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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.

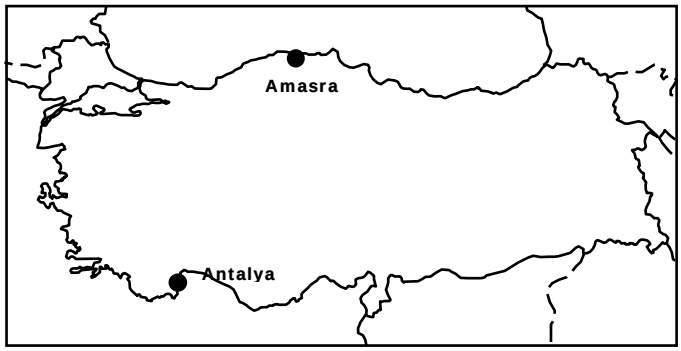

Figure 1. Locations of the Sampling Stations.

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.

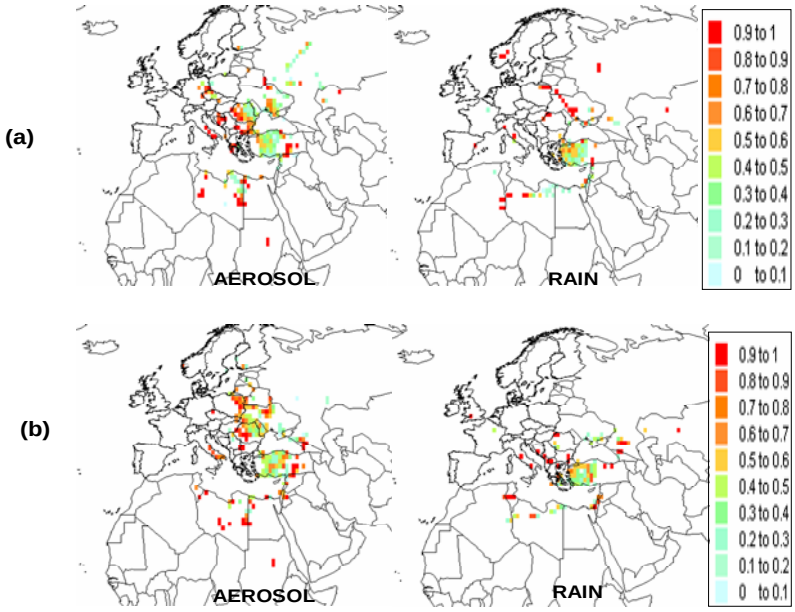

Figure 2. (a) Distribution of PSCF calculated for factor 1 in aerosol FA and factor 2 in rainwater FA at Antalya, (b) Distribution of PSCF calculated for factor 4 in aerosol and rainwater FA at Antalya

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.

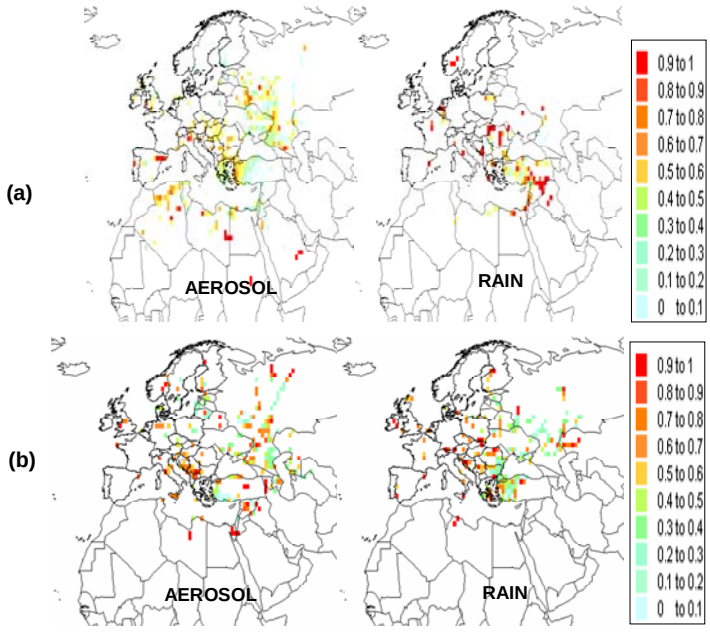

Figure 3 (a) Distribution of PSCF applied to rain water and aerosol Sulfate concentrations obtained at Antalya, (b) Distribution of PSCF applied to rain water and aerosol Sulfate concentrations obtained at Amasra

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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