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Precipitation Chemistry as an Indicator of Urban Air Quality in Mersin, North-Eastern Mediterranean Region

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Abstract The chemical composition of precipitation in the city of Mersin on the Mediterranean coast of Turkey has been studied. Spatial and temporal variability of rainwater constituents have been determined from samples collected at two central and two suburban stations for the December 2003–May 2005 period. A total of 246 samples covering all precipitation events were analyzed to determine pH, conductivity, as well as major anion (Cl^-, NO_3^-, SO_4^{2-}); major cation (H^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+) and formaldehyde (HCHO) concentrations. The pH varied within a range of 4.8–8.5, with only 8 out of 246 samples being acidic (pH<5.6), and the remaining highly alkaline samples being neutralized by either NH_4^+ in rainwater, or by $CaCO_3$ resulting from wet deposition of atmospheric dust. The volume weighted mean ΣAnion/ΣCation ratio was 0.49. The equivalent concentration of major ionic species followed the order: $Ca^{2+} > HCO_3^- > SO_4^{2-} > Cl^- > NH_4^+ > Na^+ > Mg^{2+} > NO_3^- > K^+ > H^+$. Formaldehyde concentrations varied in the range of 0.01–17.9 μM, and was found to be dependent on precipitation volume. Relatively higher NH_4^+, SO_4^{2-}, NO_3^- and HCHO concentrations, mainly of anthropogenic origin, measured near the city center suggest increased pollution from local anthropogenic sources, e.g., residential heating, industrial and/or traffic emissions. In general, the results of this study suggest local precipitation chemistry is more strongly influenced by natural (mineral dust and marine) sources compared to anthropogenic ones.

Keywords Eastern Mediterranean · Formaldehyde · Major ions · Mersin · Red rain · Precipitation chemistry

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1 Introduction

The deposition of atmospheric pollutants play an important role in controlling their concentration in the atmosphere and the earth surface, as well as providing essential nutrients to land and marine ecosystems. Because wet deposition often plays a more important role in flux compared to dry deposition (GESAMP 1985), chemical analyses of precipitation enables a partial assessment of local air quality (Berlyand et al. 1982; Lacaux et al. 1992).

The eastern Mediterranean coastal city of Mersin has been affected by increased levels of air pollution parallel the rapid increase of its population in recent years. Yet, research to determine air pollution levels for the city has been lacking, excluding rather intermittent measurements of gaseous SO_2 and particulate matter performed by the Regional Directorate of Environment of İçel (İçel Çevre İl Müdürlüğü). Precipitation events have been sampled for a continuous period of one and a half year, at four different urban stations in Mersin. The samples were analyzed for pH, conductivity, as well as major anion (Cl^-, NO_3^-, SO_4^{2-}); major cation (H^+, Na^+, K, Ca^{2+}, Mg^{2+}, NH_4^+) and formaldehyde (HCHO) concentrations. The aim of the study was to determine the ionic content of precipitation and to compare pollutant levels in rain water with previous results from other urban sites for a partial assessment of air pollution and its wet deposition affecting the area.

2 Experimental

2.1 General Characteristics of the Study Area

Mersin, an industrialized city with approximately a million inhabitants and a busy port, supports various industries (e.g., petroleum refinery, thermal power plant, soda, chromium, fertilizer and glass production), almost all situated in the industrial district, NE of the city. The study area approximately covers 36° 01′–37°00′N and 32°56′–34°57′E. The ground consists of terrigenous carbonates, derived from limestone, dolomite and calcretes (Yetiş et al. 1995), and bordered by the calcareous–karstic Taurus mountains, mostly of Paleozoic and Mesozoic formations, reaching heights of 600–1,500 m on the north (Kapur et al. 2000). Climatically, the region is characterized by generally wet and warm winters (November through to February) and hot/dry summers (June through to September). The transitional seasons, spring and autumn, are generally short. The relatively longer spring season (March through May) is noted for some periods of unsettled winter-type weather associated with an increased occurrence of North African cyclones; otherwise very similar to summer. Autumn usually lasts only one month (October) and is characterized by an abrupt change from the summer to the unsettled weather of winter (Özsoy 1981; Milliman et al. 1992). Mean annual precipitation based on the long term (1990–2003) measurements of the Turkish Meteorological Service, Mersin station, located within the city center, is 587.5 mm. The prominent wind directions during precipitation events of cyclonic passages are typically from the S–SW and SE, and therefore do not transport pollution towards the city from the industrial district located on the NE of the city.

Previous long-term studies (Kubilay and Saydam 1995; Kubilay et al. 2000) have revealed that the region is under the influence of crustal material mainly derived from the North-African arid and semi-arid regions, particularly in spring and occasionally in winter months. Dust originating from arid regions is carried into the eastern Mediterranean either by the Scirocco and Khamsin local wind systems or by mid-latitude atmospheric depressions passing along the Mediterranean–European region and usually washed-out by rain. The precipitation events coinciding with dust transport, identified by the reddish or yellowish color of membrane filters used in filtering the rainwater are called as “red rain”. The local or sporadic desert-derived dust is calcareous and contains large fractions of calcite. Neutralization of acidity by dust $CaCO_3$ and consequent changes in pH of precipitation has been reported elsewhere (Loye-Pilot et al. 1986; Al-Momani et al. 1995a; Özsoy and Saydam 2000).

