Trace elements in urban and suburban rainfall, Mersin, Northeastern Mediterranean

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ABSTRACT

Spatial/temporal variabilities of rainwater constituents are examined based on soluble/insoluble trace elements, pH and electrical conductivity measurements in rainfall sampled during December 2003–May 2005 at two urban and two suburban sites in Mersin, an industrialized city of 850,000 inhabitants on the southern coast of Turkey. In the analyses, backward air mass trajectories for rainy days were used in addition to factor analyses, enrichment factors, phase distributions and correlations between trace elements. The pH varied from 4.8 to 8.5 with an average value of 6.2, reflecting a mainly alkaline regime. Mean concentrations of trace elements collected from urban and suburban sites are spatially variable. Based on the overall data, total concentrations of trace elements were ordered as Ca>Na>Fe>Al>Mg>K>Zn>Mn>Sr>Pb>Ni>Cr>Ba>Cu>Co>Cd. Mainly terrigeneous (Ca, Fe, Al) and, to a lesser extent, sea salt particles (Na, Mg) were shown to be the major source of trace elements. Excluding major cations, the solubilities of trace elements were found to be ordered as Sr>Zn>Ba>Mn>Cu>Ni>Cr>Fe>Al, confirming the lower solubility of crustal elements. Cd, Co and Pb were excluded from the above evaluation because of the low numbers of soluble samples allowing quantitative measurements. The solubilities of Al, Fe, Mn and particularly of Ni were found to be considerably lower than those reported for various sites around the world, most likely due to the effect of pH. During the entire sampling period, a total of 28 dust transport episodes associated with 31 red rain events were identified. Extremely high mean concentration ratios of Al (8.2), Fe (14.4) and Mn (13.1) were observed in red rain, compared to normal rain. The degree of this enhancement displayed a decrease from crustal to anthropogenic origin elements and the lowest enhancements were found for anthropogenic origin elements of Zn and Cd (both having a ratio of 1.1). Aerosol dust was found to be the main source of almost all analyzed elements in Mersin precipitation, regardless that they are crustal or anthropic derived elements. The magnitude of crustal source contribution to trace element budget of precipitation was at its highest levels for crustal originated elements, most probably due to much higher scavenging ratios of crustal elements compared to anthropogenic ones.

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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, Nriagu, 1996). Their chemistry in the atmosphere is influenced by different sources of gases and aerosols that 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 these 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;

Fig. 1. The location of the rainwater sampling stations in Mersin.

Pirrone and Keler, 1996; Wong et al., 2003). For most trace elements the predominant removal mechanism from the atmosphere is by wet deposition which might be three or four times as large as the dry deposition rate (Baeyens et al., 1990; Duce et al., 1991; Migon et al., 1991). 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. Precipitation data can also be used to understand transport of pollutants, acidity and trace elements from atmosphere to aquatic and terrestrial ecosystems. The impact of such transportation in either worsening (Poissant et al., 1994; Thalmann et al., 2002; Deboudt et al., 2004) or reclamation (Bruland et al., 1991; Avila et al., 1998; Guerzoni et al., 1999; Özsoy, 2003) of various components of these ecosystems can also be assessed by this way. However, the data for elemental composition of atmospheric wet deposition are very scarce for all over the world due to much more difficult sampling and analysis protocols of rainwater compared to the ones for atmospheric aerosols.

Mersin is a big and industrialized city located on the southeastern 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 Mersin (Mersin Çevre İl Müdürlüğü). A comprehensive research on the composition of atmospheric aerosols is already being conducted at a rural site in the close vicinity of Mersin (at Institute of Marine Sciences located 45 km east

of Mersin) since 1991. Elemental composition of atmospheric aerosols has been studied in detail (Kubilay and Saydam, 1995; Kubilay et al., 2000; Koçak et al., 2004) and dry depositional fluxes of trace elements have also been calculated (Koçak et al., 2005). The results of these studies have clearly revealed that atmospheric aerosol over the eastern Mediterranean is strongly influenced by sporadic dust transport from the Saharan Desert, occuring mainly during transitional seasons in March, April, May and October (Koçak et al., 2004). However, research on elemental composition of atmospheric wet deposition on either an urban or a rural site of Northeastern Mediterranean is missing, excluding the study conducted towards the iron speciation in atmospheric precipitation in the same region (Özsoy and Saydam, 2001). Precipitation samples have been collected continuously for one and a half year (over seventeen months) period at four different stations (two urban and two suburban sites) in Mersin City. The samples were analyzed for pH, electrical conductivity (EC) 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. Major ionic compositions of the same samples were also determined and the results have been reported elsewhere (Özsoy et al., 2008).

The aim of this study was to determine the elemental composition of precipitation in urban and suburban sites of Mersin in the Northeastern Mediterranean. Different origins of trace elements were discussed with the preliminary data obtained on the soluble and insoluble phases of rainwater samples collected between December 2003 and May 2005, using factor analysis, enrichment factors, phase distributions

and correlations between trace elements. Spatial and temporal variations in concentrations were investigated. Backward air mass trajectories corresponding to the rainy days were also analyzed to determine potential geographical origin of these elements and to assess potential contribution of sporadically transported red dust to the total rainwater concentrations of trace elements in the region.

2. Materials and methods

2.1. Sampling stations

Mersin, as an industrialized city with almost one million inhabitants, is the site for various industries (*e.g.* petroleum refinery (active until mid 2004), thermal power plant, soda, chromium, fertilizer, cement and glass production), almost all situated in the industrial district, northeast of the city. The city has an unresolved solid waste deposition problem for a long time. At present, approximately more than 700 tons of daily municipal solid waste (MSW) are just dumped to a vast open area, named Çavuşlu municipal landfill, nearly 10 km away from the shoreline, at north. This is an uncontrolled, irregular landfill site where no management strategy in regards to either recovering, reusing or composting of wastes is applied. There is no regular system in order to collect landfill gas and huge trash piles which have been accumulated within long time periods are burning by itself due to emission of biogas, generated by anaerobic decomposition of organic materials. Occasionally, in order to reduce the amount of solid wastes these piles are incinerated in open air. Therefore, in addition to various industrial complexes, MSW disposal area may act as a continuous and significant emission source for various trace elements (*e.g.* Zn, Cd, Pb, K).

Four sampling stations (two urban and two suburban) were selected within the residential area of the city (Fig. 1), located at roofs of private buildings based on practical and safety considerations. St.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. St.2 is located on the roof of a private building in the newly developing residential area of Yenişehir, 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 was deployed at St.2. The urban stations St.3 and St.4 were located at roofs of a private house and a business center, respectively, 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.

2.2. Analytical procedure and data quality

Precipitation samples collected on an event basis were immediately brought to the laboratory after cessation of the particular rain event. Precipitation was recorded at sampling increments of 0.1 mm by a rain-gauge (Akım Elektronik,

Pluviograph, Model PHD5-02) installed at St.2. 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. 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. 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. Utmost care has shown to avoid contamination of samples due to difficulty in the analysis of trace elements in rain water samples.

Membrane filter 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 25 mL volume by double distilled deionized 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). EC measurements were performed with a DIST H198300/3-4 Conductivity/TDS Meters with automatic temperature compensation. A Varian Liberty II Model Inductively coupled plasma atomic emission spectroscopy (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 s with three replicates. The analytical detection limits, defined as three times the standard deviation of five replicate blank measurements, of Ca, Mg, Na and K were found to be 0.010, 0.003, 0.004 and 0.005 mg L^{-1}, respectively. The reproducibility (coefficient of variation, CV %) defined as the standard deviation of seven replicate analysis of subsamples was better than 0.3%, 1.3%, 0.9% and 4.0% for major cations in the same order. The accuracy of the data was cross-checked by participating in semi-annual WMO/GAW (World Meteorological Organisation/Global Atmosphere Watch) precipitation chemistry laboratory intercomparison. The accuracy was found to be better than 3.7% for pH and conductivity, 5.0% for K, better than 9.8% for Ca and Mg. Relative error was found to be relatively high for Na analysis (<15%) on the average of simulated acid rain samples.

The detection limits for the soluble fractions of other elements, in μg L^{-1}, were: 2.0, 0.1, 0.3, 0.7, 0.4, 0.5, 3.0, 2.0, 0.7, 2.0, 0.9 and 3.0 for Al, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sr and Zn, respectively and the CV% was better than 2.6% for Al, Ba,

Table 1
Percentage of mean airflow directions of 78 rain events at five different (1000, 900, 850, 700, 500 hPa) barometric pressure levels during December 2003–May 2005 in Mersin (Özsoy et al., 2008).

hPa	Sector 1 (NE)	Sector 2 (NW)	Sector 3 (SW)	Sector 4 (SE)
1000	10	18	44	28
900	12	23	28	37
850	9	23	45	23
700	3	27	69	1
500	2	35	63	0

Fe, Mn, Sr and Zn and better than 8.8% for Cr, Cu and Ni. The reproducibility was found to be relatively high (<12.0%) for Cd, Co and Pb analysis. Additionally, around in half of the total soluble samples, Cd, Co and Pb concentrations were found to be below the analytical detection limits (BDL) of these elements (0.3, 2.0 and 0.7 $\mu g\ L^{-1}$, respectively). Therefore, ICP-AES method was found not to be sufficiently sensitive and competent for the analysis of Cd, Co and Pb in soluble fraction of precipitation samples. Since these are the preliminary data on elemental composition of wet deposition in the region, values below the detection limit of trace elements were considered as one-half of the respective detection limit for statistical calculation and the data have been evaluated cautiously. Since our approach might have led to possible bias introduced in the solubility of Cd, Co and Pb, those elements were excluded from the discussion on solubility.

