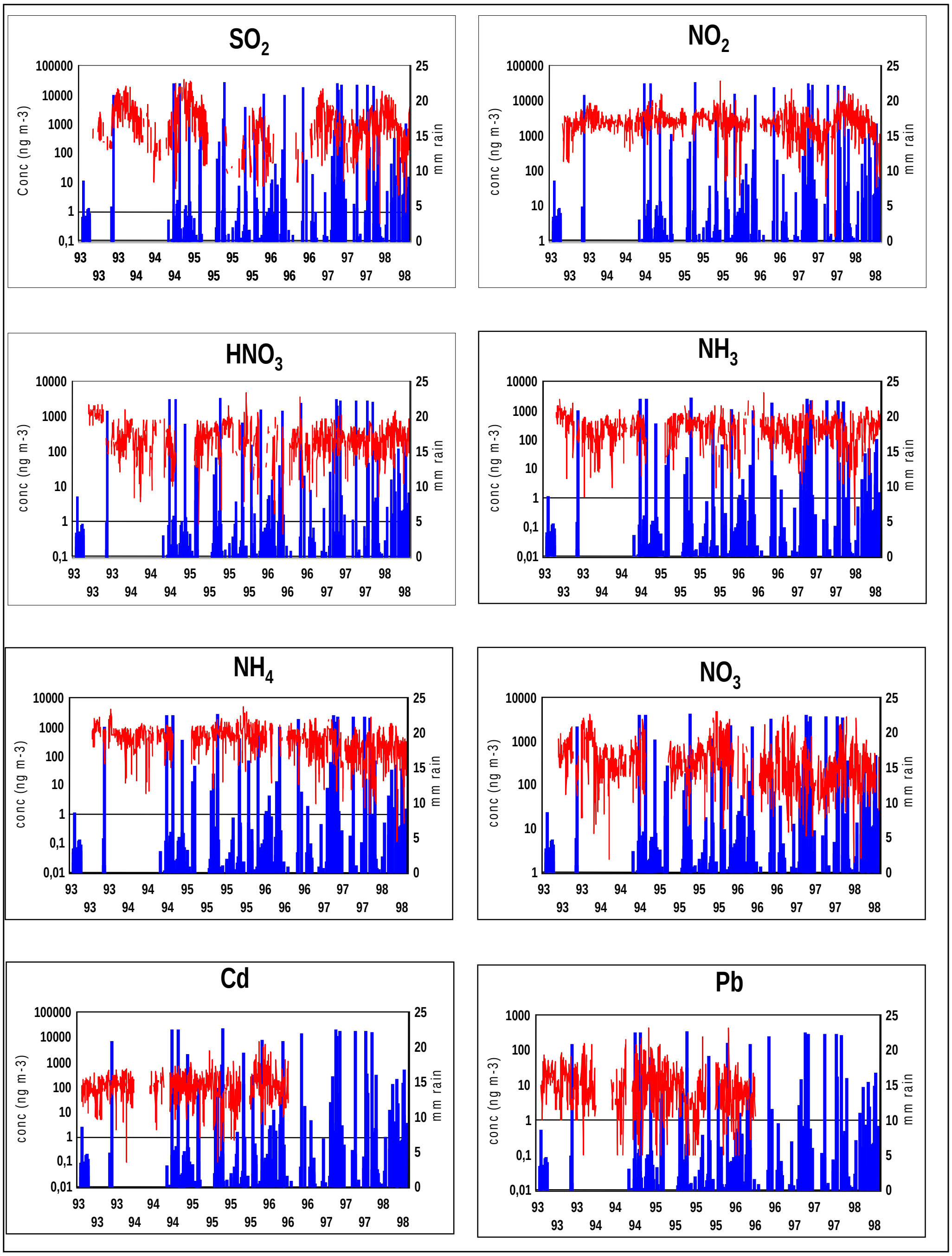

Figure 2. Daily variation in concentrations of selected species in rain and aerosol samples collected at Çubuk Station.

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.

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ELEMENTAL COMPOSITION OF RAINWATER IN MERSİN, AN URBAN SITE IN THE NORTH EASTERN MEDITERRANEAN

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ABSTRACT

Rainwater samples collected at urban sites of Mersin, an industrialized city 800,000 population on the southern coast of Turkey, during the year 2004 were analyzed to determine soluble and insoluble concentrations of trace elements, pH and conductivity. The soluble phase was obtained by filtering of rainwater from 0.45 μm size filters and the insoluble phase by HF:HNO_3 digestion of the material collected on filter paper. Al, Ba, Cd, Cr, Co, Cu, Fe, Mn, Ni, Pb, Sr and Zn were analyzed in both phases and Na, K, Ca and Mg in the dissolved phase by ICP-AES. Precipitation sampled at two central and two suburban sites were used to examine the spatial and temporal variability of rainwater constituents. The pH varied from 4.8 to 8.5 with an average value of 6.0, therefore considered alkaline. Concentrations of trace elements were in the order of Ca > Na > Fe > Mg > Al > K > Zn > Sr > Mn > Pb > Ni > Cr > Cu > Co > Ba > Cd. Terrigeneous particles were shown to be the main source of trace elements. Trace elements grouped according to crustal Enrichment Factors (EFs calculated with respect to Al normalization) showed the precipitation not to be enriched in Ba, K, Fe, Mn and Mg compared to the upper crust composition. Na, Sr, Cr, Ca, Ni, Cu and Co are moderately enriched while Zn, Pb and Cd are highly enriched, most probably by other sources; e.g. sea, vegetation and human activities.

Key Words: Rainwater, Trace elements, North-Eastern Mediterranean, Enrichment factors, Mersin

1. INTRODUCTION

There is considerable interest in the atmospheric trace elements since they are increasingly being introduced into the environment as pollutants (Nriagu and Pacyna, 1988). Their chemistry in the atmosphere is influenced by different sources of gases and aerosols both can be originated from natural (crustal, marine biogenic) and/or anthropogenic emissions. During precipitation events, these gases and aerosols are incorporated into raindrops and this so-called washed-out processes play an important role in atmospheric deposition mechanisms of trace elements to the aquatic and/or terrestrial ecosystems (Barrie *et al.*, 1987). From this point of view, it is possible to obtain important information about the atmospheric trace element reservoirs and the air quality of the local atmosphere through chemical analyses of precipitation.

Mersin is a big and industrialized city located on the south-eastern coast of Turkey, affected by increased air pollution following a rapid increase in its population in recent years. Serious research to determine air pollution levels for the city has not been conducted until present, excluding the intermittent measurements of gaseous SO_2 and particulate matter performed by the Regional Directorate of Environment of İçel (İçel Çevre İl Müdürlüğü). Precipitation samples have been collected continuously for one year at four different urban stations in Mersin. The samples were analysed for pH, conductivity and trace elemental composition. Al, Ba, Cd, Cr, Co, Cu, Fe, Mn, Ni, Pb, Sr and Zn were analyzed in both soluble and insoluble phases while Na, K, Ca and Mg were analyzed only in the soluble phase by ICP-AES.

The aim of this study was to determine the elemental composition of Mersin precipitation. For this purpose different origins of trace elements are discussed with the preliminary data obtained on the total, soluble and insoluble phase of rainwater samples collected between December 2003-June 2004, using enrichment factors, phase distribution and correlations between trace elements.

2. EXPERIMENTAL

2.1. Sampling Stations

Mersin as an industrialized city with more than a million inhabitants is the site for various industries (e.g. petroleum refinery, thermal power plant, soda, chromium, fertilizer and glass production), almost all situated in the industrial district east of the city. Four sampling stations were selected within the residential area of the city (Figure 1), located at roofs of private buildings based on practical and safety considerations. Station 1 is located in Çiftlikköy Campus of Mersin University, at an appoximate height of 60 m from sea-level, on the slopes of Taurus Mountains. The campus is surrounded by agricultural land, mainly lemon groves. Sampling buckets of 30 cm diameter made out of HDPE (high density polyethylene) were deployed at the roof of Mersin Vocational School, a building with central heating and therefore no active chimney. Station 2 is located on the roof of a private building in the newly developing residential area of Yenişehir - Menteş Mahallesi, surrounded by a low density of small private houses and gardens, far from active chimneys. A rain-gauge (Akım Elektronik, Pluviograph, Model PHD5-02) with a special facility for rainwater sampling were deployed at Station 2. Station 3 and Station 4 were located at roofs of a private house and a business center, both heated by electricity, near the highly populated center of the city under the direct influence of other residential heating and dense traffic activity in the area.