2.2 Sampling Sites

Four sampling stations 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 approximate 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. A rain-gauge (Akım Elektronik, Pluviograph, Model PHD5-02) with a special facility for rainwater sampling were deployed at St. 2. The sampler consisted of a 25 cm diameter HDPE funnel, a one liter capacity PE collection bottle and a coarse filter at the interface between the funnel and the bottle. St. 3 and St. 4 were

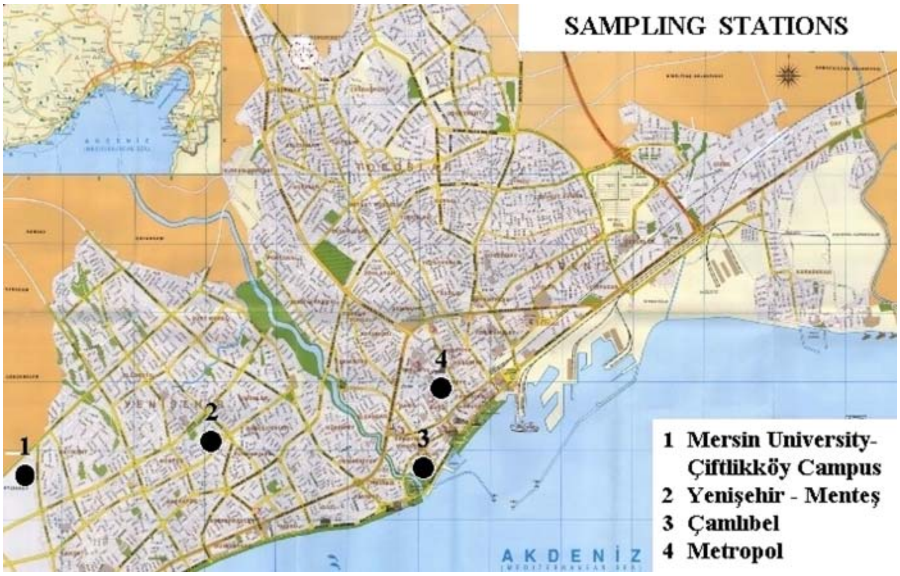

Fig. 1 Location of the sampling stations of precipitation in Mersin

located at the roof 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.

2.3 Analytical Procedure and Data Quality

Precipitation samples 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. Sample quality was ensured by screening the sample to exclude any visible contamination. After measuring their volume, samples were filtered through a 0.45 μm pore size membrane filter (MFS, cellulose acetate, 47 mm diameter) to remove insoluble particles by applying gentle negative pressure and divided into aliquots for analyses. Samples reserved for major anion analysis were filtered through a 0.22 μm pore size membrane filter (Sartorius, cellulose acetate, 47 mm diameter) in order to protect the anion exchange column. Subsamples of precipitation were transferred in rigorously cleansed PE (polyethylene) bottles and preserved at 4°C until analysis time. Aliquots for major cation analysis were preserved by acidification with 0.1 M HNO_3 before storage. Ammonium and formaldehyde analyses have been performed as soon as possible, since these species are unstable with respect to oxidation. In order to prevent microbial decomposition of formaldehyde, 100 μl of $CHCl_3$ was added to the samples which were stored at 4°C in the dark until analysis.

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 Meter with automatic temperature compensation. Ammonium has been analyzed using a Shimadzu UV-1601, UV-VIS Spectrophotometer. Samples were colored with Nessler reagent and absorbance of the colored solution was measured at 425 nm in a cell with 1.0 cm optical thickness. The detection limit defined as three times the standard deviation of the blank value was 0.005 mg l^{-1} and reproducibility defined as the standard deviation of seven replicate analysis of subsamples was better than 9%. Formaldehyde was analyzed using the Nash method (Nash 1953). The yellow colored complex formed by the reaction of Nash reagent with formaldehyde was determined spectrophotometrically at 412 nm wavelength. The detection limit was 0.3 μM and the coefficient of variation was better than 10%. An HP1090 model HPLC equipped with UV-DAD detector and auto-sampler coupled with a VYDAC 302 IC anion exchange column was used for the analysis of Cl^{-}, NO_3^{-} and SO_4^{2-}, at the Central Research Laboratory of Mustafa Kemal University (MKU) in Antakya. The detection limits of Cl^{-}, NO_3^{-} and SO_4^{2-} ions were found to be 0.075, 0.070 and 0.090 mg l^{-1}, respectively. The reproducibility was found to be 7% for Cl^-, 3% for NO_3^- and 4% or SO_4^{2-} ions. A Varian Liberty II model ICP-AES at the Central Research Laboratory of MKU was used for the analysis of Na^+, K^+, Ca^{2+} and Mg^{2+}. 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 detection limits of Na^+, Ca^{2+}, K^+ and Mg^{2+} ions were found to be 0.004, 0.010, 0.005 and 0.003 mg l^{-1}, respectively. Reproducibility of results was better than 4% for all major cations. The same procedures have been applied to five field blanks collected within the sampling period. The concentration of field and laboratory blanks measured throughout the study were all below the detection limit of the measured species.