Elemental mesurements in insoluble phase of precipitation were performed by a teflon torch of ICP-AES instrument and the digested samples were diluted to 25 mL, therefore the detection limits, expressed in $\mu g\ L^{-1}$, became in the same order: 0.7, 0.01, 0.3, 0.3, 0.3, 0.5, 0.3, 0.04, 0.3, 1.4, 0.5 and 0.2. Standard solutions for trace elements have been prepared daily from 1000 ppm stock MERCK ICP Multi-element Standard solution IV. Cross-check methods of standard additions were used. The qualities of standards for the analysis of insoluble fractions of precipitation samples were controlled by the digesting and analyzing CRM-142 R Standard Reference Material. The relative errors were found to be −3.2, −5.3, 1.0, −0.1, 1.3, 3.9, −2.7 and 0.4% for Cd, Co, Cu, Mn, Ni, Pb, Cr and Zn, respectively. The same procedures have been applied to five field blanks collected within the sampling period. Approximately 200 mL of distilled, deionized water was poured into the cleaned sampling bucket and deployed at the precipitation sampling stations. The concentrations of field and laboratory blanks measured throughout the study were all below the detection limit of the measured trace elements.

2.3. Air mass back trajectories

Three-dimensional, 3-day backward trajectories of air masses subjected to scavenging by precipitation and arriving at this station (36° 47′ 25″ N latitude and 34° 37′ 36″ E longitude) at the beginning of every particular rain event, at 1000, 900 and 850 hPa pressure levels (assumed to be within the boundary layer) and 700 and 500 hPa (assumed to be within the free troposphere) were calculated. The three-dimensional trajectory model developed at the European Center for Medium Range Weather Forecasts (ECMWF) in Reading, England by Ray McGrath of the Irish Meteorological

Service is used with a spectral truncation of t-213, a time step of 1 h going backward in time, for each trajectory. The model uses direct calls to the ECMWF atmospheric data archive system MARS to retrieve global model derived wind fields and generates its own internal index to mimic the original wind database and the model does not give any information about precipitation events during the excursion of the air masses (Özsoy et al., 2008).

3. Results and discussion

3.1. Rainfall data and air masses back trajectories of rainy days

Based on fourteen years of climatological data from Mersin (Turkish Meteorological Service, Mersin Station), mean annual precipitation and the number of rainy days were 587.5 mm and 67 respectively, for the period 1990–2003. The annual precipitation corresponding to the period of our sampling (from 26 December 2003 till 26 December 2004) was 554 mm and the number of rainy days was 48 during the same period (data obtained from the rain-gauge deployed at St.2), which are quite lower than the mean climatological values. The mean annual precipitation values were 591, 529, 469 and 468 mm respectively for stations 1, 2, 3 and 4. As a result of heat island effects near the city center, relatively lower precipitation values have been measured at St.3 and St.4. Cumulative precipitation for a total of 74 rainy days during the sampling period of December 2003–May 2005 was 735.4 mm. Minimum and maximum rainfall were 0.2 mm and 49.8 mm respectively, for individual precipitation events. During the study period (December 2003–May 2005) a total of 252 samples have been collected and 6 of these samples were rejected due to insufficient amount of precipitation (<0.1 mm).

In order to identify the mean directions of the air masses carrying precipitation to Mersin, trajectories have been classified according to four 90° sectors of arrival. Each trajectory was assigned to the sector in which it spent most of its three days of excursion. The trajectory classification for rainy days was performed at 1000, 900, 850 hPa levels (likely to be in the planetary boundary layer) (PBL) and at 700, 500 hPa levels (free trophosphere), respectively. The results of this classification are presented in Table 1, where the percentage in each direction is given for a total of 78 trajectories during rain events during December 2003–May 2005.

Table 1 shows that the highest percentages belong to Sector 3, SW direction. This result is consistent with the long term observation of the Turkish Meteorological Service, Mersin station indicating prominent wind directions of S–SW and SE during rainy days. The secondary prominent trajectory direction was found to be SE, Sector 4, particularly for the air masses that move within the planetary boundary layer during rainy periods, which do not lead to transport towards the city from the industrial district located on the NE of Mersin (Özsoy et al., 2008).

3.2. pH and electrical conductivity

The mean pH of precipitation, calculated from the volume weighted H^+ concentration, was found to be 6.22, which is in
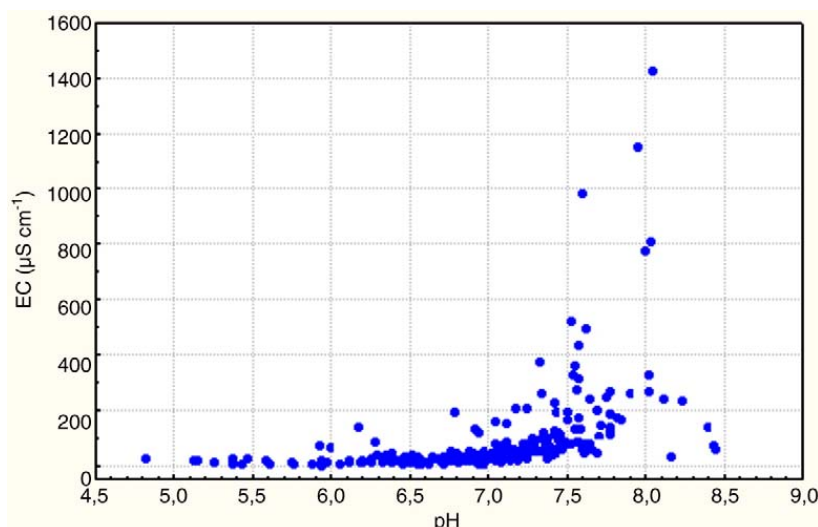
Fig. 2. EC *vs* pH in Mersin precipitation.

the alkaline range as compared to 5.6 pH of rainwater at equilibrium with atmospheric CO_2. Out of 246 samples, 97% reflects alkaline pH of precipitation. 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. There have been only 8 acidic events (3% of the total samples), mostly after continuous rains when the dust in the atmosphere had been washed-out, therefore resulting in decreased buffering potential (Özsoy et al., 2008).

EC of the precipitation samples was found to be highly variable, within a range of 0–1427 µS cm^{-1}. The geometric mean conductivity of the 246 samples was 47.8 µS cm^{-1}. A very high positive correlation ($R^2 = 0.88$) was found between EC and calcium concentration (Özsoy et al., 2008). Precipitation samples with relatively high concentrations of calcite mineral, hence mineral dust, had very high conductivity, most likely 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. Conductivity as a function of pH for all the precipitation samples is presented in Fig. 2. This relationship can be expressed by a logarithmic model: $\log y = -5.69 + 1.36x$, where the conductivity is positively correlated with pH ($R^2 = 0.71$, $p < 0.05$).

3.3. Mean trace element concentrations

The volume weighted mean (VWM) concentrations and their standard deviations (SDVWM), and minimum and maximum concentrations of trace elements in soluble and insoluble fractions of Mersin precipitation are presented in Table 2. Standard deviations of the VWM were calculated using the formula of Galloway et al. (1984).

Based on the whole data, total concentrations of trace elements were in the order of Ca>Na>Fe>Al>Mg>K>Zn>Mn>Sr>Pb>Ni>Cr>Ba>Cu>Co>Cd. This order of

Table 2
The volume weighted mean concentrations (VWM) and their standard deviations (SDVWM), and minimum and maximum concentrations (µg L^{-1}) of trace elements in soluble and insoluble fractions of Mersin precipitation, n: 246.

Element	VWMC ± SDVWMC			Minimum			Maximum		
	Soluble	Insoluble	Total	Soluble	Insoluble	Total	Soluble	Insoluble	Total
Al	6.48 ± 1.07	478 ± 49	484.5 ± 49.5	0.03	1.00	1.97	446	101,145	101,191
Ba	1.63 ± 0.16	3.51 ± 0.54	5.14 ± 0.64	0.04	0.01	0.06	107	991	1098
Cd [a]	0.50 ± 0.07	0.31 ± 0.03	0.81 ± 0.09	0.02	0.005	0.06	10.2	31.6	31.7
Co [a]	1.35 ± 0.16	0.72 ± 0.06	2.07 ± 0.19	0.08	0.01	0.43	25.9	149.9	66.0
Cr	1.05 ± 0.18	4.67 ± 0.41	5.72 ± 0.43	0.01	0.25	0.43	33.3	2498	2500
Cu	1.62 ± 0.20	2.32 ± 0.17	3.94 ± 0.27	0.15	0.02	0.65	19.7	649	669
Fe	3.21 ± 0.44	740 ± 115	743.2 ± 115	0.08	1.13	2.63	460	336,600	336,640
Mn	3.23 ± 0.25	15.8 ± 2.43	19.03 ± 2.55	0.03	0.01	0.49	211	4987	5069
Ni [a]	2.58 ± 0.44	4.65 ± 0.32	7.23 ± 0.51	0.03	0.64	0.73	105	904	956
Pb [a]	5.07 ± 0.73	6.29 ± 0.33	11.36 ± 0.81	0.21	0.23	2.21	174	1742	1804
Sr	12.6 ± 2.35	3.03 ± 0.40	15.6 ± 2.52	0.19	0.03	0.49	2064	1472	3537
Zn	36.9 ± 5.54	13.3 ± 1.55	50.2 ± 6.06	0.16	0.11	1.96	4977	2864	5238
Ca	3890 ± 370			34.0			186,400		
Mg	380 ± 80			3.0			177,400		
Na	1020 ± 150			8.0			169,600		
K	180 ± 20			1.0			28,090		

[a] Soluble concentrations that are below the detection limit of Cd (0.3 µg L^{-1}), Co, Ni (0.7 µg L^{-1}), and Pb (2.0 µg L^{-1}) elements were considered as one-half of the corresponding detection limits for statistical calculation.