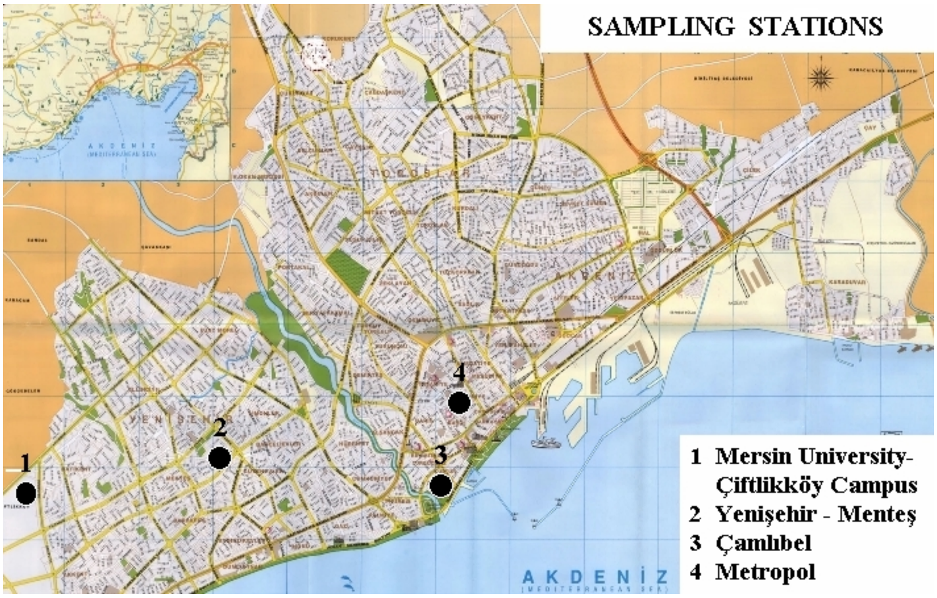

Figure 1. The location of the sampling stations of precipitation in Mersin.

2.2. Analytical Procedure

Sampling buckets, bottles and all glassware used in the laboratory have been washed first with detergent and rinsed with double distilled deionized water. Laboratory equipment have been additionally soaked in 1 M HNO_3 washing solution for 48 h and rinsed with distilled, deionized water several times prior to usage. Precipitation samples collected on an event basis were immediately brought to the laboratory after cessation of the particular rain event. The buckets were tightly sealed with a clean plastic lid in order to avoid contamination during transport to the laboratory. After measuring their volume, the samples were filtered through a 0.45 μm pore size membrane filter (MFS, cellulose acetate, 47 mm diameter) to seperate insoluble particles by appling gentle negative pressure and divided into aliquots for different analyses. Subsamples of precipitation were transferred in rigorously cleansed PE (polyethylene) bottles and preserved at +4°C. Aliquots for major trace metal analysis were preserved by acidification with 0.1 M HNO_3 before storage. Filter samples were preserved at -18°C in a deep-freeze until analysis time.

Membrane fitler samples have been digested according to the procedure given in UNEP (1995), using a microwave digestion oven (MARS 5, Microwave Accelerated Reaction System, CEM Microwave Technology Ltd.) at the Central Research Laboratory of Mustafa Kemal University. Total (HF) decomposition method has been applied with little modification in the adjustment of the microwave oven's power and timing. In digestion of samples HF and Aqua Regia (1:3 v/v HNO_3 and HCl) mixture have been used. Digested samples were diluted to 50 mL volume by double distilled de-ionized water and then transferred into polyethylene bottles in order to preserve them at +4°C until analysis time.

The pH in rainwater was measured by a Mettler Toledo MP120 pH-meter (accuracy of 0.01 pH unit). Conductivity measurements were performed with a DIST H198300/3-4 Conductivity/TDS Meters with automatic temperature compensation. A Varian Liberty II Model ICP-AES at the Central Research Laboratory of Mustafa Kemal University was used for the analysis of trace elements in both soluble and insoluble phases of precipitation. The ICP-AES with axial torch was controlled by PC Pentium III. Plasma power was 1.0 kW and integration time was 1.5 sec. with three replicates. The detection limits of Na, Ca, K and Mg were found to be 0.004, 0.010, 0.005 and 0.003 mg/L, respectively. The reproducibility was better than 4 % for these metals. Detection limits for the other elements were 3.0 $\mu g\ L^{-1}$ for Fe and Zn, 2.0 $\mu g\ L^{-1}$ for Al and Mn, 1.4 $\mu g\ L^{-1}$ for Pb, 0.9 $\mu g\ L^{-1}$ for Sr, 0.7 $\mu g\ L^{-1}$ for Co and Ni, 0.5 $\mu g\ L^{-1}$ for Cu, 0.4 $\mu g\ L^{-1}$ for Cr, 0.1 $\mu g\ L^{-1}$ for Ba and Cd. Standard solutions for trace elements have been prepared daily from 1000 ppm stock MERCK ICP Multi-element Standard solution IV.

The same procedures have been applied to five field blanks collected within the sampling period. Approximately 200 mL of distilled, de-ionized water was poured into the cleaned sampling bucket and deployed at the precipitation sampling stations. The concentration of field and laboratory blanks measured throughout the study were all below the detection limit of the measured trace elements.

3. RESULTS AND DISCUSSION

3.1. pH and Conductivity

A total of 158 samples collected during one year period from four different stations in Mersin. The mean pH of precipitation, calculated from the volume weighted H^+ concentration, was found to be 6.0. Out of 158 samples, 95 % reflects alkaline pH of precipitation, as compared to 5.6 pH of rainwater at equilibrium with atmospheric CO_2. The observed alkalinity of rainwater is mostly due to the high loading of particulate matter present in the local atmosphere of Mersin. The suspended particulate matter which is rich in carbonate/bicarbonate of calcium, buffers the acidity of rainwater (Özsoy and Saydam, 2000).

Electrical conductivity of the precipitation samples was found to be highly variable, within a range of 0 -1300 $\mu S\ cm^{-1}$. The geometric mean conductivity of the 156 samples was 39.7 ± 3.53 $\mu S\ cm^{-1}$. The volume weighted mean total aluminium concentration of 101 precipitation samples was 347.8 $\mu g\ L^{-1}$. The relationship between electrical conductivity and total aluminium concentration is presented in Figure 2, representing a high positive correlation (r = 0.81) between the two parameters. Precipitation samples with relatively high concentrations of aluminium, hence mineral dust, had very high conductivity, most probably due to the high content of soluble solids, high ion adsorption capacity of mineral dust surfaces and adsorption-desorption processes taking place between the solid and liquid phases.

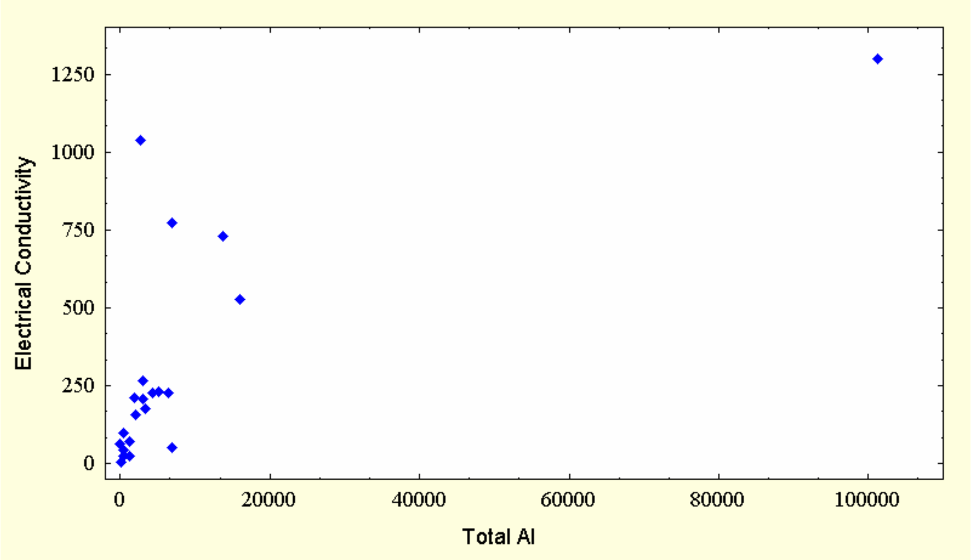

Figure 2. The relationship between the electrical conductivity (μS cm^{-1}) and total aluminium concentrations (μg L^{-1}) in Mersin precipitation.