The accuracy of the data are 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, conductivity, sulphate, nitrate and chloride, 5.0% for potassium, better than 9.8% for calcium and magnesium. Relative error was found to be relatively high for sodium and ammonium analyses (better than 15.0%) on the average of simulated acid rain samples.

2.4 Air Mass Back Trajectories

Precipitation was recorded at sampling increments of 0.1 mm by a rain-gauge (Akım Elektronik, Pluviograph, Model PHD5–02) installed at St. 2. 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.

3 Results and Discussion

3.1 Precipitation Data and the Trajectories of the Precipitation Carrying Air Masses

Based on 14 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. There are significant differences in precipitation among our sampling stations. 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 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 six of these samples were rejected due to insufficient amount of precipitation (<0.2 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 3 days of excursion. Figure 2 shows the location of the sampling site (St. 2) along with the sectors used in trajectory classification of rainy days. Percentage values of mean airflow directions at the 850 hPa barometric pressure level are shown for each sector. The trajectory classification for rainy days was performed at 1,000, 900, 850 hPa levels (likely to be in the planetary boundary layer; PBL) and

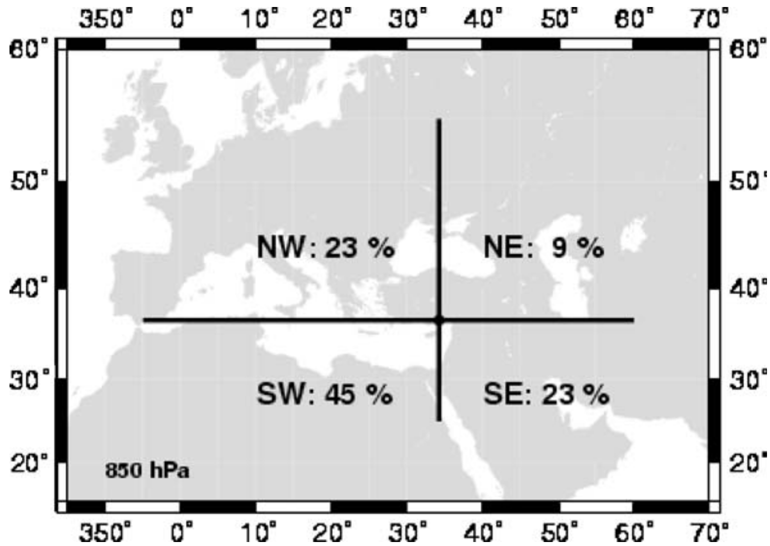

Fig. 2 Sectors used in trajectory classification for a total of 78 rain events with the percentage values of mean airflow directions at the 850 hPa barometric pressure level during December 2003–May 2005

at 700, 500 hPa levels (free trophosphere), respectively. The results of this classification are presented in Table 1, where the percentage in each direction are given for a total of 78 trajectories during rain events during December 2003–May 2005.

Table 1 shows that the highest percentages belong to the sector 3, SW direction. This result is consistent with the long term observation of 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.

3.2 Ionic Balance

Ion balance was applied to 246 samples in order to check the completeness of measured parameters. The volume weighted mean ΣAnion/ΣCation ratio was 0.49, which is very low than unity, most probably due to exclusion of bicarbonate ion, as frequently reported for the Mediterranean region (Samara et al. 1992; Al-Momani et al. 1995b; Al-Momani et al. 2000; Hontoria et al. 2003). Since no direct method is available for the measurement of bicarbonate, the concentration of this anion was estimated from the theoretical relation between pH and HCO_3^-. When the sample is in equilibrium with atmospheric carbon dioxide (365 ppm) and pH is higher than 5.6, HCO_3^- concentration is calculated as follows (Granat 1972): $\left[HCO_3^-\right] = 10^{-11.26+\mathrm{pH}}$ This equation was safely applied to our data since most of the pH values measured in Mersin precipitation were above 5.6. and the volume weighted mean ΣAnion/ΣCation ratio was found to be 1.02 when the bicarbonate ion was included in the ionic balance.