Table 3
Comparison of the total trace element VWM concentrations ($\mu g\ L^{-1}$) with the data reported from various locations around the world.

Element	[a]Mersin (U)	[b]Ankara (U)	[c]Mexico City (U)	[d]Athens (U)	[e]Antalya (R)	[f]N. Jordan (R)	[g]S. Jordan (R)
Al	484.5 ± 49.5	980 ± 2900	50.7 ± 5.40	5.87 ± 8.67	580 ± 758	382 ± 323	–
Ba	5.14 ± 0.64	–	–	–	–	–	–
Cd	0.81 ± 0.09	9.5 ± 12.0	0.41 ± 0.04	0.20 ± 0.14	4.9 ± 6.4	0.42 ± 0.63	42.00 ± 22.86
Co	2.07 ± 0.19	–	–	–	–	–	–
Cr	5.72 ± 0.43	3.0 ± 7.8	0.52 ± 0.03	1.29 ± 0.97	9.0 ± 11.6	0.77 ± 0.84	–
Cu	3.94 ± 0.27	6.1 ± 9.5	–	15.41 ± 14.51	4.9 ± 6.4	3.08 ± 1.61	40.00 ± 26.99
Fe	743.2 ± 115	750 ± 2370	–	4.38 ± 2.54	–	92 ± 104	21.50 ± 32.84
Mn	19.03 ± 2.55	–	9.64 ± 1.35	3.61 ± 3.68	–	2.11 ± 1.56	–
Ni	7.23 ± 0.51	4.1 ± 6.4	3.37 ± 0.60	4.14 ± 3.97	24 ± 26	2.62 ± 2.87	1.75 ± 1.36
Pb	11.36 ± 0.81	19.1 ± 37.6	2.48 ± 0.33	0.88 ± 1.05	10 ± 14	2.57 ± 2.33	51.00 ± 36.40
Sr	15.6 ± 2.52	–	–	–	–	–	–
Zn	50.2 ± 6.06	0.03 ± 0.03	–	33.46 ± 40.81	137 ± 510	6.52 ± 7.84	32.00 ± 32.61
Ca^{2+}	3890 ± 370	2640 ± 2180	26.44 ± 5.92	–	2200 ± 2300	2164 ± 1461	192.10 ± 40.42
Mg^{2+}	380 ± 80	240 ± 480	2.46 ± 0.52	–	1400 ± 2500	373 ± 298	133.60 ± 17.71
Na^+	1020 ± 150	530 ± 800	7.00 ± 1.56	–	9900 ± 19,200	1150 ± 1208	85.10 ± 24.99
K^+	180 ± 20	139 ± 207	2.16 ± 0.75	–	620 ± 1440	434 ± 375	51.10 ± 15.48

U: urban area, R: rural area.
[a] This study.
[b] Kaya and Tuncel (1997).
[c] Baez et al. (2007).
[d] Kanellopoulou (2001).
[e] Al-Momani et al. (1998).
[f] Al-Momani (2003).
[g] Al-Khashman (2005).

concentration clearly demonstrates that the highest contributions to the atmospheric concentration of trace elements are from terrigeneous particles (Ca, Fe and Al) and marine sources (Na, Mg) in Mersin atmosphere. The total as well as the soluble concentrations of all elements exhibits a steady decrease with increasing precipitation volume being in a hyperbolic relationship, due to dilution effect.

Our results were compared to the data reported for various locations around the world in Table 3. For comparison only the mean values were taken into account since the way of standard deviation calculations of volume weighted mean concentrations has not been reported in any of other studies. It is notable that crustal elements such as Ca, Al, Fe and Mn mean concentrations in Mersin precipitation are the highest. Among anthropogenic elements the mean Cu concentration of Mersin precipitation is lower than the values reported for almost all other places. The mean Ni, Cr and Zn concentrations

in Mersin rainwater are found to be higher than the other values, except for Antalya; another Northeastern Mediteranean City like Mersin. Higher concentrations of Ni and Cr in Mersin and Antalya rainwater can be explained by natural contribution of local soil which is particularly rich in Ni and Cr contents of ophiolitic minerals (Çağatay et al., 2002) to the atmospheric precipitation concentrations of these elements.

3.4. Spatial and temporal variabilities of trace elements

Due to the dynamic nature of the atmosphere, concentrations of atmospheric particulate and reactive gaseous constituents are highly variable in space and time. In order to display spatial variability among elemental concentrations in Mersin precipitation the VWM concentrations of the measured elements along with their standard deviations from each station are calculated and the Student's *t* test (two-tail at

Table 4
VWM and SDVWM concentrations ($\mu g\ L^{-1}$) of trace elements in precipitation collected at four different sites from December 2003 to May 2005.