3.2. Solubility of Trace Elements

Volume weighted mean (VWM) concentrations of the trace elements in the soluble and insoluble phases of precipitation are presented in Table 1. Concentrations of trace elements were in the order of Ca > Na > Fe > Mg > Al > K > Zn > Sr > Mn > Pb > Ni > Cr > Cu > Co > Ba > Cd. Terrigeneous particles were shown to be the main source of the measured elements.

Percentage solubilities of trace elements are found to be in the order of Fe < Al < Mn < Cr < Ba < Cu < Ni < Pb < Cd < Co < Zn < Sr. According to their solubility, measured elements can be evaluated into three groups: The first group includes crustal elements such as Fe, Al and Mn which have less than 15% solubility in precipitation The second group includes Cr, Ba, Cu, Ni and Pb which are moderately soluble in precipitation (solubilities ranging between 20 and 50 %. The third group includes the soluble and mainly anthropogenic elements such as Cd, Co and Zn (ranging between 50 and 80%). Our data are similar to Guieu *et a*l., 1997 concerning Al, Cu, Pb and Zn. On the other hand, the solubility of Fe (0.3%) in Mersin precipitation was found to be much lower than the value (6.2%) reported for Erdemli-Mersin (a rural-coastal area) precipitation (Özsoy and Saydam, 2001). Solubilities of trace elements are a function of several parameters such as pH, the amount of precipitation and the type of aerosols scavenged from the atmosphere during wash-out processes (Chester *et al*., 1993a; Spokes *et al*., 1994). This study have been conducted in the urban atmosphere and the volume weighted mean pH value of this study (6.0) was found to be higher than the pH value of 4.95 reported for the precipitation conducted in rural atmosphere of Mersin. Therefore, pH and the aerosol type might be the reason of the discrepancy between the solubility of iron found in this study and reported in Özsoy and Saydam, 2001.

Table 1. Volume weighted mean concentrations of the measured trace elements in Mersin precipitation. Concentrations are in μg L^{-1}. n refers to the number of samples.

Element	n	Soluble	Insoluble	Total	%Solubility
Ca^{2+}	153	3360	-	3360	-
K^{+}	153	170	-	170	-
Mg^{2+}	153	410	-	410	-
Na^{+}	153	990	-	990	-
Al	101	6.5	341.3	347.8	1.9
Ba	101	1.14	2.57	3.71	30.7
Cd	101	0.45	0.41	0.86	52.3
Co	101	3.06	1.94	5.00	61.2
Cr	101	1.54	6.11	7.65	20.1
Cu	101	2.63	3.43	6.06	43.4
Fe	101	2.42	766.5	768.9	0.3
Mn	101	2.05	13.52	15.57	13.2
Ni	101	3.99	5.11	9.10	43.9
Pb	101	6.12	7.15	13.27	46.1
Sr	101	14.8	3.75	18.53	79.8
Zn	101	36.3	10.4	46.7	77.7

3.3. Enrichment Factors

Enrichment Factors (EFs) provide information on the extent to which trace metal concentrations in aerosols or precipitation are enriched or depleted relative to crustal and marine sources (Duce *et al.*, 1975; Chester *et al.*, 1993b). They are often used to emphasize the natural or anthropic metals enrichment. A value of 10 is generally used to highlight this enrichment. Other sources, different than the crustal or marine ones, explain enrichment factors higher than 10.

The enrichment factor for an element x is defined as:

$$EF_{crust} = (x/Al)_{rain} / (x/Al)_{crust} \qquad (1)$$

$$EF_{marine} = (x/Na)_{rain} / (x/Na)_{marine} \qquad (2)$$

Where x, Al and Na are concentrations, the subscript “rain” denotes the concentration ratio in the precipitation, and the subscripts “crust” and “marine” denote the ratios in the appropriate reference materials (Zoller *et al.*, 1974). In this study, the average composition of upper crust (Rudnick and Gao, 2003) was used as crustal reference materials. The crustal EFs, based on volume weighted mean total concentrations of trace elements are presented in Table 2.

Table 2. Enrichment Factors (EFs) of trace elements in Mersin precipitation, with respect to crust.

Element	EF_{crust}
Ba	1
Fe	5
Mn	5
Mg	6
Ca	31
Na	10
K	2
Cd	2274
Co	68
Cr	20
Cu	51
Ni	45
Pb	183
Sr	14
Zn	164

EF_{crust} for trace elements presented in Table 2 have been grouped into non-enriched, moderately enriched and highly enriched classes, as in the following:

1. Non-enriched elements: Al (the crustal indicator), Ba, K, Fe, Mn, Mg, Na, with volume weighted mean EF_{crust} values of 1-10.

2. Moderately enriched elements: Sr, Cr, Ca, Ni, Cu, Co, with EF_{crust} values in the range of 10-10^2.

3. Highly enriched elements: Zn, Pb and Cd, having volume weighted mean EF_{crust} values in the range of 10^2->10^3

Among the highly enriched elements Zn and especially Pb and Cd are predominantly of anthropogenic origin. Zn and Cd have many common sources, the non-ferrous metal industry accounting for the largest fraction of Zn and Cd emitted (Nriagu and Pacyna, 1988). The largest contribution of Pb to the atmosphere is gasoline combustion, accounting for about 60% of the total anthropogenic emission in Europe (Pacyna, 1984). EF_{crust} values of mainly anthropogenic elements e.g. Zn, Cd, Pb, obtained from this study were found to be approximately, order of magnitude lower than the EF_{crust} values reported for İskenderun (EF_{Zn}:1333, EF_{Cd}:25055, EF_{Pb}:1474, Örnektekin and Çakmaklı, 2003) most likely due to the difference between the volume weighted mean Al concentrations of Mersin (347.8 µg L^{-1}) and İskenderun precipitation (30.04 µg L^{-1}). Enrichment Factors might be evaluated as pollution indicators with respect to upper crust mean composition. However, the EF values have to be used with caution in this type of comparisons. This caution is needed especially when anthropogenic elements are used as tracers, since part of the variability in EF can come not from the element itself but from the variability of the reference element (Al concentration).

3.4. Wet Deposition Fluxes

Wet deposition flux of the trace elements (F_w = mg m^{-2}) can be calculated using the relationship;

$$F_w = C_w \, . \, P \qquad (3)$$

Where C_w is the total (soluble+insoluble) trace element concentration in precipitation and, P is the rainfall. Since, trace element analyses have not been completed yet, approximate annual wet deposition fluxes have been calculated based on the volume weighted mean concentrations of the measured trace elements and cumulative precipitation, The total wet deposition flux of aluminium was found to be 564 mg m^{-2} during the sampling period (December 2003 – June 2004). This value corresponds to an annual flux of approximately 1128 mg m^{-2}. This value is in good agreement with the value reported for a rural area in Mersin (1118 mg m^{-2}, Özsoy and Saydam, 2000). These wet deposition fluxes of aluminium are the highest values among reported values from various stations around the world. These results confirm that the eastern Mediterranean atmosphere is heavily loaded by mineral dust sporadically transported from arid regions (Özsoy and Saydam, 2000).

Among the mainly anthropogenic elements, the wet deposition flux of Zn (76 mg m^{2}) was found to be considerably higher than those of the other anthropogenic elements e.g. Pb, Ni, Cr, Cu, Co and Cd.

4. CONCLUSIONS

Rainfall samples collected during the December 2003 – June 2004 period were analyzed to determine the trace elemental composition and to describe general characteristics of precipitation in Mersin. The results show that the rainwater in Mersin is typically of alkaline character with volume weighted mean pH of 6.0. Mainly Ca^{2+} ions were found to be responsible for neutralizing the acidity of rainwater. Electrical conductivity of the precipitation samples was found to be highly variable. Precipitation samples with relatively high concentrations of aluminium, hence mineral dust, had very high conductivity, most probably due to the high content of soluble solids. Solubilities of the measured trace elements have been investigated and the lowest solubilities were found for the crustal elements (*e.g.* Fe, Al and Mn) while the highest solubilities were obtained for mainly anthropogenic elements (*e.g.* Cd, Co and Zn). Trace elements grouped according to crustal Enrichment Factors, showed the precipitation not to be enriched in Ba, K, Fe, Mn and Mg compared to the upper crust mean composition. Na, S

r, Cr, Ca, Ni, Cu and Co are moderately enriched while Zn, Pb and Cd are highly enriched, most probably by other sources; *e.g.* sea, vegetation and human activities. Wet depositional fluxes of trace elements were in the order of Ca > Na > Fe > Mg >

Al > K > Zn > Sr > Mn > Pb > Ni > Cr > Cu > Co > Ba > Cd. The highest wet depositional fluxes calculated for both marine originated (Ca, Na, Mg) and crustal (Fe and Al) elements suggest that Mersin is under the influence of natural atmospheric sources rather than anthropogenic sources.