Table 1 Percentage of mean airflow directions of 78 rain events at five different (1,000, 900, 850, 700, 500 hPa) barometric pressure levels during December 2003–May 2005 in Mersin

hPa	Sector 1 (NE)	Sector 2 (NW)	Sector 3 (SW)	Sector 4 (SE)
1,000	10	18	44	28
900	12	23	28	37
850	9	23	45	23
700	3	27	69	1
500	2	35	63	0

3.3 Electrical Conductivity and pH Variation

Figure 3 presents the percent frequency distribution of pH for 246 rain events collected during one and a half year period from four different stations. The pH varied within a range of 4.8–8.5. The average pH of rainwater for the entire data set is observed to be 6.22, which is in the alkaline range. Out of 246 samples, 97% reflects alkaline pH of precipitation, as compared to 5.6 pH of rainwater at equilibrium with atmospheric CO_2. The observed alkalinity of rainwa-

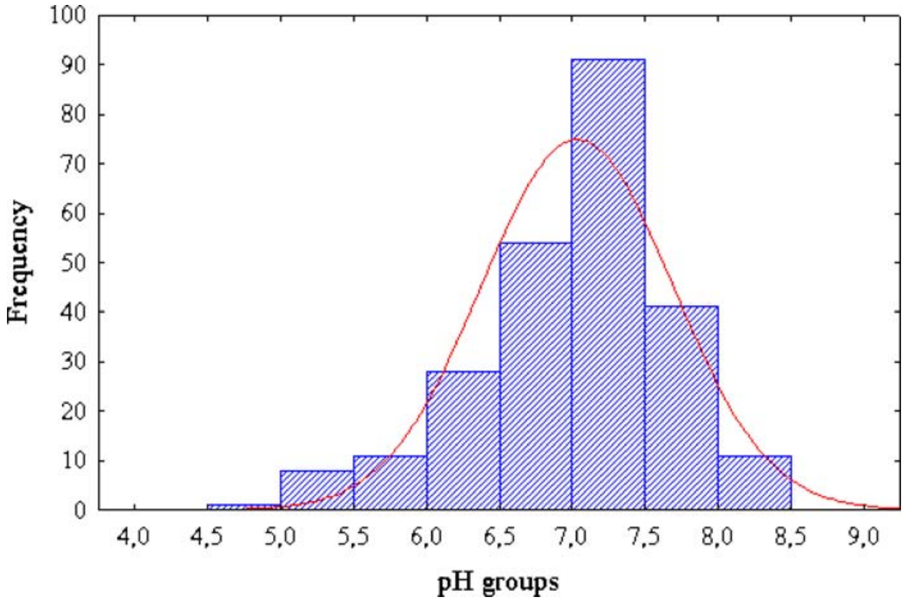

Fig. 3 Frequency distribution of measured pH values at Mersin

ter 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). There have been only eight 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.

Electrical conductivity of the precipitation samples was found to be highly variable, within a range of 0–1,427 μS cm^{-1}. The geometric mean conductivity of the 246 precipitation samples was 47.8 μS cm^{-1}. The relationship between electrical conductivity and calcium concentration is presented in Fig. 4, representing a high positive correlation (R^2=0.88) between the two parameters. Mineral dust particles having high content of calcite mineral most probably act as host for soluble solids.

3.4 Mean Ionic Composition and Spatial Variability

The volume weighted mean (VWM) concentrations of the measured parameters in Mersin precipitation from each station are presented in Table 2. The concentration of major ionic species has the following order: $Ca^{2+}>HCO_3^->SO_4^{2-}>Cl^-> NH_4^+>Na^+>Mg^{2+}>NO_3^->K^+>H^+$, which respectively account for 29, 27, 11, 10, 8, 6, 4, 4, 1, 0.1% of the total ionic mass. Dominant ions are calcium and bicarbonate because of the natural influence of calcareous mineral dust, but sulfate, chloride and ammonium concentrations are also notable. Calcium represents 59% of total cations, while sulfate represents 22% of the total mass of anions. Similar dominance was also observed in other studies carried out in the Mediterranean Basin (Jaradat et al. 1999; Tuncer et al. 2001; Hontoria et al. 2003). Anthropogenic ions SO_4^{2-}, NO_3^- and NH_4^+ account for approximately one third and natural ions Ca^{2+}, Cl^-, Na^+, Mg^{2+}, and K^+ account for the remaining two thirds of the ionic mass, when we exclude bicarbonate from the ionic balance. Although the contribution from anthropogenic ions is significant, the H^+ ion accounts for only <0.1% of the total ionic mass due to extreme neutralization of acidity, as will be discussed in subsequent sections (see Section 3.6).

Generally, an elevation trend was observed in VWM concentrations of almost all parameters from St.1 to St. 4. Particularly, anthropogenic constituents (e.g., SO_4^{2-}, NO_3^-, NH_4^+ and HCHO) were found to have higher concentrations at central stations (St. 3 and St. 4), while the highest values were obtained at St. 4 (Table 2). This observation might be a consequence of two factors:

1. Relatively high level of human activities (e.g. dense traffic and population) can be found at St. 3 and St. 4. Additionally, these central stations are closer to the industrial zone of the city.