| Element	St.1 (*n*: 67)	St.2 (*n*: 78)	St.3 (*n*: 51)	St.4 (*n*: 50)
Al	458.3 ± 81.7	376.6 ± 60.7	640.6 ± 157.5	621.0 ± 143.7
Ba	4.54 ± 1.01	4.19 ± 0.95	6.52 ± 1.71	6.77 ± 1.74
Cd	0.846 ± 0.134	0.895 ± 0.173	0.670 ± 0.124	0.646 ± 0.117
Co	2.00 ± 0.29	2.13 ± 0.32	1.95 ± 0.36	2.12 ± 0.52
Cr	5.95 ± 0.94	4.36 ± 0.61	7.57 ± 1.12	6.97 ± 1.03
Cu	4.15 ± 0.43	3.60 ± 0.41	3.94 ± 0.55	4.55 ± 0.76
Fe	720.8 ± 226.9	663.3 ± 198.4	813.6 ± 239.6	891.0 ± 230.0
Mn	19.46 ± 5.26	18.33 ± 4.48	18.54 ± 4.70	20.42 ± 4.66
Ni	10.14 ± 1.58	5.53 ± 0.79	7.57 ± 0.81	7.94 ± 0.85
Pb	13.52 ± 0.98	9.56 ± 1.20	11.26 ± 1.96	13.55 ± 2.57
Sr	25.37 ± 9.66	12.08 ± 2.90	12.06 ± 3.73	16.78 ± 4.54
Zn	163.4 ± 26.7	16.60 ± 1.82	25.76 ± 3.76	32.72 ± 5.92
Ca^{2+}	4082.8 ± 795.2	3104.4 ± 398.5	4440.9 ± 1076.4	5063.8 ± 1125.7
Mg^{2+}	448.5 ± 36.9	400.4 ± 23.4	263.2 ± 96.6	348.5 ± 118.6
Na^+	1154.4 ± 356.0	822.2 ± 156.0	1181.7 ± 457.0	1193.7 ± 364.2
K^+	261.1 ± 39.6	137.8 ± 22.7	196.6 ± 50.3	206.9 ± 45.6
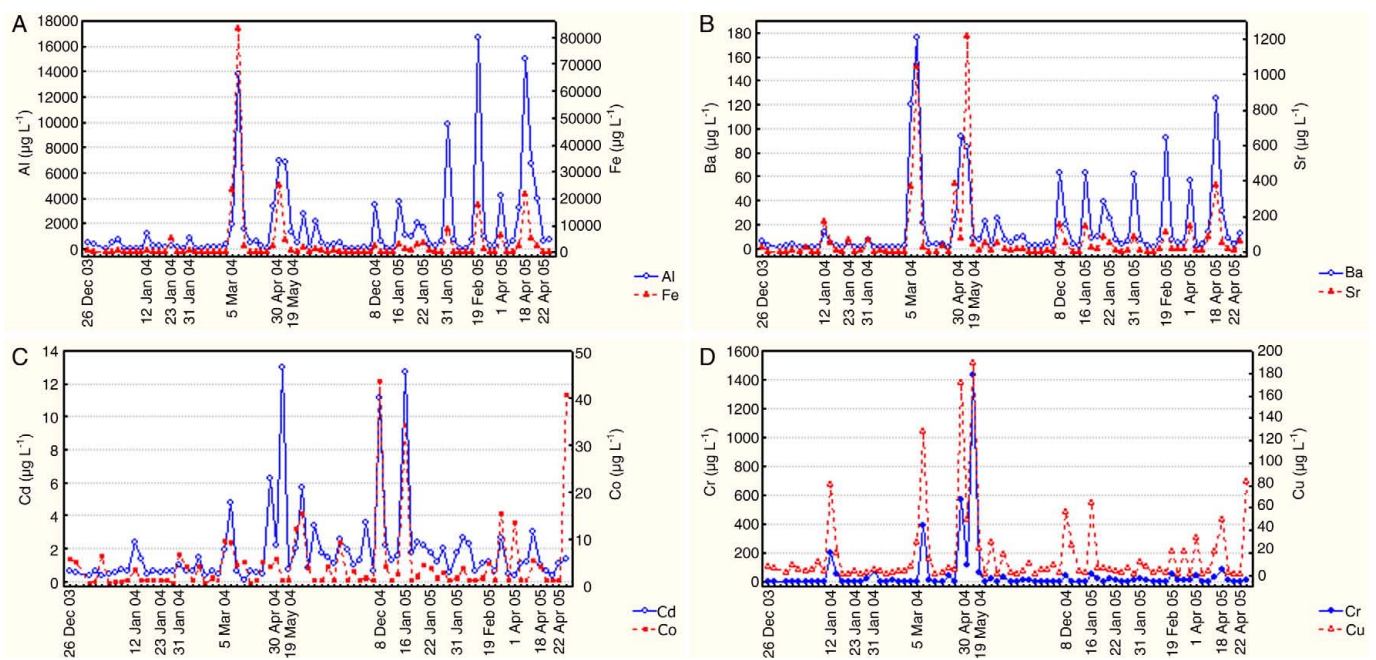
Fig. 3. Time series of total A) Al *vs* Fe, B) Ba *vs* Sr, C) Cd *vs* Co, D) Cr *vs* Cu, E) Pb *vs* Ni, F) Mn *vs* Zn concentrations and soluble, G) Ca²⁺ *vs* Mg²⁺, and h) Na⁺ *vs* K⁺ concentrations measured in precipitation samples collected at St.2 during December 2003–May 2005 in Mersin.
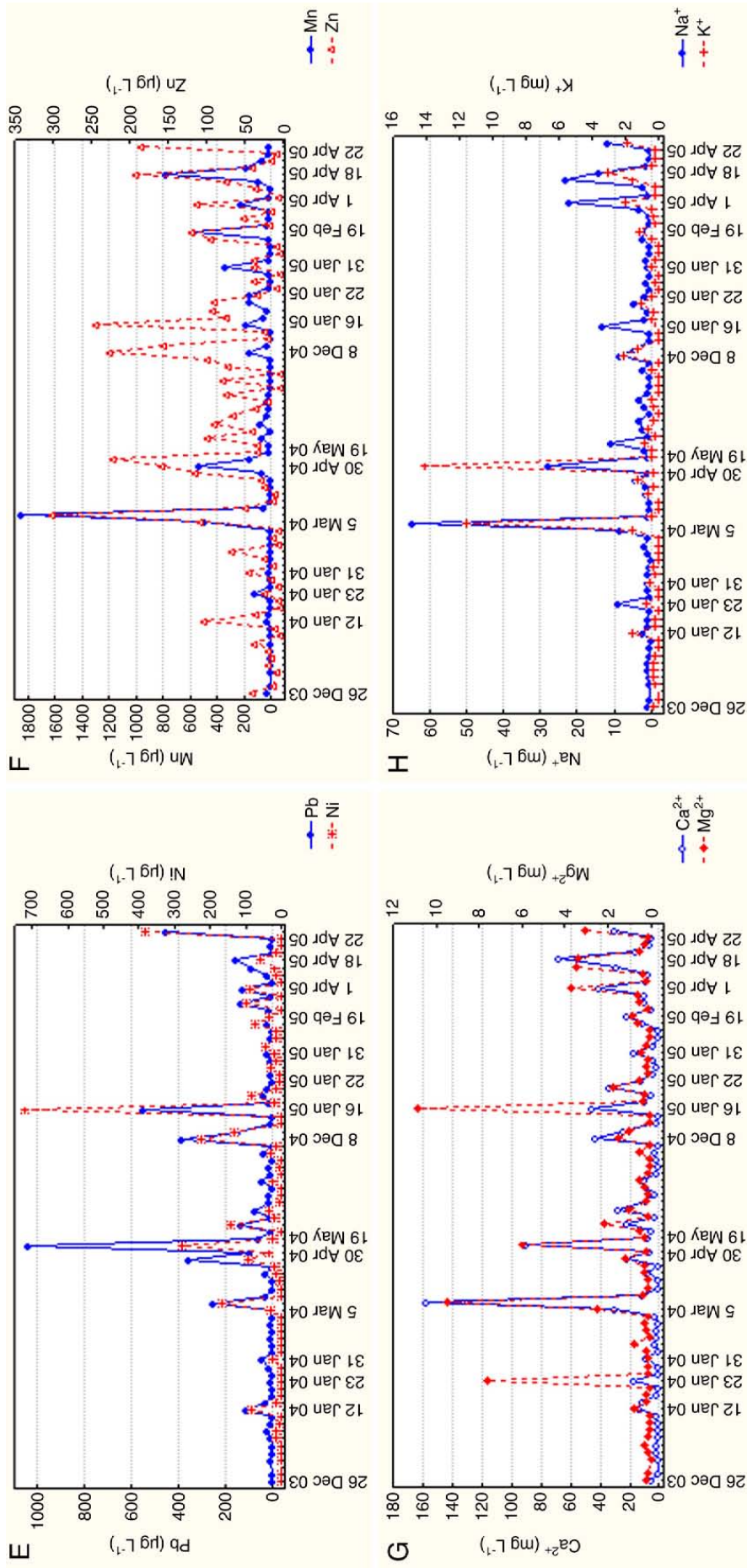
Fig. 3 (*continued*).

5%) is applied to the data. The results are presented in Table 4. Among the sampling sites, St.2 has the minimum mean trace element concentrations, except for Cd and Co of which should be evaluated cautiously (refer to Section 2.2). Owing to local meteorological conditions mainly two factors might have caused the observed spatial variability: 1—the differences in the total amount of precipitation collected from every station (refer to Section 3.1) and 2—variation in source contributions, such as the level of anthropogenic activities in the close vicinity of sampling stations (*e.g.* dense traffic, agriculture, population) and the degree of contribution to the atmospheric trace element budget of every station from remote sources, (*e.g.* long range transportation). Even though the mean elemental concentrations calculated for urban stations of St.3 and St.4 are close to each other, the mean Cu, Mn, Ni, Pb, Sr, Zn, Ca^{2+} and Mg^{2+} concentrations of St.4 are found to be significantly higher than the mean St.3 values of the respective elements at $p<0.05$.

Total Al, Ba, Cr, Cu, Fe, Mn and soluble Ca^{2+} and Na^+ mean concentrations of urban samples (St.3 and 4) are found to be relatively higher than the ones collected from suburban stations (St.1 and 2) and the differences between Al, Ba, Cr, Fe, Ca and Na mean concentrations of urban and suburban samples are statistically significant at the 95% confidence level. Since human activities are high and the amount of precipitation is lower in the urban stations about half of the elements appear to be more concentrated as a consequence. We would expect to observe the minimum mean elemental concentrations at St.1 since it has received the highest total amount of precipitation (591 mm) and is not under the direct influence of combustion sources by being located at suburban of the city. However, relatively higher levels of Ni, Sr, Zn, Mg^{2+} and K^+ concentrations are observed at this station and particularly, the mean Zn concentration in St.1 is approximately an order of magnitude higher than the mean Zn values of other stations (Table 4). As it is indicated in Section 2.1, St.1 is located in Mersin University Campus and surrounded by agricultural land, mainly lemon groves. Application of potassium salts such as K_2O, K_2SO_4 and zinc salts such as $ZnSO_4$ as fertilizers to the vegetable and citrus tree fields and to spray ZnO and MnO aqueous solutions to the leaves of citrus trees are very common around the region (İ. Yavuz, agriculturist, pers. comm.). Therefore, local agricultural activities might be responsible for relatively higher Zn and K^+ levels in precipitation samples of this suburban station. Similar aerosol Zn enhancement particularly during summer in the Levantine Basin of the Eastern Mediterranean has also been attributed to agricultural activities (Koçak et al., 2004). Another reason for relatively higher Zn and K^+ mean concentrations of St.1 samples might as well be relatively higher influence of biomass burning emissions from the MSW deposition area, depending on the changing wind direction over this particular location.

In order to display temporal variability of trace element concentrations in Mersin precipitation, St.2 data are evaluated since the highest number of data has been obtained from this station. Time series of total Al, Fe, Ba, Sr, Cd, Co, Cr, Cu, Pb, Ni, Mn and Zn concentrations and soluble Ca^{2+}, Mg^{2+}, Na^+ and K^+ concentrations measured in St.2 samples during the sampling period are presented in Fig. 3. The dates marked at the time scale belong to the most intense dust transport episodes originated either from remote or local sources during the sampling period. It is noteworthy that almost all elements display high concentration peaks on those days depending on the intensity of aerosol dust load over the local atmosphere. However, some elements such as Zn, Cd, Co and to a lesser extent Cu and Pb display somewhat a different temporal variability than that of crustal originated elements (*e.g.* Al, Fe), suggesting that contributions from other sources (*e.g.* fossil fuel and biomass burning, fertilizers) to the atmospheric concentration levels of these elements are prominent. Present rainwater data are preliminary for the region and as a specific application dealing with issue, the sale of gasoline containing TEL (tetra ethyl lead) additives has been banned in Turkey on the summer of 2004 in accordance with the European legislation. Since the timing of this abatement coincides with our rainwater sampling period we would expect a decreasing trend in Pb concentrations in Mersin rainwater at least after October 2004. However, such a trend is not apparent in Fig. 3e, most likely a one year time scale is not sufficient to detect such a diminishing trend due to the possible time lag in the effectuation of the new legislation.