5. ACKNOWLEDGEMENTS

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ACID RAINS AND RAINS CAUSING ACIDITY OF SOILS IN SRI LANKA

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ABSTRACT

Acid rains are not a common phenomenon in Sri Lanka, though there is some suspicion of acid rains from polluted atmosphere. However, in the context of atmospheric air pollution, rains that cause soil acidity and subsequent destruction of the crop is equally important and as bad as acid rains *per se*.

Raindrops can combine with NO_2 and SO_2 to yield acid droplets. Although acid rains were not considered a problem in the country, recent research indicates that it occurs in some parts of the country. High levels of sulphur and nitrogen interception by fog in Horton plains supports the suspicion that forest die back at the site is due to acid rains. However it may also possible because of the country's position that the pollutants reaching Horton plains are not from national sources but from cross national boundaries due to wind effects.

Rainfall causing soil acidity and saline conditions was commonly observed during the last three decades in rain-fed paddy lands of southern Sri Lanka. Nilwala Ganga Flood Protection and Drainage project in Matara, was completed in late 1980's and caused nearly 8,000 ha of paddy lands uncultivable due to excessive drainage and subsequent acid sulphate conditions. The paddy farmers who are the poorest of the poor in Sri Lanka were thrown from the 'frying pan to the burning fire'. .Research conducted found that it was due to the oxidation of acid sulphate causing parent material present in the soil catena at about 1 to 1.5 feet below the surface which move upwards to the root zone and causes soil acidity and parched up the broadcast sown or transplanted rice plants.

Paddy soils in the project area have pH values ranging from 4.2 to 2.8, together with the appearance of orange yellowish 'jarosite like material' on the soil surface. Moreover, during the dry weather with the sharp increase in acidity there was a slow but steady increase in salinity too. Owing to erratic rainfall, the young rice crop is subjected to acid sulphate conditions and other toxicities, namely aluminium and iron toxicities, together with low phosphate availability causing the death of rice plants.

Key words: Acid rains, Soil acidity, Atmospheric Pollution, Jarosite, Rain fed Paddy

1. INTRODUCTION

Acid rain is a common term used to describe any form of acid precipitation (rain, snow, hail, fog, etc.). Atmospheric pollutants, such as oxides of Sulphur and Nitrogen, can cause rain to become more acidic when converted to Sulphuric and Nitric acids and therefore relates to the chemistry of air pollution and moisture in the atmosphere. Acid rain is really a series of interactions and reactions among various factors in environment and society and to better understand it we can trace it through five stages, emission, transport, transformation, deposition and effects (Zhao Dianwu and Zhang Xianshan (1981). Because of its nature in transport acid rains has become a global problem instead of a localized problem.

Rainfall is naturally weakly acidic due to the presence of carbon dioxide in the atmosphere which combines with rainwater to form weak carbonic acid. Coal, oil and gas are called fossil fuels because they form over millions of years through the decay, burial and compaction of rotting vegetation on land (coal), and marine organisms on the sea floor (oil and gas). The combustion of fossil fuels produces waste gases such as oxides of N and S and to a lesser extent, chloride. Coal was the first fossil fuel to be exploited on a large scale during the 19th century with the beginning of the Industrial Revolution.. These pollutants such as NO_2 and SO_2, chlorides, can be converted, through a series of complex chemical reactions, into sulphuric acid, nitric acid or hydrochloric acid, increasing the acidity of the rain or other type of precipitation, such as snow and hail.

Rainfall acidity is measured in pH units. ‘Normal’ or ‘unpolluted’ rainfall has a pH of 5.6. This is slightly acidic due to the presence of carbon dioxide in the atmosphere which forms weak carbonic acid in water. The pH scale in acid rain takes a logarithmic scale, and there is a ten fold increase in acidity with each pH unit. Pollutants can be carried many hundreds of kilometers by winds cutting across boundaries of different countries, thus, acid pollutants emitted in one country may be deposited as acid rain in other countries. Some countries emit small quantities of pollutants yet deposition can be several times greater. Thus acid deposition has become an international problem in today’s context. This problem is highlighted by the fact that emissions of a particular pollutant from one country do not equal the deposition of that pollutant in the same country. The most recent UNECE Convention on Long Range Trans-boundary Air Pollution protocol was signed by 27 countries in December 1999. The Gothenburg Protocol, designed to Abate Acidification, Eutrophication and Ground-level Ozone aims to cut emissions of four pollutants: SO_2 NOx, volatile organic compounds (VOCs), and ammonia (NH_3), by setting country-by-country emission ceilings to be achieved by the year 2010.

The UK is committed to reducing sulphur emissions through the 1998 Gothenburg protocol. This Protocol requires UK to reduce sulphur emissions by 85% and nitrogen emissions by 49% by year 2010 (from 1980 levels). To meet these requirements, emissions of sulphur dioxide in UK are being reduced, through the use of cleaner technology within the power generation industry, and the use of cleaner fuels and car engines in the transport sector.

Impacts of Acid Rain

Unpolluted rain normally has a pH of 5.6 it is somewhat acidic because carbon dioxide in the atmosphere combines with water to form carbonic acid. Virtually all plants and animals can neutralize the acidity in normal rainfall and therefore not damaging. However when large quantities of pollutants are expelled in to the air, oxides of N and S, acids are formed and pH values of rainfall can drop. Acid rains can affect the natural ability of plants and animals and their habitats to neutralize acids. When terrestrial and aquatic ecosystems can no longer handle the stress of extra acidity, i.e. they cannot neutralize, and system becomes acidic. Acid deposition, more commonly known as acid rain, results from man-made emissions of SO_2 and NO_x through the burning of fossil fuel for energy and transportation. Acid rain has negative effects on the environment in which we live. Since acid rain is a trans-boundary pollution problem, acidic emissions produced by one country can be deposited in another. Sweden and Norway, for example, both receive more than 90% of their sulphur pollution from abroad. In Sri Lanka the scientists suspects the death of forest plants in the central hills is due to acid rain experienced in the area. If large quantities of acid rain are deposited they may have detrimental consequences for wildlife, forests, soils, freshwater and buildings. Acid rain acidifies the soils and waters where it falls, killing off plants and animals. Surface water acidification can lead to a decline in, and loss of, fish populations and other aquatic species including frogs, snails and crayfish. Acid rain affects trees by damaging their leaves. Certain types of building stone can also be dissolved in acid rain.

Effect on Environment

Acid rain can have serious impacts on trees and forests. Acid rain does not usually kill trees directly. Instead, it is more likely to weaken them by damaging their leaves, limiting the nutrients available to them in the soil, or poisoning them with toxic substances. The main atmospheric pollutants that affect trees are nitrates and sulphates. Forest decline is often the first sign to show that trees are in trouble due to air pollution. Sometime it takes many years of acid deposition for effects to be noticeable.

Scientists believe that acidic water once deposited on soil dissolves the nutrients and other helpful minerals in the soil and then washes them away before absorption by the flora. At the same time, the acidity that develops in the soil causes the release of toxic substances such as aluminum into the soil. These are very harmful to trees and plants, even in minute quantities. If large quantities of acid rain are deposited they may have detrimental consequences for wildlife, forests, soils, freshwater and buildings. Acid rain acidifies the soils and waters where it falls, killing off plants and animals. Surface water acidification can lead to a decline in, and loss of, fish populations and other aquatic species including frogs, snails and crayfish. Certain types of building stone can be dissolved in acid rain.

Forests in high mountain regions receive additional acid from the acidic clouds and fog that often surround them. These clouds and fog are often more acidic than rainfall. When leaves are frequently bathed in this acid fog, their protective waxy coating can wear away. The loss of the coating damages the leaves and creates brown spots.