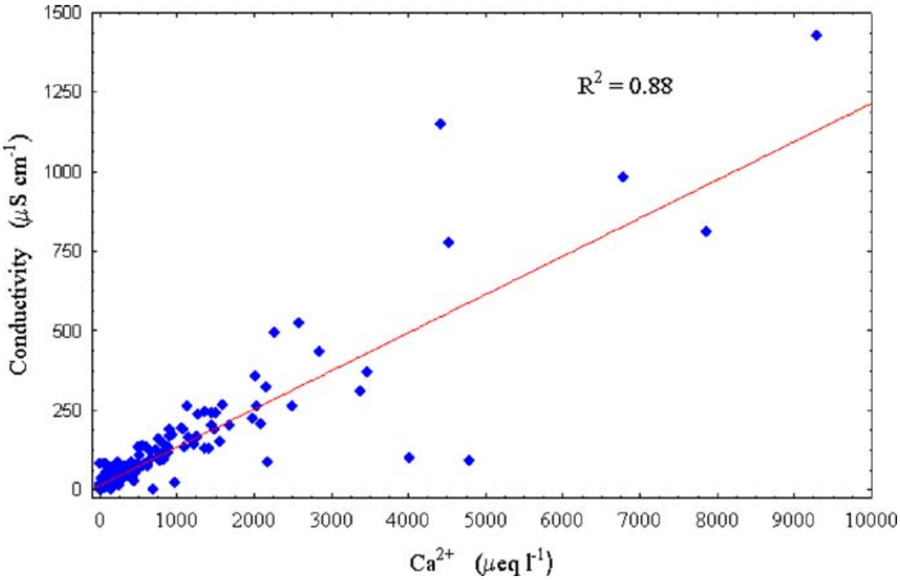

Fig. 4 Relationship between the electrical conductivity (μS cm^{-1}) and calcium concentrations (μeq l^{-1}) in Mersin precipitation

2. The total amount of rainfall in these central stations for one year sampling period was less than the suburban stations. In fact, the total amount of precipitation was found to be in decreasing order of 591, 529, 469 and 468 mm for stations 1, 2, 3 and 4, respectively.

To test for significant differences among ionic concentrations in precipitation between the sampling sites, the standard deviations of the VWM were calculated using the formula of Galloway et al. (1984) and the Student's *t* test (two-tail at 5%) was applied. The results of this statistical test indicate that there were significant differences between the sampling sites particularly for anthropogenic parameters. The differences in SO_4^{2-} and NH_4^+ mean concentrations between St. 3 and St. 4 and the difference in NO_3^- concentrations between St. 2 and St. 4 were found to be insignificant. In contrast to the central stations, ionic concentrations in the suburban stations,

Table 2 Volume weighted means (VWM) concentrations (μeq l^{-1}) and standard deviations of the concentrations of major ions (μeq l^{-1}) and of formaldehyde (μM) in Mersin precipitation collected at four sites from December 2003 to May 2005

Parameter	St. 1 (*n*:67)	St. 2 (*n*:78)	St. 3 (*n*:51)	St. 4 (*n*:50)	All (*n*:246)
pH	6.21	6.37	6.15	6.28	6.22
Conductivity[a]	39.5	48.5	53.0	54.1	47.8
HCO_3^-	64.5 (17.4)	99.7 (45.0)	250.6 (202.1)	263.7 (212.1)	180.7 (86.3)
Cl^-	55.7 (16.6)	71.6 (19.1)	74.2 (33.2)	66.1 (24.2)	65.5 (13.5)
NO_3^-	25.6 (2.7)	32.4 (3.6)	27.5 (2.6)	31.8 (4.9)	28.5 (2.1)
SO_4^{2-}	64.7 (7.2)	75.6 (9.6)	80.8 (11.3)	83.7 (11.8)	75.9 (6.0)
H^+	0.62 (0.22)	0.43 (0.16)	0.71 (0.42)	0.52 (0.27)	0.60 (0.16)
NH_4^+	40.3 (4.3)	52.1 (5.2)	60.5 (7.4)	62.4 (8.4)	53.6 (4.1)
Na^+	50.2 (15.5)	35.5 (6.8)	51.4 (19.9)	51.9 (15.8)	44.2 (6.2)
K^+	6.7 (1.0)	3.5 (0.6)	5.0 (1.3)	5.3 (1.2)	4.7 (0.4)
Ca^{2+}	203.7 (39.7)	152.5 (19.9)	221.6 (53.7)	252.7 (56.2)	192.8 (18.2)
Mg^{2+}	36.9 (15.8)	32.8 (12.6)	21.7 (7.9)	28.7 (9.8)	30.9 (6.8)
HCHO	0.66 (0.09)	1.28 (0.16)	1.51 (0.20)	1.66 (0.28)	1.27 (0.10)

Standard deviations of the VWM were calculated using the formula of Galloway et al. (1984) and presented in parentheses.

[a] Conductivity was measured in μS cm^{-1} unit. Geometric mean of the data is presented in the table.

particularly in St.1, are generally lower (except for K^+ and Mg^{2+}). Since human activities are less and the amount of precipitation is higher in the suburban area, pollutants appear to be more diluted as a consequence. Relatively high level of K^+ concentration in St.1 might be attributed to the application of potassium salts such as K_2O and K_2SO_4 as fertilizers to the vegetable and citrus tree fields in the close vicinity of this station. The highest mean Cl^- concentration observed in St. 3 is most likely due to the closer location of this station to the sea (Fig. 1). VWM Cl^- concentration of St. 1 was significantly lower than the rest of the other sites. But the differences among the mean Cl^- concentrations of St. 2, 3 and 4 were insignificant.