3.5. Solubility of trace elements and relationship with pH

In literature, major cations such as Ca^{2+}, Mg^{2+}, Na^+ and K^+ are usually analyzed only in soluble fraction of rainwater, since it was considered that the solubility of these alkaline (Na and K) and earth alkaline (Ca and Mg) elements are high. In order to have an idea about the solubility of these major cations, Ca, Mg, Na and K analysis has been performed to the insoluble fractions of only 21 arbitrarily selected precipitation and the results are presented in Table 5 along with solubility data reported from various locations around the world. In a variable number of soluble samples the concentrations of trace elements (particularly for Cd, Co, Pb) were below the detection limit of the ICP-AES method. To eliminate possible bias, these elements were not evaluated with respect to their solubility.

The percentage solubilities of trace elements are found to be in the order of Ca>Sr>Na>Mg>Zn>Ba>Mn>Cu>Ni>Cr> K>Fe>Al in Mersin precipitation (Table 5). According to this order, the highest solubilities (>70%) are observed for Ca, Sr, Mg (earth alkaline) and Na (alkaline) whereas the lowest solubilities belong to the mainly crustal elements of Fe and Al ($\leq$5%).

In general, large variations of trace element solubility appear in the literature (Table 5) as in our samples and this variability has usually been attributed to the pH of the final rainwater solution as well as ligands, ionic strength, amount of precipitation and the type of aerosols scavenged from the atmosphere during wash-out processes (Chester et al., 1993a; Losno et al., 1993; Spokes et al., 1994). In a couple of research, the solubilities of trace elements have been investigated for different subsets of samples having pH <5 and pH >5 (Kaya and Tuncel, 1997; Garcia et al., 2006; Baez et al., 2007). We could not apply this classification to our data since the number of samples having pH <5 is not sufficient for statistical analysis. Solubility of Al in Mersin precipitation (4.8%) was found to be significantly lower than the values reported for Cap Farrat (17.0%, Chester et al., 1997); Tour du Valat (19%, Guieu et al., 1997) and Mexico City (42.6%, Baez et al., 2007). Our data are similar to Kaya and Tuncel (1997)

Table 5
Percentage solubility (%) of trace elements in precipitation samples of Mersin and various locations around the world.

Element	[a]Mersin		[b]Ankara	[c]Mexico City	[d]Tour du Valat
	*n	pH: 6.2	n: 76 pH: 4.7	n: 81 pH: 5.1	n: 45 pH: –
Ca	21	93.9 ± 5.0	94 ± 10	–	–
K	21	24.0 ± 21.4	69 ± 28	–	–
Mg	21	72.9 ± 14.2	61 ± 26	–	–
Na	21	73.9 ± 18.0	76 ± 20	–	–
Al	243	4.8 ± 12.4	14 ± 14	42.6 ± 30.4	19 ± 26
Ba	243	42.3 ± 26.3	–	–	–
Cr	233	25.9 ± 24.8	35 ± 29	46.3 ± 25.4	–
Cu	243	34.8 ± 30.4	49 ± 27	–	71 ± 21
Fe	243	5.2 ± 12.9	17 ± 16	–	11 ± 16
Mn	244	40.6 ± 25.1	–	79.7 ± 18.5	63 ± 28
Ni	189	30.1 ± 34.1	72 ± 31	78.6 ± 20.9	58 ± 36
Sr	243	74.2 ± 22.4	–	–	–
Zn	242	62.6 ± 33.8	43 ± 29	–	68 ± 30

*n refers to the number of samples for which quantitative measurements were obtained in both the soluble and insoluble fractions. Due to a low number of quantitative measurements of the soluble Cd (n: 137), Co (n: 125) and Pb (n: 128) samples the solubilities of these elements were not evaluated.
 [a] This study.
 [b] Kaya and Tuncel (1997).
 [c] Baez et al. (2007).
 [d] Guieu et al. (1997).

concerning Ca, Mg, Na and to a lesser extent Cr and Cu. However, in addition to Al the solubility of Fe, K, Mn and Ni in Mersin precipitation was found to be significantly lower than the data reported from all other stations presented in Table 5. This difference might be attributed to the effect of pH factor. The mean pH of Mersin precipitation (6.2) is higher than the mean pH of Ankara (4.7) and Mexico City (5.08) samples (Table 5). Besides, significantly lower trace element solubilities were reported for the subset of precipitation samples having pH >5 in Ankara, *e.g.* $11 \pm 15\%$ for Cr; $30 \pm 27\%$ for Cu and $18 \pm 21\%$ for Ni (Kaya and Tuncel, 1997) and also in Mexico City (Garcia et al., 2006).

Among trace elements atmospheric iron has particularly attracted considerable research interest since it is a key element for marine biogeochemistry and too many studies have been conducted addressing its solubility (Zhuang et al., 1995; Zhu et al., 1997; Kieber et al., 2001, 2003), its relationship with atmospheric dust (Jickells and Spokes, 2001; Özsoy and Saydam, 2001; Mahowald et al., 2005; Jickells et al., 2005) and combustion sources (Chen and Siefert, 2004; Chuang et al., 2005; Guieu et al., 2005; Luo et al., 2008). On the basis of arithmetic means, the percentage of Fe solubility in Mersin precipitation (5.2%) was found to be much lower than the value reported for Erdemli–Mersin (a rural–coastal area) precipitation (9.6%, Özsoy and Saydam, 2001). The present study has been conducted in the urban and suburban atmosphere of Mersin and aerosol type is supposed to be a mixture of natural (mineral dust, sea salt) and anthropogenic (combustion) sources. Among scientific community there is an uncertainty in which type of iron is more soluble: iron in mineral dust aerosols or iron emitted from combustion sources? Even though it has previously been assumed that iron in mineral aerosols is relatively insoluble (Duce and Tindale, 1991; Zhu et al., 1997; Fung et al., 2000), recently it has been suggested that iron in mineral aerosol might become more soluble during pollution related atmo-

spheric processes (Luo et al., 2008 and references therein). Therefore, it is not possible to explain lower solubility percentage of Fe in Mersin precipitation by the mixed origin type of aerosols. On the other hand, pH effect is again apparent on the solubility of Fe, as a major factor. The mean pH of the present study (6.22) is most likely responsible for the relatively lower solubility (5.2%) of Fe when compared to the mean pH of 4.95 reported for the rural atmosphere of Erdemli–Mersin precipitation where relatively higher Fe solubility (9.6%) was observed (Özsoy and Saydam, 2001). Even though, the distance between the sampling stations of these studies is only 40 km, most likely pH is the main reason of this discrepancy between the Fe solubilities of the two almost similarly conducted studies.

Recently, Koçak et al. (2007) have investigated trace metal solid speciation in Erdemli aerosols. In order to reflect the contrasting mixtures of aerosol material, three stage sequential leach scheme was applied to two populations of samples, which were classified as "anthropogenic" (n: 14) and "Saharan" (n: 16) dominated aerosols. The results were given as the proportion of trace elements (Al, Fe, Cu, Pb, Cd, Zn, Mn) present in the (a) "exchangeable", (b) "carbonate-oxide" and (c) "refractory" phases. Considering the "exchangeable" phase control of the potential availability of trace metals for rainwater dissolution, the results of this study are compared to our solubility data in Table 6.

According to Koçak et al. (2007), crustal derived elements (Al and Fe) are predominantly incorporated into the resistant refractory solid phase and trace elements influenced by anthropogenic sources (Zn, Pb and Cd) are being dominated in the exchangeable phase, even though the variability was comparatively high (12–64% for Zn, 19–85% for Pb and 40–100% for Cd). The solubility of Al, Fe, Mn, Zn and Cu in Mersin precipitation is consistent with the proportion of these elements in exchangeable phase of Erdemli aerosols (Table 6).

In order to display the variation of trace element solubility with respect to pH, percentage solubilities of trace elements (Al *vs* Fe, Ba *vs* Sr, Mn *vs* Cu and Zn *vs* Cr) are plotted against pH values in Fig. 4a–d, respectively. A very high scattering of data can be noticed for almost all elements. In order to evaluate the dependency of trace element solubility on pH factor, linear regression lines are provided with the regression equations written above each plot at $p < 0.05$. Almost all elements display a decrease in their solubilities as pH increases, which is consistent with the results of previous studies (Losno et al., 1988; Lim et al., 1994; Chester et al., 1997). However, Sr which is known as a radioactive earth alkaline element (Herut et al., 1993; Negrel and Roy, 1998) displays a very unique type of variation with respect to pH; its

Table 6
Comparison of the proportion of trace elements in exchangable fraction of Erdemli aerosols (Koçak et al., 2007) with their solubility percentages in Mersin precipitation.