Industrial revolution

Over the past several decades scientists have been keeping records of pH values of precipitation and compare the past and the present. Amount of acid in rains is insignificant in early 1800. Industrial revolution increased burning of coal and oils sending many acid forming gasses and particles into the air. In 1872 Robert Smith UK indicated the link between coal burning to rusting of metals, fading of dyes in areas where coal is used heavily. In the year 1900 it was reported that the fishes in the Norwegian and Swedish lakes are been affected by acid rains. During 1960's increase in S & N in polluted air caused respiratory illnesses in UK and found pH vales of rain is 100 times more than normal. 1979 average pH of rainfall is 4.1 in Ontario, Canada and New York in USA. 1992 the western UDA had an average pH value of 4.2 much more acidic than normal. The emission of SO_2 in 1960's is 31 million mt per year in USA which was reduced to 23 with the government intervention where as NOx it was 1970's which stands at 16 million mt has risen to 18.9 million in 1985

Trans-boundary Pollution

Stationary emission sources, such as coal-fired and oil-fired power stations, and mobile sources, such as cars, ships and aircrafts emit a complex mixture of pollutants, including SO_2 and NOx (the precursors to acid rain). It is now well established that this air pollution is transported over hundreds or even thousands of kilometers. Consequently, when acidic pollution is finally deposited, its environmental impacts are felt in areas far away from their sources. Since this air pollution has no regard for national boundaries, it has been termed trans-boundary pollution. The critical loads for total acidity of sulphur and nitrogen need to be determined so that a coherent international agreement can be reached with regard to abatement policies. There are numerous methods that are available for obtaining critical loads. In order to obtain values for the critical loads, an ecosystem has to be chosen and then a suitable indicator species is selected to represent the ecosystem. A chemical limit is subsequently defined. Svanke Oden (1960) reported acidity in Scandinavian lakes have been affected by pollution carried on the wind from UK and Western Europe.

2. ACID RAINS IN SRI LANKA

Geographical positioning of Sri Lanka has its advantages on acid deposition. Since the country is surrounded by the sea, the tropical monsoon winds and the sea and land breeze during the inter-monsoon period help the country to lower the concentration of atmospheric pollutants and disperse them. Raindrops can also combine with NO_2 and SO_2 to yield acid droplets. Although acid rains were not considered a problem in the country, recent research indicates that it occurs in some parts of the country. Illeperuma & Premakeerthi (1998) have monitored acid rains in several parts of the Island and the data obtained are given in Table 1 where Matara recording a pH of 6.00 in rain water.

Table 1. Incidence and quality of acid rains monitored at different locations of Sri Lanka.

Location	pH	Cl^- (ppm)	NO_3 (ppm)	SO_4 (ppm)
Colombo	5.89	2.22	0.57	2.95
Galle	6.45	18.06	0.90	2.44
Matara	6.00	13.46	1.25	2.10
Hambantota	5.89	10.00	1.89	2.00
Peradeniya	6.26	2.77	0.19	0.76
Puttalama	7.00	2.56	0.43	2.47
Anuradhapura	6.00	1.63	0.74	0.05

High levels of sulphur and nitrogen interception by fog in Horton plains supports the suspicion that forest die back at the site is due to acid rains. However it may also possible because of the country's position that the pollutants reaching Horton plains are not from national sources but from cross national boundaries due to wind effects.

Rain causing acidity in Sri Lanka

Rain causing acidity is much more serious in Sri Lankan context than acid rains *per se* because the suspected rains in the central highlands do not possess high acidity like in other countries. Further, the suspected acid rain damage in the central hills of the country may again be due to trans-boundary effect as there were no heavy industries within the country. In the south west coast of Sri Lanka low lying lands between 0.3 m above mean sea level(MSL) there are approximately 28,350 ha of poorly drained, flood prone, half bog and bog soils (Cooray 1967, Arumugam 1969, Douglas et al 1969) together with 3000-3400 ha of mineral alluvial soils of variable drainage and texture. In these lands a total of 32,000 to 36,000 ha were presently grown to rice regularly or occasionally. Below MSL there are approx. 8,900 to 11,000 ha where, despite acute hydrologic and coastal salinity related problems, a single, long aged crop is cultivated in favourable years, hence a total extent of 42,000 ha of high risk and low productivity lands. Since the removal of forest canopy in the central highlands the water flow in the river receded and during the dry periods of the year there was sea water movement upstream along the river and deposited the sulphate in the river bank which reacted with ferrous ions to form jarosite. This process has been there for several decades but due to reduced conditions and high water table in the area they remained as un-harmful.

Bog soils have more than 30 % organic matter and consist of black or brownish muck, mucky peat or peat (Dimantha 1977). Dimantha and Jinadasa (1981) have cautioned that Bog and half Bog soils have a fair amount of sulphides in the wet anaerobic conditions and if these soils are drained too much and get aerated sulphates would form and soils become extremely acidic. Half bog soils contain 15-30% organic matter and similar in reaction to bog soils though they have better bearing capacity.

During the rainy weather the removal of flood waters from low elevation lands is impeded owing to the rapid rise of ground water to the soil surface, and even above, which prevents vertical drainage. Furthermore the weak seaward gradient drastically reduces horizontal drainage. Consequently, during rainy weather the land gets quickly water logged with standing water of a few cm riding from 30 to 60 cm for periods ranging from a few days to 2-3 months.

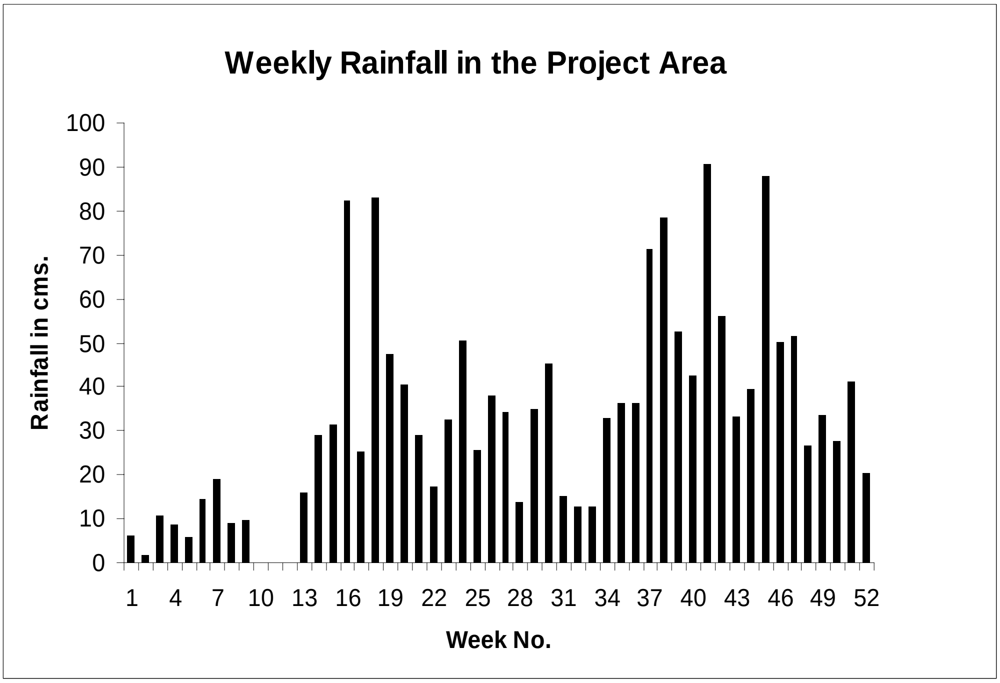

Figure 1. Weekly rainfall in the Project Area, Matara, Sri Lanka during 1995-1999

The rainfall data in the project area (Figure 1) shows that the rainfall during the first 13 weeks is less than one cm and during this period there is oxidation of jarosite due to oxidized conditions present in the soil. This enables the oxidation of sulphide producing hydrogen sulphide (H_2S) or sulphur dioxide (SO_2) which will be released from the soil. The H_2S and SO2 will then move upwards due to the evaporation pull and when it reaches the root zone and with the onset of dry season (*yala*) rains proper, reacts with rain water producing sulphuric acid. Normally land preparation for *yala* rice crop starts by the 13th week and the broadcasting rice seeds are the normal practice. When there is good rain by about the 16th week the plants are small and get killed due to acid conditions formed in the soil. Once again by the 30th week onwards (before the onset of wet (*maha*) season) there is a period of drought and the process gets repeated. This phenomenon is well described in Table 2 where monthly variation of pH and EC values over a year is given. Data clearly shows that the pH values drops severely and EC values are higher during the first 13 weeks of the year where there is less rainfall.