3.5 Marine Contribution

In order to calculate marine contribution to the ionic budget of Mersin precipitation, sea salt fractions (SSF) and enrichment factors with respect to sea water (EF_{marine}) have been calculated. For this purpose, sodium was taken into account as a reference element because the chloride concentration was higher than that of sodium. Even though several authors have referred to a crustal contribution of sodium around 10–35% in the Mediterranean region (Al-Momani 1995b; Tuncel and Ungör 1996; Jaradat et al. 1999) we preferred using sodium, due to non-conservative character of chloride as a result of reactions with acidic species (Wall et al. 1988). The sea water (μequivalent) ratios used to calculate the proportion of ions that were not of marine origin were: sodium (1); chloride (1.1650); sulphate (0.1205); magnesium (0.2272); calcium (0.0439) and potassium (0.0218; Riley and Skirrow 1975). Table 3 shows ionic ratios of Mersin precipitation enrichment factor EF_{marine} with respect to sodium and the corresponding non sea salt and sea salt fractions. The Ef_{marine} was calculated as follows:

$$EF_{marine} = (X/Na^+)_{rain}/(X/Na^+)_{marine}$$

where X is the ion of interest.

All ratios in Mersin precipitation were found to be higher than that of seawater due to contribution of other sources. The highest non sea salt fractions (NSSFs) were calculated for Ca^{2+} and SO_4^{2-} most probably due to the contributions of crustal and anthropogenic sources to the atmospheric budgets of these ions. EF_{marine} values based on the VWM concentrations of these ions also show that Ca^{2+} is significantly enriched, while SO_4^{2-} is moderately enriched relative to marine sources. Marine contributions to the atmospheric concentrations of Mg^{2+} and K^+ are also significant.

3.6 Acid Neutralization and Neutralization Factors

If all the $NSS-SO_4^{2-}$ (69.6 μeq l^{-1}) and NO_3^- existed in the free acid forms, as the sum of the volume weighted mean concentrations of these species is 98.13 μeq l^{-1}, the precipitation pH would have been 4.01 which is 2.21 pH units lower than the measured mean value of pH (6.22). This discrepancy indicates that the precipitation has been excessively neutralized by other species, e.g., crustal components and ammonia. Taking the difference of the sum of $NSS-SO_4^{2-}$ and NO_3^- from H^+, we can estimate that about 99.4% of the acidity is in neutralized form. The role of Ca^{2+}, Mg^{2+} and NH_4^+ has been evaluated by calculating neutralization factors (NF) as follows:

$$NF_{Ca} = Ca^{2+}/\left(NO_3^- + SO_4^2\right);$$
$$NF_{Mg} = Mg^{2+}/\left(NO_3^- + SO_4^{2-}\right);$$
$$NF_{NH4} = NH_4^+/\left(NO_3^- + SO_4^{2-}\right)$$

Table 3 Comparison of sea water and precipitation ionic ratios (μequivalent), enrichment factors $Ef_{marine,}$ non sea salt (NSSF) and sea salt (SSF) fractions

Ionic ratio	Seawater[a] ionic ratio	Precipitation ionic ratio	EF_{marine}	NSSF (%)	SSF (%)
Cl^-/Na^+	1.1650	1.484	1.27	10.7	89.3
SO_4^{2-}/Na^+	0.1205	1.718	14.26	91.7	8.3
Mg^{2+}/Na^+	0.2272	0.699	3.08	67.5	32.5
Ca^{2+}/Na^+	0.0439	4.366	99.5	99.0	1.0
K^+/Na^+	0.0218	0.1064	4.9	79.6	20.4

[a] Based on the data in Riley and Skirrow (1975)

The respective values of neutralization factors for Ca^{2+}, NH_4^+ and Mg^{2+} were 1.85, 0.51 and 0.30, suggesting that the main neutralization has occurred due to Ca^{2+}. Therefore, calcite content of atmospheric dust particles, either originated from local soil or sporadically transported from North Africa and/or Middle East (Özsoy and Saydam 2000) seem to be the major component responsible for neutralization of Mersin precipitation.

3.7 Formaldehyde and Variation with Precipitation Volume

Formaldehyde is the most abundant carbonyl compound in the atmosphere since it occurs as a stable intermediate in the oxidation of methane and of other volatile organic compounds (VOCs) (Possanzini et al. 1996). It can be directly emitted in the atmosphere either by anthropogenic (Cleveland et al. 1977) and/or natural biogenic sources (Sakugawa et al. 1993). Contributions from biomass burning are also significant (Benning and Wahner 1998). Among the anthropogenic sources motor vehicle exhaust is the most important direct source of HCHO particularly in urban atmosphere. HCHO has been detected in the atmosphere in gas phase (Klemm et al. 1998; Weller and Schrems 2000), particle phase (Deandrade et al. 1995; Liggio and McLaren 2003) and in precipitation (Zafiriou et al. 1980; Khare et al. 1997; Kieber et al. 1999).