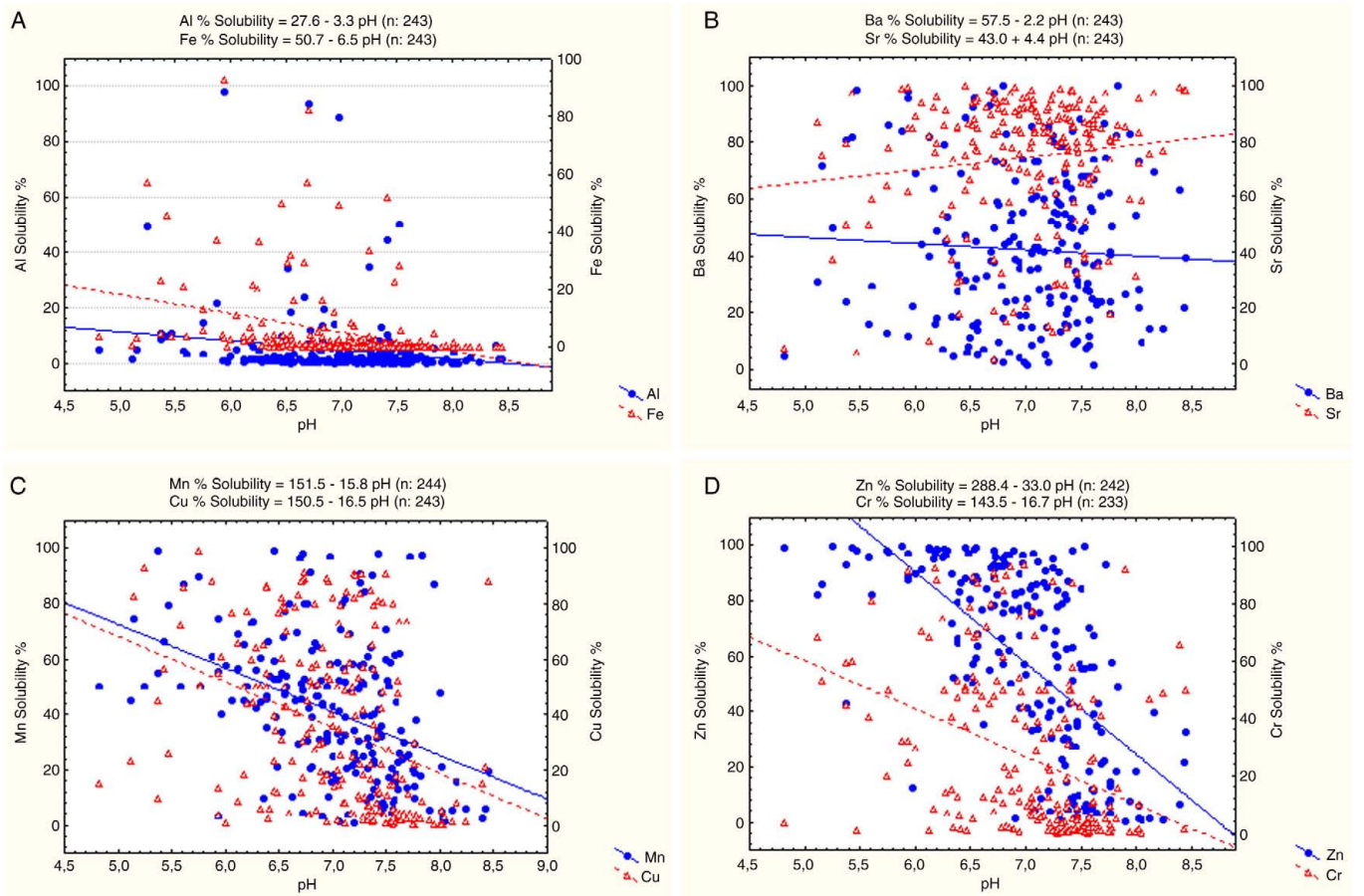| Element	Sol. % in rain	Ex. % in Saharan aerosols	Ex. % in Anthropic aerosols
Al	4.8 ± 12.4	1.0 ± 0.5	3.9 ± 1.2
Fe	5.2 ± 12.9	0.9 ± 0.6	2.6 ± 1.1
Mn	40.6 ± 25.1	35.3 ± 10	52.9 ± 4.1
Zn	62.6 ± 33.8	38.5 ± 14.9	65.6 ± 8.6
Cu	34.8 ± 30.4	35.7 ± 3.4	37.0 ± 4.4

Fig. 4. pH *vs* solubility percentage of A) Al *vs* Fe, B) Ba *vs* Sr, C) Mn *vs* Cu, and D) Zn *vs* Cr (within 0.95 confidence interval) in Mersin precipitation.

solubility increases as pH increases (Fig. 4b). Since our basic pH–solubility data are not sufficient to explain the reason of its opposite trend of solubility/pH relation, this issue requires further investigation.

From the slope of regression equations it is predicted that Zn displays the highest variation rate in its solubility with respect to pH. The pH–% solubility relationship of Cr, Cu and Mn follows Zn, in a decreasing order.

3.6. 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 metal 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 the 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 7 along with the crustal EFs of Erdemli aerosols (Kubilay, 1996), although they are not directly comparable.

EF$_{crust}$ values for trace elements in Mersin precipitation, presented in Table 7 were grouped into non-enriched, moderately enriched and highly enriched classes, as in the following:

1. Non-enriched elements: Al (the crustal indicator), Ba, Fe, Mn, Mg, Na, K, Sr and Cr with volume weighted mean EF$_{crust}$ values of 1–10.
2. Moderately enriched elements: Ca, Co, Cu, and Ni with EF$_{crust}$ values in the range of 10–10^2.
3. Highly enriched elements: Pb, Zn and Cd, having volume weighted mean EF$_{crust}$ values in the range of 10^2 to >10^3.

According to the same classification, Al, Fe, Mn, Mg, Ca, Na, Co, Cr and Ni were non-enriched; Zn was moderately enriched; Cd and Pb were highly enriched elements over the rural Erdemli region (Kubilay, 1996).

Among the highly enriched elements Zn, Pb and Cd are predominantly of anthropogenic origin. Zn and Cd have many common sources for instance, the non-ferrous metal industry accounting for the largest fraction of Zn and Cd emitted (Nriagu and Pacyna, 1988). MSW incinerators are also important sources for Cd (Pinzani et al., 2002) and Zn (Nriagu and Pacyna, 1988; Pacyna, 1989) emissions. Agricultural source and natural biomass burning (Artaxo et al., 1990) of Zn are also common while the manufacturing and disposal of Cd batteries and the wearing of automobile tires might be

additional potential sources of Cd emissions (Mugica et al., 2002). The largest contribution of Pb to the atmosphere is gasoline combustion, accounting for about 60% of the total anthropogenic emission in Europe (Pacyna, 1984). Pb is also emitted from MSW incinerators and smelters (Sobonska et al., 1999). There has been a significant mitigation in aerosol Pb (Migon and Nicolas, 1998; Flament et al., 2002) and rainwater concentrations (Baez et al., 2007) within the last decades due to the reduction of Pb in fuels and hence emissions from vehicular transport. Approximately, 40% decrease has been reported for aerosol Pb concentrations in Erdemli–Mersin compared to the previous data of 1991–1992 (Koçak et al., 2004). Since there is no previous rainwater Pb data for this region, it is not possible to derive the same conclusion from the present research unless long term monitoring study is performed. After all, it might be interesting to compare the crustal EFs of Pb in Mersin precipitation and Erdemli aerosols, only to give an insight into the issue. Relatively lower EF$_{crust}$ of Pb (112) in Mersin precipitation than previously reported EF$_{crust}$ (295) for Erdemli aerosols (Kubilay, 1996) might as well be an indication of the mentioned mitigation of atmospheric Pb concentrations in the region. Parallel to the significant differences among the VWM Zn concentrations of four stations (Table 4), Zn is found to be highly enriched in St.1 samples, with respect to crust (EF$_{crust}$ values of Zn are found to be 403, 50, 46 and 60 respectively, for St.1, 2, 3 and 4). EF$_{crust}$ values of Zn, Cd, Pb, obtained from this study were found to be almost an order of magnitude lower than the EF$_{crust}$ values reported for İskenderun (EF$_{Zn}$: 1333, EF$_{Cd}$: 25,055, EF$_{Pb}$: 1474, Örnektekin and Çakmaklı, 2003) most likely due to more than an order of magnitude higher difference between the VWM Al concentrations of Mersin (347.8 μg L^{-1}) and İskenderun precipitations (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 comparison. 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).

Table 7
Enrichment Factors (EFs) of trace elements in Mersin precipitation and Erdemli aerosols (Kubilay, 1996) with respect to crust.

Element	EF$_{rainwater}$	EF$_{aerosol}$
Ba	1.4	–
Fe	3.6	1.6
Mn	4.1	1.8
Mg	4.3	6.2
Ca	26	9.1
Na	7.1	9.6
K	1.3	–
Cd	1515	123
Co	20	2.2
Cr	10.5	10.3
Cu	24	–
Ni	26	9.0
Pb	112	295
Sr	8	–
Zn	126	33

Table 8
Varimax rotated factor matrix, applied to the logarithmic data and corresponding probable source type for the data set.