Table 2. Fluctuations in pH and EC in Channels, Fields and River during the period 1986-1990

Month	Rain Fall in mm 1917-1955	Drainage Channel		Malimboda Paddy Field		Nilwala River	
		pH	EC ms/cm	pH	EC ms/cm	pH	EC ms/cm
January	60	2.8	1.9	2.8	2.1	6.1	0.8
February	50	2.7	2.2	2.7	2.2	6.2	1.2
March	100	2.7	2.1	2.8	2.1	6.3	0.9
April	150	2.8	2.3	2.7	2.5	6.1	0.8
May	265	2.8	1.7	3.2	0.9	6.2	0.8
June	190	3.3	1.1	3.7	0.8	6.1	0.9
July	140	4.1	0.9	4.1	0.9	6.1	2.1
August	145	3.1	1.2	3.7	1.2	6.2	2.4
September	180	3.4	1.2	3.8	1.1	6.3	1.2
October	280	3.7	0.8	3.8	1.1	6.3	0.8
November	240	4.1	0.7	4.1	0.7	6.1	0.9
December	165	3.9	0.7	4.1	0.7	6.1	0.8

Table 2 also shows that during droughty weather in some areas strong soil acidification occurred, with pH values in the range of 4.2 to 2.8 together with the appearance of orange yellowish jarosite like material on the soil surface. Moreover in the dry weather with decreasing surface water and corresponding sharp increase in acidity there was a slow but steady increase in salinity too. However, before threshold toxic salinity values are reached the pH dropped sharply below 3.5 bringing about lethal acid sulphate conditions. On such soils owing to erratic rainfall, the rice crop particularly the young crop is subjected to the devastating effects of acid sulphate conditions namely aluminum and iron toxicities together with low phosphate availability. Hence the death of rice plants in coastal areas during droughty weather often attributed by the farmers to ‘kiula’ is in fact frequently due to a combination of injurious factors associated with soil acidification, salinity and water stress.

The different soils types described above namely bog, half bog and mineral soils are comparatively high in organic matter. Oxidation of organic matter due to high drainage conditions also produce organic acids increasing the soil pH which do not get leached because of low rainfall. This process also contributes to soil acidity in the area. Since these paddy tracts are cultivated under rainfed conditions acid saline conditions are developed and was not leached down. Thus the paddy cultivation in these tracts collapsed totally over the years.

The above discussion shows that though Sri Lanka is fairly safer from acid deposition through rainfall due to geographical positioning and comparatively low industrialization, acid deposition below ground due to manmade causes have similar detrimental effect on the vegetation and is equally serious.

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COMPARISON OF SOURCES AFFECTING CHEMICAL COMPOSITIONS OF AEROSOL AND RAIN WATER AT THREE DIFFERENT LOCATIONS IN TURKEY

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ABSTRACT

In this study, relationship between chemical compositions of atmospheric aerosol and rainwater is investigated using receptor-oriented methods utilizing long-term data collected at Antalya and Amasra stations in Turkey. Factor analysis (FA) performed to aerosol and rainwater data sets yielded that source types affecting chemical compositions of rain and particles are generally the same, but contribution of each source type to rain and aerosol compositions shows differences. Potential source contribution calculations were also performed to investigate if the source regions affecting chemical composition of rain and particles are identical.

Key Words: Aerosol, Rainwater, Factor analysis, Potential source contribution function

1. INTRODUCTION

Receptor oriented models are used to provide information regarding source characteristics from the measurements of chemical composition at a sampling site and to determine the contributions of each source to the measured pollution level. In air pollution studies, among all multivariate statistical approaches, factor analysis (FA) have been most commonly applied to arrays of pollution variables, to aerosol and precipitation elemental composition data, or to the spatial pollution distributions in order to derive information about pollution sources influencing the data (Al-Momani, 2005; Gao et al., 2002; Plaisance et al., 1997). A receptor model that explicitly combines the results of FA with meteorological data in a unique analysis scheme to produce a probability field for source emission potential, called potential source contribution function (PSCF), might be suitable for such a task (Plaisance et al., 1997). The PSCF calculations was first performed by Malm et al. (1986), than successfully used to determine source regions affecting pollutant concentrations at various receptors (Liu et al., 2003; Stohl et al., 2002; Polisar et al., 1998).

In this study, FA and PSCF calculations are performed to investigate if the source types and the source regions affecting chemical compositions of particles and rain measured at Antalya and Amasra stations in Turkey are identical or not.

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 and aerosol (Karakaş, 1999) and rainwater (El-Agha, 2000) compositions at Amasra Station. A brief description of experimental techniques is presented in the following paragraphs as detailed description of methods used for sampling and analysis of both aerosols (Güllü, 1996; Karakaş 1999) and rain water (Al-Momani, 1995; El-Agha, 2000) are given elsewhere.

2.1. Sampling Site

The data sets used in this study are generated at two stations located in different parts of Turkey. Amasra Station was located approximately 20 km east of Amasra town and 3.5 km away from the Black Sea (32.29 longitude east of Greenwich and 41.47 latitude north of Equator). Antalya Station was located on a land owned by the Ministry of Forestry that is approximately 20 km away from the city of Antalya,. The locations of the sampling stations are depicted in Figure 1.

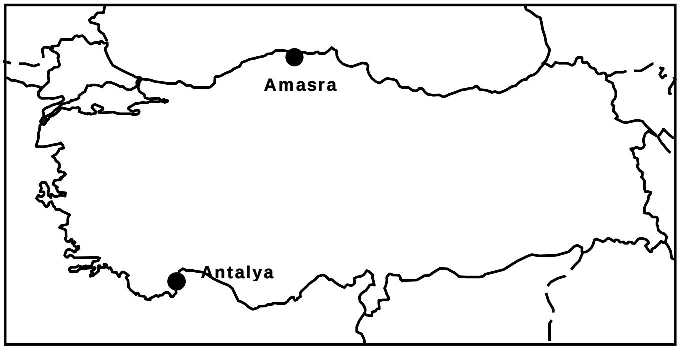

Figure 1. Locations of the Sampling Stations.

2.2. Sampling and Analysis Methodology

Aerosol samples were collected on cellulose filters (Whatman-41), for 24-hour periods using an Andersen Hi-Vol sampler at Amasra and Antalya stations. Rainwater samples were collected using Andersen wet and dry sampler that enable collection of wet and dry deposition samples separately at both stations. A modification was made on wet and dry sampler so that rainwater was first collected with a funnel, then passed through a filtration unit equipped with a 0.47 μm pore sized cellulose acetate membrane filter and ended up in the sampling bottle. The analysis of residue on the filter and solution in the sampling bottle provided determination of fractions of elements and ions in particulate phase and dissolved in rainwater separately. In this study, total concentrations (dissolved + particulate) of elements and ions are used in statistical treatment of data.

Samples collected on filters were digested by a HNO_3-HF mixture. Then the samples were analyzed for elements Al, Fe, Pb, Mg, Zn, Cu, Ba, Mn, Na, K, Ca Ni, Cr, Cd, Pb and V using a Perkin Elmer 1100B Atomic absorption spectrometry. Concentrations of SO_4^{2-}, NO_3^-, Cl^- and NH_4^+ in aerosol and rainwater samples were measured by ion chromatography and spectrometric methods. Aerosol samples collected at both stations were also analyzed by instrumental neutron activation analysis.

3. RESULTS AND DISCUSSION

In this study, factor analysis was performed to the data collected at Antalya and Amasra stations. In this analysis, the Statgraphics Statistics Software with varimax rotation is used to improve orthogonality of resolved factors.