Since the concentration of soluble species is a function of the precipitation volume (Baeyens et al. 1990), the binary correlation coefficients of the measured parameters with the amount of precipitation were calculated and presented in Table 4.

The formaldehyde concentration is plotted against precipitation volume in Fig. 5. In contrast to the studies carried out by Khare et al. 1997; Kieber et al. 1999 and Pena et al. 2002 formaldehyde concentrations, like all the other measured parameters in Mersin precipitation, were found to be negatively correlated with precipitation volume (Table 4, Fig. 5). This fact indicates that the concentration of all chemical species is affected by precipitation volume (their concentration tends to decrease with increasing precipitation volume), and thus their concentrations are mostly controlled by dilution.

The same result was also reported for Los Angeles by Sakugawa et al. (1993). This result suggest that scavenging mechanisms of particle phase formaldehyde play an important role in Mersin atmosphere which is heavily loaded with dust particles rather than continuous supply of gaseous formaldehyde during rain events or in situ photochemical production in the aqueous phase. A gradual increase in volume weighted mean formaldehyde concentrations from St. 1 to 4 is noticable (Table 2), most probably due to the increased traffic activity towards the city center. Formaldehyde is also positively correlated with NH_4^+ (R^2=0.76), NO_3^- (R^2=0.57) and NSS – SO_4^{2-} (R^2=0.67) all of which are mainly of anthropogenic origin. Volume weighted mean formaldehyde concentration of Mersin precipitation is compared to data from around the world in Table 5.

Formaldehyde concentration in Mersin precipitation is quite lower than almost all values in Table 5, except the value reported for Galicia, which is a rural area surrounding a thermal power plant in the Northwest Spain. İzmir is the only big city where formaldehyde measurements have been performed in precipitation in Turkey. Unfortunately, instead of volume weighted mean concentrations, minimum and maximum concentrations were reported for İzmir. Therefore, we made our comparison on annual wet deposition flux basis which is also reported for the third biggest city of Turkey, İzmir. Annual wet deposition flux of formaldehyde in Mersin (17.8 mg m^{-2} $year^{-1}$) is found to be considerably lower than the value given for İzmir, 31.4 mg m^{-2} $year^{-1}$ (Seyfioğlu et al. 2005). Mersin atmosphere is not heavily loaded

Table 4 Binary correlation coefficients, *R*, of the measured parameters with precipitation volume

Parameter	*R* value
Rainfall	1.00
Conductivity	−0.39
pH	−0.21
H^+	0.06
HCO_3^-	0.18
NH_4^+	−0.44
Ca^{2+}	−0.33
K^+	−0.30
Mg^{2+}	−0.19
Na^+	−0.21
Cl^-	−0.23
NO_3^-	−0.35
SO_4^{2-}	−0.30
HCOH	−0.43

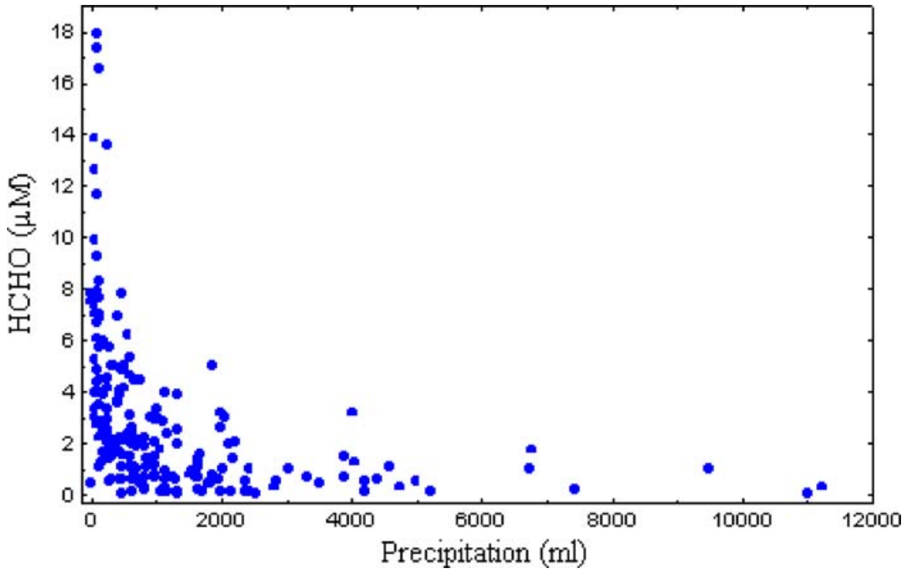

Fig. 5 Formaldehyde concentration versus precipitation. R^2=−0.43

with this constituent comparable to the other settlements around the world.