Variables	Factor 1	Factor 2	Factor 3	Communality
Al	**0.88**	0.31	0.22	0.95
Ba	**0.82**	0.40	0.27	0.90
Cd	0.17	**0.74**	0.17	0.54
Co	0.19	**0.53**	0.27	0.43
Cr	**0.52**	**0.62**	0.17	0.67
Cu	0.33	**0.72**	0.40	0.81
Fe	**0.91**	0.23	0.23	0.96
Mn	**0.87**	0.31	0.26	0.92
Ni	0.23	**0.81**	0.30	0.79
Pb	0.22	**0.85**	0.30	0.85
Sr	**0.64**	0.46	0.48	0.90
Zn	0.21	**0.78**	0.12	0.65
Ca^{2+}	**0.71**	0.39	0.45	0.89
Mg^{2+}	0.48	0.35	**0.74**	0.90
Na^+	0.39	0.37	**0.79**	0.90
K^+	0.44	0.48	**0.60**	0.79
H^+	−0.70	−0.04	−0.40	0.68
Eigenvalues	11.71	1.73	0.87	
Variance (%)	65.1	9.6	4.8	79.5
Probable source	Crustal	Anthropogenic	Marine	

3.7. Factor analysis

In order to identify probable source of the measured elements a powerful multivariate statistical method; Principal Component Factor Analysis was used. Varimax rotated factor analysis (StatSoft, Inc., 2003) was applied for logarithms of the total concentrations of twelve trace elements and five major cations (totally seventeen variables) of the data set, since element concentrations in precipitation usually exhibit logarithmic Gaussian distributions. Table 8 shows the factor loadings normalized with the Varimax rotation. Only factor loadings larger than 0.50 were considered as significant and marked as bold face in Table 8. Three factors were chosen that explained the 79.5% of the total variance. Most of the communalities are greater than 0.70, suggesting reasonable success in the three factors. The first factor is composed of a group of crustal elements (Al, Ba, Fe, Mn, Sr, Ca) and

explains 65.1% of the total system variance. The second factor which is largely associated with Cd, Cu, Ni, Pb, Zn and moderately associated with Co and Cr clearly represents the anthropogenic factor, which could be attributed to combustion sources such as Zn–Cd smelters and oil burning vehicular sources that emit Pb and Ni. This factor explains a further 9.6% of the variance. The third factor which is largely associated with Na^+ and Mg^{2+} and lowly associated with K^+ most likely represents marine sources, accounting for only 4.8% of the total system variance. Among the elements, Cr and partly Mg^{2+} and K^+ loadings are partitioned between different sources suggesting that total concentrations of these elements have been effected by both of them. This partitioning of load takes place between the crustal and anthropogenic sources (Factors 1 and 2) for Cr, whereas for Mg^{2+} it takes place between crustal and marine sources (Factors 1 and 3). The partitioning of load takes place between the marine, anthropogenic and crustal sources (Factors 1, 2 and 3) for K^+.

Cr is usually emitted from combustion of fossil fuels (Pacyna, 1984) and from electroplating processes (Garcia et al., 2006), but it has also crustal sources. Particularly, for the Mediterranean and Cilician Basin high enrichment of aerosol samples in Cr and Ni has been reported (Guerzoni et al., 1989; Kubilay and Saydam, 1995) due to the presence of Cr and Ni rich soil (ophiolitic minerals) in the Balkan Area and along the Mediterranean coast of Turkey (Tolun and Pamir, 1975; Çağatay et al., 2002). For Cr, this partitioning of load between the crustal and anthropogenic sources and the very low EF_{crust} value (10.5) are consistent with those previous findings. Enhanced aerosol Cr concentrations have also been observed at Erdemli and the aerosol Cr concentrations were found to be 3.1 times higher than those observed at Tel Shikmona, Israel (Koçak et al., 2004). We would expect a similar partitioning of load for Ni in our data due to high crustal sources of this element in this region. However, Ni has largely associated with the anthropogenic factor in Mersin precipitation. Moderately enriched character of Ni explains higher loading of this element in Factor 2 with respect to crustal sources. Partitioning of load could again be attributed to local soil

Table 9
Binary correlation matrix of precipitation data at Mersin.

Element	Al	Ba	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Sr	Zn	Ca^{2+}	Mg^{2+}	Na^+	K^+	H^+
Al	**1.00**																
Ba	**0.90**	**1.00**															
Cd	0.28	0.42	**1.00**														
Co	0.37	0.46	0.37	**1.00**													
Cr	**0.64**	**0.65**	0.34	0.35	**1.00**												
Cu	**0.58**	**0.61**	0.48	0.48	0.57	**1.00**											
Fe	**0.95**	**0.88**	0.25	0.36	**0.60**	0.54	**1.00**										
Mn	**0.90**	**0.90**	0.35	0.43	**0.64**	0.58	**0.93**	**1.00**									
Ni	**0.50**	**0.56**	0.48	0.43	**0.59**	0.72	0.43	0.49	**1.00**								
Pb	**0.53**	**0.58**	0.55	0.47	**0.62**	0.79	0.44	0.51	0.82	**1.00**							
Sr	**0.79**	**0.82**	0.37	0.39	**0.66**	0.64	**0.83**	**0.86**	0.55	0.59	**1.00**						
Zn	0.37	0.45	0.39	0.43	**0.48**	0.53	0.37	0.46	0.60	0.63	0.55	**1.00**					
Ca^{2+}	**0.81**	**0.84**	0.40	0.38	**0.63**	0.59	**0.81**	**0.84**	0.59	0.60	0.88	0.49	**1.00**				
Mg^{2+}	**0.68**	**0.69**	0.32	0.41	**0.50**	0.58	**0.67**	**0.70**	0.54	0.57	0.83	0.44	0.81	**1.00**			
Na^+	**0.60**	**0.66**	0.33	0.42	**0.50**	0.59	**0.60**	**0.63**	0.57	0.56	0.74	0.42	0.75	0.91	**1.00**		
K^+	**0.61**	**0.66**	0.30	0.41	**0.54**	0.63	**0.62**	**0.69**	0.58	0.57	0.81	0.58	0.75	0.77	0.76	**1.00**	
H^+	−0.60	−0.61	−0.21	−0.24	−0.41	−0.39	−0.65	−0.69	−0.29	−0.27	−0.65	−0.14	−0.71	−0.54	−0.49	−0.53	**1.00**

Bold correlations are significant at $p < 0.05$.

which is rich in Ni as well as Cr (Tolun and Pamir, 1975). Potassium (K) is known to be a reliable indicator element of biomass burning (Andreae, 1983) and partly loading of K^+ in anthropogenic source might be due to the contributions of uncontrolled biomass burning emissions from the MSW deposition area.

3.8. Correlation of trace element concentrations

Element concentrations in precipitation usually show log-normal Gaussian distributions, therefore correlation coefficients (r) were calculated for logarithms of the element concentrations (Shimamura et al., 2007) and presented in Table 9. Al, Ba, Fe and Mn are strongly correlated with each other ($r \geq 0.9$) indicating crustal origin of these elements. Al is also well correlated with Ca and Sr ($r = 0.8$), which are mainly crustal originated elements. No correlations between Al and Cd, Co, Zn show different origins while high correlations among Ni, Cu, Cr, Cd, Co, Zn with Pb indicate the common anthropic origin of these elements. However, this type of data must be interpreted cautiously, because sometimes significant correlations can be observed among the elements originated from different sources. For instance, Na is mainly marine (partly crustal) originated elements and it has also well correlations with anthropic elements of Cu, Ni, Pb and crustal elements of Sr, Ba, Al, Fe and Mn (Table 9). This can be explained by the similar scavenging ratio of these elements which depends on the size and hygroscopic properties of

atmospheric particles with which these elements are associated during wash-out processes (Galloway et al., 1993).

3.9. Trajectories of "red rain" events and potential source regions of trace elements

The prominent wind directions and the dominant sectors of the air masses carrying precipitation to Mersin are SW (Sector 3) and SE (Sector 4) (refer to Section 3.1). These sectors are also potential source regions of aerosol dust transportation. In order to assess potential contribution of sporadically transported red dust to the total rainwater concentrations of trace elements in the region, initially red rain events were determined by color identification along with insoluble Al measurements of filter samples and air mass back trajectory analysis of the corresponding rainy days. During the entire sampling period, totally 28 dust transport episodes associated with 31 red rain events were identified. According to the classification of trajectories 17 of these dust transport events were found to be quite outstanding, transporting material from distant sources like the North Africa or the Middle East while the rest of the 11 events are transporting material from the local sources such as the Anatolian mainland and the Cilician Basin (Özsoy et al., 2008). Air mass back trajectories originated from remote and local source regions are presented in Fig. 5a and b, respectively.