3.1. Results of FA for Antalya Dataset

The results of FA performed for the data generated at Antalya Station are given in Table 1 and Table 2 for aerosol and rainwater datasets, respectively. Factor 1 in Table 1 that is loaded with Al, Cr, K, Mg, Ca, Ni, NO_3^- and SO_4^{2-} is a crustal factor. The NO_3^- and SO_4^{2-} are anthropogenic components in this factor, but previous studies showed that some of these components are in the form of $CaSO_4$ and $Ca(NO_3)_2$ (Güllü et al., 1998) and some of the fine SO_4^{2-} and NO_3^- particles stick on coarse crustal particles (Kuloğlu, 1997). Factor 2 in Table 2 that is loaded with Al, Ca, Cr, K, Mg, Ni is a crustal factor in rainwater dataset. There are some differences between crustal factors resolved by FA from rainwater and aerosol datasets. Crustal factor accounts for 35% of variance in aerosol dataset, whereas it accounts for a smaller fraction of the system variance (i.e., 15%) in rainwater dataset. This is due to stronger influence of sea salt on the composition of rain water, whereas crustal particles has stronger influence on composition of aerosol.

Factor 2 in Table 1 and Factor 1 in Table 2 that is loaded with Na, Cl, Mg, K and Ca represents marine factor in aerosol and rainwater datasets, respectively. The most important difference between rain and aerosol FA results is that the marine factor explains a significantly greater fraction of system variance in rainwater as it accounts for a larger fraction of the ionic mass in rain. This suggests that amount of sea salt in rainwater cannot be explained only by wash-out of sea salt in particles present at station site. Sea-salt in rainwater samples are also introduced by rain-out process at which cloud itself brings sea salt while it is transported to Mediterranean. Factors 3 in Table 1 and Factor 4 in Table 2 are anthropogenic factors in aerosol and rainwater datasets, respectively.

The results of FA performed for aerosol and rainwater data generated at Antalya Station demonstrate that crustal and marine components, which have strong local sources, show differences for aerosol and rainwater datasets. On the other hand, components that are transported from distant sources and anthropogenic components are similar both for aerosol and rainwater datasets.

Table 1. Results of FA for Antalya aerosol dataset.

	Factor 1	Factor 2	Factor 3	Factor 4	Communality
Al	**0.81**				0.74
Ca	0.36	0.19	**0.66**		0.61
Cl		**0.94**			0.90
Cr	0.60		**0.49**		0.62
K	0.76	**0.50**			0.84
Mg	0.39	**0.77**			0.84
Na		**0.87**			0.78
NH_4^+			**0.70**	0.24	0.58
Ni	0.84				0.73
NO_3^-	0.78			0.32	0.72
Pb				**0.81**	0.72
SO_4^{2-}	0.75			**0.42**	0.81
Eigenvalue	4.22	2.37	1.39	0.92	
% variance	35.13	19.74	11.62	7.64	74.14

Table 2. Results of FA for Antalya rainwater dataset.

	Factor 1	Factor 2	Factor 3	Factor 4	Communality
Al		**0.70**			0.56
Ca	**0.55**	**0.49**	**0.36**		0.73
Cl	**0.92**				0.89
Cr		**0.55**	**0.30**		0.51
K	**0.86**	0.31			0.84
Mg	**0.84**	0.20			0.80
Na	**0.90**				0.85
NH4			**0.81**	0.22	0.71
Ni		**0.74**			0.56
NO3				**0.65**	0.45
Pb				**0.68**	0.47
SO4			**0.64**		0.55
Eigenvalue	3.68	1.89	1.25	1.11	
% variance	30.67	15.78	10.40	9.23	66.08

3.2. Results of FA for Amasra Dataset

The results of FA performed for aerosol and rainwater datasets generated at Amasra Station are given in Table 3 and Table 4, respectively. Factor 2 in Table 3 that is highly loaded with Al and Fe and moderately loaded with Ca, Cr, K, Mg, Ni, NO_3^-, SO_4^{2-} and V is a crustal factor in aerosol dataset. Similarly, Factor 1 in Table 4 that is mainly loaded with Al, Fe, K, Mg, Na and moderately loaded with Ca, Cd and V is a crustal factor in rainwater dataset. Although there are some differences, these factors clearly represent crustal component in rainwater and aerosol data collected at Amasra atmosphere.

Factor 3 in aerosol and Factor 2 in rainwater FA results are anthropogenic components with similar basic compositions. Factor 3 in Table 3 is loaded with NH_4^+, SO_4^{2-}, NO_3^- and other anthropogenic elements such as Cd, Pb and Zn. Factor 2 in Table 4, however, is loaded with NH_4^+, SO_4^{2-}, NO_3^- and Cd. As a matter of fact, both in aerosol and rain data this factor is a neutralized acidity factor.

Factor 4 of aerosol dataset is a clear marine factor that is loaded with Na, Cl, Mg, K and NO_3^-. Factor 5 of rainwater dataset is also a marine factor with similar loadings. Factor 5 of aerosol dataset is another crustal factor loaded with Al, Ca, Cd, Fe, Mg, NH_4^+, Pb and Zn. Presence of Cd, NH_4^+, Pb and Zn suggests mixing of some anthropogenic components into this factor. Corresponding crustal factor in rainwater dataset is Factor 4 that is loaded with Ca, Cl, Fe, NH_4^+, Ni and Zn. These two factors probably represent the same components in aerosol and rainwater that is a mixed crustal-anthropogenic component. This component is clearly identified in aerosol dataset but it is not as clear in rainwater dataset. This is probably due to smaller number of rainwater samples included in the analysis compared to aerosols. Factor 6 of rainwater and aerosol datasets shows differences. This factor is an anthropogenic component for both datasets, but loaded with different elements and ions. This could either indicates a component brought to station from distant sources or an artifact in statistical tool used.

Table 3. Results of FA for Amasra aerosol dataset.

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Comunality
Al		**0.87**			**0.33**		0.88
Ca		0.19			**0.86**	0.12	0.80
Cd	**0.48**		**0.40**		0.11	**0.42**	0.59
Cl				**0.92**			0.87
Cr	**0.82**	0.13					0.70
Fe	0.19	**0.88**			0.23		0.88
K		0.25		0.13		**0.83**	0.79
Mg	0.14	**0.38**		0.29	**0.80**		0.90
Na				**0.91**			0.85
NH_4^+	0.15		**0.82**		0.17		0.74
Ni	**0.63**	**0.38**	0.11			0.14	0.61
NO_3^-	0.16	**0.39**	**0.40**	**0.54**		0.21	0.67
Pb	**0.72**		**0.33**		0.23		0.71
SO_4^{2-}		0.20	**0.86**				0.78
V	**0.51**	**0.37**	**0.53**			0.19	0.72
Zn	**0.39**		0.15		0.17	**0.68**	0.69
Eigen value	4.36	27.23	1.63	1.41	1.25	1.07	
% variance	2.47	15.46	10.16	8.84	7.82	6.71	76.21

Table 4. Results of FA for Amasra rainwater dataset.

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Communality
Al	**0.92**		0.15				0.88
Ca	**0.46**	0.13		**0.64**		0.13	0.66
Cd	0.18	**0.54**	**0.34**			**0.34**	0.58
Cl		0.13		0.11	**0.78**		0.66
Cr						**0.45**	0.29
Cu	0.21				0.10	**0.77**	0.65
Fe	**0.93**			0.13		0.18	0.92
H	0.11						0.39
K	**0.91**		0.11			0.14	0.86
Mg	**0.87**		0.22				0.82
Mn	**0.46**			0.27	0.21	**0.53**	0.61
Na	**0.52**				**0.34**	0.26	0.47
NH4		**0.65**		**0.36**			0.62
Ni			**0.43**	0.18	**0.58**	0.25	0.62
NO3		**0.81**			0.18		0.70
Pb	**0.35**		**0.72**				0.65
SO4	0.14	**0.59**			**0.43**		0.64
V	0.16		**0.80**				0.68
Zn				**0.78**	0.23		0.68
Eigen value	4.93	1.99	1.63	1.48	1.27	1.08	
% variance	25.94	10.49	8.59	7.80	6.70	5.70	65.22

3.3. Potential Source Contribution Function

In this study, PSCF calculations are applied to factor scores obtained from FA at Antalya and Amasra stations, and source regions of similar factor components of rain and aerosol are compared. Similarities in factors involve particular uncertainty in calculations. In order to reduce the uncertainties, PSCF calculations are applied to SO_4^{2-} concentrations in rainwater and aerosol samples collected at Antalya and Amasra stations.

3.3.1. Results of PSCF for Antalya Dataset

As explained in previous sections, Factor 1 of aerosol dataset and Factor 2 of rainwater dataset resolved by FA represents crustal component. Distribution of PSCF values calculated for crustal components of aerosol and rainwater are depicted in Figure 2(a). Source regions for crustal components in aerosol and rainwater samples are not exactly the same. The main difference is that sources of crustal component are more local for rainwater dataset. Crustal material that forms this component in rainwater are located in the western parts of Turkey, where as crustal particles that arrive from regions in Europe also contribute crustal component in Eastern Mediterranean aerosols.

Distribution of PSCF values for rainwater and aerosol Factor 4 scores are given in Figure 2(b). Factor 4 has the same composition for both aerosol and rainwater dataset, suggesting that rainwater and aerosol compositions are affected from similar source types, but there are significant variations in the source regions identified by PSCF calculations. PSCF calculations for aerosol dataset suggest that sources effecting Factor 4 are located in the western part of Turkey. On the other hand, PSCF calculations for rainwater suggests that sources located at the central Anatolia are mostly responsible for species associated with this factor. There are significant source areas in central Europe (e.g., Romania, Bulgaria, Ukraine) Factor 4, but these distant source areas do not appear when PSCF is calculated for Factor 4 of rainwater.

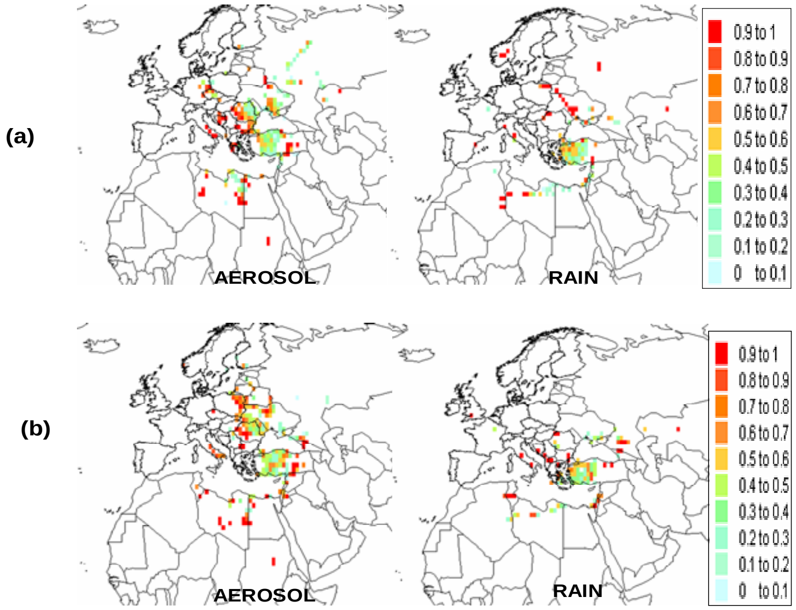

Figure 2. (a) Distribution of PSCF calculated for factor 1 in aerosol FA and factor 2 in rainwater FA at Antalya, (b) Distribution of PSCF calculated for factor 4 in aerosol and rainwater FA at Antalya

3.3.2. Results of PSCF for Amasra Dataset

Factor 1 of aerosol and Factor 2 of rainwater datasets resolved by FA are found to represent anthropogenic component. Source regions do not exactly match for these anthropogenic components of aerosol and rainwater datasets. However, general pattern is similar as observed for Antalya Stations with affecting source regions for both aerosol and rain being located to the north of the Black Sea.

Factor 2 and Factor 1 resolved by FA represent crustal component for aerosol and rainwater datasets, respectively. Source regions for crustal component of rainwater data are located to the north of the Amasra Station. Source regions for crustal component of aerosol dataset are generally from Balkan countries in addition to sources at north. However, unlike at Antalya Station, there is no indication that source regions affecting rain factor is more local compared to source regions assigned to this factor in aerosol FA.

As explained in previous sections, Factor 3 of aerosol and rainwater dataset resolved by FA represents the same anthropogenic component. When distribution of PSCF scores for rainwater and aerosol datasets are compared, similar distributions are observed with the results of the previous factors. Source regions are generally located at north of Black Sea for both aerosol and rainwater, but just like the other factors, there is no exact match for these regions. West of Aegean and even Africa coasts are observed as source regions for anthropogenic component of aerosols. These source regions could not be observed in the anthropogenic component of rain.

3.3.3. Results of PSCF for Sulfate

Potential source contribution function calculations are also performed for SO_4^{2-} concentrations in rainwater and aerosol datasets generated at Antalya and Amasra stations. Results are depicted in Figure 3(a) and 3(b) for Antalya and Amasra sations, respectively. As in the case of Antalya dataset, distributions of PSCF values calculated for SO_4^{2-} concentrations measured at Amasra Station have similar spatial distribution observed for the PSCF values obtained from FA. It is observed that, SO_4^{2-} concentrations both in rainwater and aerosol samples are generally affected from the sources located at north of Europe. Some parts of Turkey, Ukraine, Russia and some regions at Balkans have a contribution to the SO_4^{2-} concentrations both in rainwater and aerosol samples.

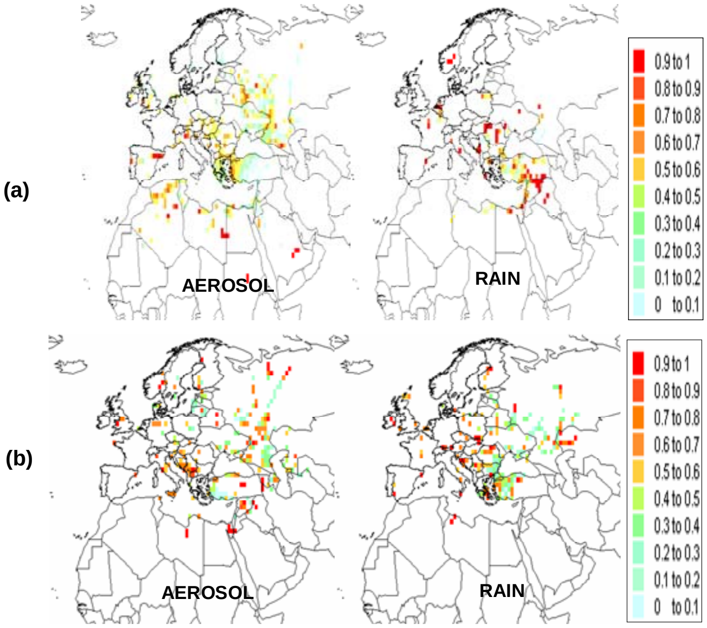

Figure 3 (a) Distribution of PSCF applied to rain water and aerosol Sulfate concentrations obtained at Antalya, (b) Distribution of PSCF applied to rain water and aerosol Sulfate concentrations obtained at Amasra

PSCF calculations applied for both SO_4^{2-} concentrations and factors obtained from FA at Antalya, clearly indicate that rainwater compositions are affected from local sources more than aerosol does. On the other hand, there is not a clear indication of higher influence of local sources on rainwater than on aerosol at Amasra. It is not possible to explain the reason for the variation between stations by the current knowledge. This variation could be due to the differences of airflow climatology at different heights and seasons. In order to understand this mechanism completely, a comprehensive modelling study is needed.

CONCLUSIONS

Factor analysis performed for the aerosol and rainwater data generated at Antalya and Amasra stations yielded generally similar components suggesting that wash-out of local aerosol particles has a profound influence on the composition of rainwater collected at both stations. However, lack of exact match between crustal and marine factors in Antalya and anthropogenic components in Amasra indicates that the fraction of natural anthropogenic species brought by clouds to sampling site can not be totally ignored in explaining chemical composition of rain in these two stations. Another possibility for the observed similarity between factors obtained in aerosol and rain FA exercises is that the composition of rain might be totally independent of aerosol composition at the sampling location. But the source types not necessarily affecting chemical composition of rainwater and aerosol sampled at the stations may be very similar. In such a case factors obtained in aerosol and rain FA would be similar as observed in this study.

PSCF calculations are performed using both aerosol and rain composition data at Antalya and Amasra, to determine if the source regions affecting chemical composition of rainwater and aerosol particles are the same or different. The general pattern observed in distribution of source regions in rainwater and aerosol datasets showed some similarities in both stations, but there are substantial differences in detail. The most notable difference between PSCF results in Antalya and Amasra is that source regions affecting composition of rainwater in Antalya are much more local compared to source regions affecting compositions of particles. Such difference is not observed in Amasra.

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