Totally, 96 red rain samples were collected from two urban and two suburban stations during the entire sampling period. In order to understand whether there are any significant
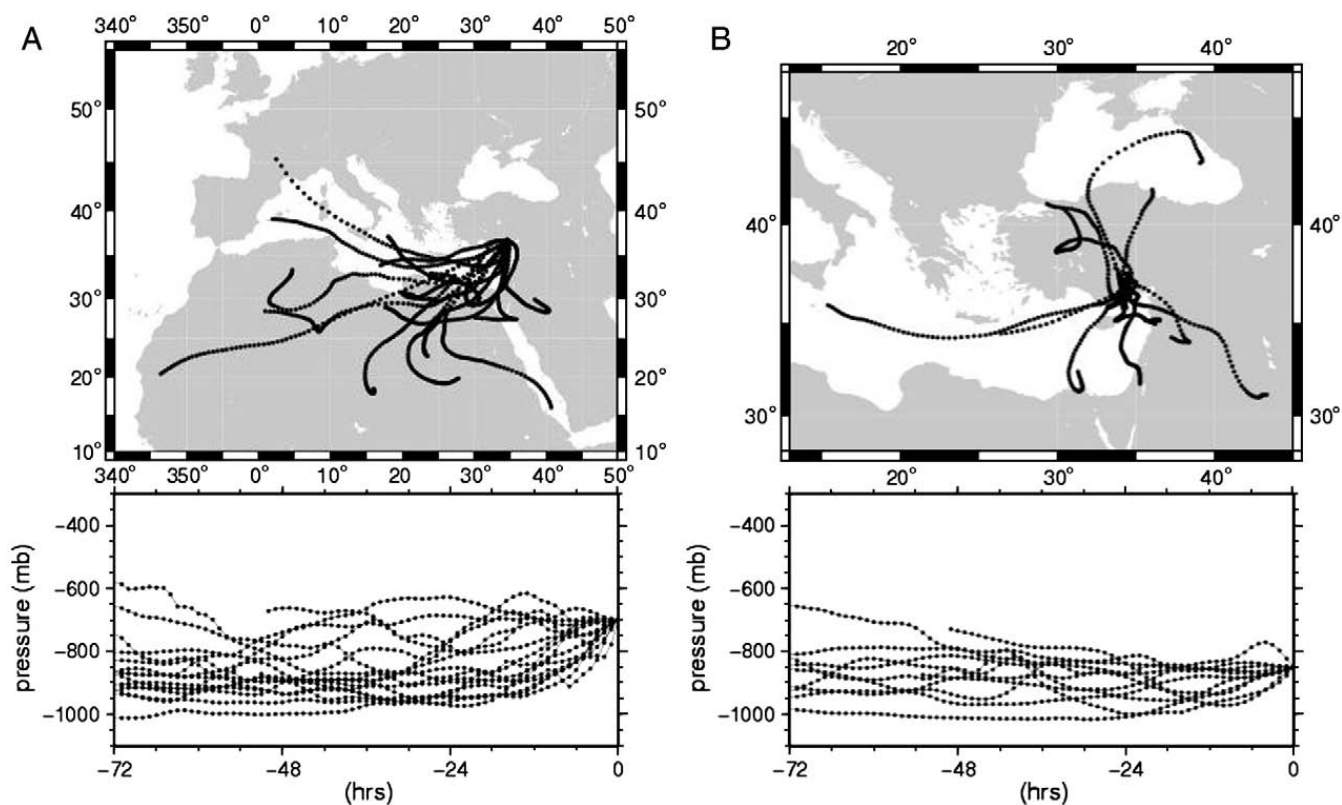

Fig. 5. A) Trajectories of air masses arriving 700 hPa pressure level at Mersin, originated from remote sources (*e.g.* North Africa, Middle East); B) trajectories of air masses arriving 850 hPa pressure level at Mersin, originated from local sources (*e.g.* Anatolia, Cilician Basin). Trajectories of remote and local sources are plotted for 17 and 11 events, respectively (Özsoy et al., 2008).

Table 10
Comparison of the VWM and SDVWM of pH, H^+ and total trace element concentrations ($\mu g\ L^{-1}$) associated with normal *vs* red rain events.

Parameter	Red rain (*n*: 96)	Normal rain (*n*: 150)	Factor
Rainfall	635	2034	0.31
pH	7.21	6.10	
H^+	0.0615 ± 0.0171	0.792 ± 0.222	0.078
EC*	121.4 (2.6)	26.2 (2.8)	4.6
Na^+	2542 ± 595	601 ± 78	4.2
K^+	431.4 ± 61.0	117.4 ± 14.3	3.7
Mg^{2+}	1001 ± 336	205 ± 50	4.9
Ca^{2+}	9701 ± 1393	2291 ± 248	4.2
Al	1555 ± 199	189.9 ± 20.6	8.2
Ba	15.2 ± 2.5	2.37 ± 0.40	6.4
Cd	0.865 ± 0.121	0.783 ± 0.106	1.1
Co	2.83 ± 0.47	1.86 ± 0.21	1.5
Cr	12.4 ± 1.5	3.89 ± 0.36	3.2
Cu	7.19 ± 0.79	3.05 ± 0.26	2.4
Fe	2753 ± 493	190.8 ± 29.0	14.4
Mn	69.0 ± 10.7	5.27 ± 0.67	13.1
Ni	15.2 ± 1.3	5.05 ± 0.54	3.0
Pb	20.7 ± 1.8	8.81 ± 0.91	2.3
Sr	41.9 ± 7.6	8.29 ± 2.40	5.0
Zn	56.0 ± 5.7	48.5 ± 7.5	1.1

Rainfall is the cumulative amount of precipitation in mm. Factor, represents the red rain/normal rain concentration ratio. SDVWM concentrations are calculated according to the formula given by Galloway et al. (1984).

*EC is in $\mu S\ cm^{-1}$ unit. Geometric mean of the data and its standard deviation are presented in the table.

differences in total trace elemental compositions of the "red" and "normal" rain samples, the VWM values of the trace element concentrations associated with respective events are presented in Table 10.

The comparison of the two data sets clearly demonstrates extremely higher (order of magnitude) mean concentrations of crustal elements; Al ($\times 8.2$), Fe ($\times 14.4$) and Mn ($\times 13.1$) in red rain compared to normal rain. Enhancement in Ba, Sr and major cations mean concentrations in red rain are also significant (varying between 6.4 and 3.7). Most likely due to the contribution of local crustal sources, Cr and Ni concentrations in red rain are enriched 3.2 and 3.0 times than normal rain, respectively. The importance of local sources for Cr inputs to the Eastern Mediterranean marine aerosol was also highlighted by Koçak et al. (2004) by categorising samples into "local" and "non-local" groupings depending upon their air mass influence. In contrast to crustal elements, the enhancements in Cd and Zn mean concentrations of red rain (1.1. times) are very low. However, the differences between the VWM Cd and Zn concentrations of red rain and normal rain samples are statistically significant, within 95% confidence interval. These results suggest that aerosol dust whether it is derived from remote or local source regions is the main origin of almost all analyzed elements in Mersin precipitation regardless that they are crustal or antropic derived elements and the magnitude of this contribution is at its highest levels for crustal elements, most probably due to their much higher scavenging ratios than that of anthropogenic ones (Chester et al., 1997). Similar enhancement of anthropic elements in atmospheric aerosols during dust transportation in the Eastern Mediterranean has also been reported by Güllü et al. (1996) and Koçak et al. (2004).

4. Conclusion

Rainwater samples collected from urban and suburban locations of Mersin during the year of 2004 were analyzed to determine the trace elemental composition and to describe general characteristics of precipitation in Mersin. The results show that precipitation is typically of alkaline character with an average pH of 6.2. Electrical conductivity of the precipitation samples was highly variable, rainfall samples with relatively high concentrations of Al, hence mineral dust, called as "red rain" had very high conductivity, due to the high content of soluble solids. Relatively higher total concentrations of crustal and marine originated elements suggest that Mersin is under the influence of natural sources rather than anthropogenic sources. Most of the elements displayed statistically significant inter-stational differences in their VWM concentrations. Considerably higher Zn and K^+ concentrations have been observed in one of the suburban station (St.1) samples most likely, due to relatively higher contributions from agricultural sources and emissions from the MSW landfill area. Percentage solubilities of trace elements and pH-dependent solubilities were investigated and the lowest solubilities were found for the crustal elements (Fe, Al). In contrast to most of the previous findings, the mean solubility of some anthropogenic elements such as Ni was found to be quite low. For almost all elements except Sr, the percentage solubilities decreased in a variable extent with increasing pH values. The highest pH-dependent solubility was observed for Zn while the lowest were observed for Ba and Al. Trace elements grouped according to the crustal enrichment factors, calculated with respect to Al normalization showed that Ba, Fe, Mn, Mg, Na, K, Sr and Cr are not enriched; Ca, Co, Cu and Ni are moderately enriched while Zn, Pb and Cd are highly enriched in Mersin precipitation compared to the upper crust mean composition, most probably due to the influence of other sources; *e.g.* vegetation, agricultural activities and combusion sources. Mineral dust was found to be the main origin of almost all elements in Mersin precipitation regardless that they are crustally or anthropogenically derived. Enhancement in red rain samples of mean concentration was found to be the highest for crustal elements (Fe, Mn, Al), while it was the lowest for anthropic elements (Zn, Cd, Pb), as a result of their association with fine particles ($<1\ \mu m$) with relatively low scavenging ratios.

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