3.8 Red Rain

The precipitation events coinciding with dust transport, identified by the reddish or yellowish color of membrane filters used in filtering rainwater are called as "red rain" (Avila et al. 1998; Özsoy and Saydam 2001). In our study, color identification of filter samples and air mass back trajectory analysis of the corresponding rainy days revealed 28 dust transport episodes associated with 31 "red rain" events, during the entire sampling period. Trajectory classification shows that 17 of these dust transport events were quite outstanding and they have transported material from distant sources (e.g. from the North Africa or the Middle east). As shown by free trophospheric back trajectories in Fig. 6, without exception all 17 events have originated from North Africa while the remaining 11 cases originated from the local sources (e.g. from the Anatolian mainland and Cilician Basin, presented in Fig. 7).

Table 5 Comparison of the volume weighted mean concentrations of formaldehyde with the data reported from various cities around the world

Location	HCHO (μM)	Reference
Mersin	1.27	This study
Camarillo, CA, USA	2.00	Grosjean and Wright 1983
Wilmington, NC, USA	2.70	Kieber et al. 1999
Heraklion, Crete	3.05	Economou and Mihalopoulos 2002
Agra, India	4.40	Khare et al. 1997
Galicia, Northwest Spain	0.42	Pena et al. 2002
İzmir	0.33–10.00	Seyfioğlu et al. 2005

Totally, 96 red rain samples have been collected from four different stations during the entire sampling period. In order to understand whether there are any significant differences in ionic compositions of the red and normal rain samples, the VWM values of measured parameters associated with normal versus red rain events are presented in Table 6.

The results of the Student's *t* test (two-tail at 5%) applied on the data revealed that the VWM of major ion and formaldehyde concentrations of red rain samples are significantly higher than the normal rain values, except H^+, the latter resulting from extreme neutralization by the high carbonate/bicarbonate content of red rain. Based on our data we can safely conclude that red rain is quite a rich source of all major ions and formaldehyde and mineral dust particles act as a host for all these measured species in Mersin atmosphere.

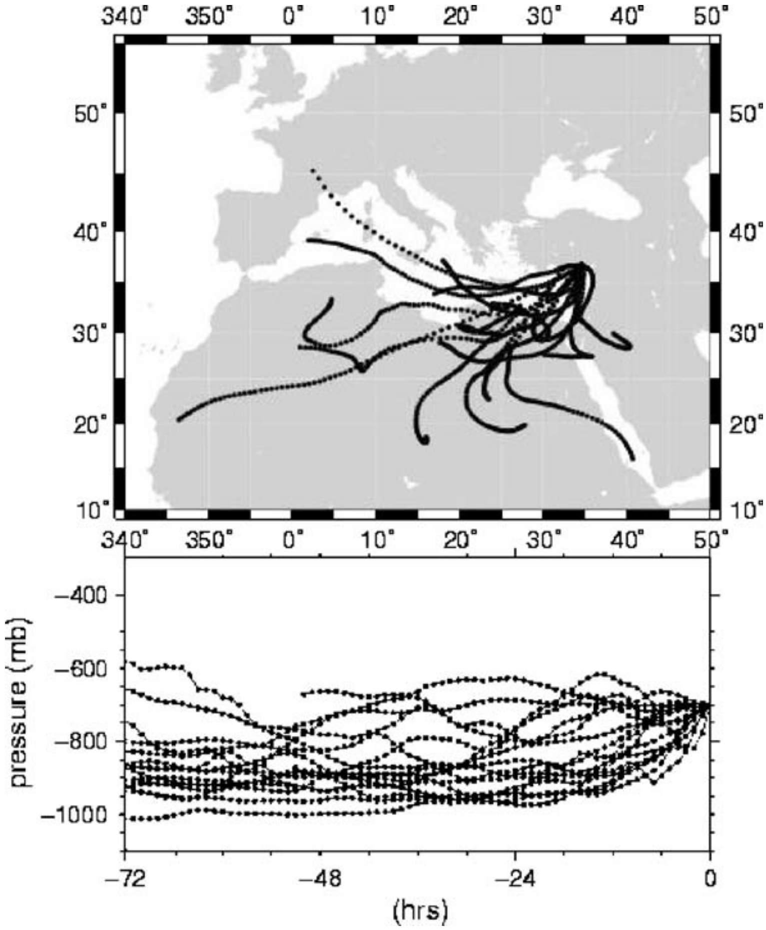

Fig. 6 Trajectories of air masses arriving 700 hPa pressure level at Mersin, having mineral dust carrying capacity from North Africa and Middle East. Trajectories are plotted for 17 events

3.9 Comparison of the Data

In order to evaluate the air quality of Mersin, the data obtained from this study was compared in Table 7 with data reported from various urban locations around the world. Especially for this purpose, anthropogenic species e.g., SO_4^{2-}, NO_3^- and NH_4^+ were used in the comparison. Ca^{2+} was used as an indicator of mineral dust influence at a particular location.

In Table 7, it is notable that the stations under the influence of mineral dust have very high levels of Ca^{2+} particularly for the cases of İskenderun, Madrid and Jordan. The lowest Ca^{2+} concentration belongs to Singapore, where no dust activity has been reported. The mean Ca^{2+} concentration of Mersin precipitation is higher than the values reported for İzmir, Athens, Bordeaux, Irbid and Mexico City. The mean SO_4^{2-} concentration of Mersin rainwater is quite lower than most of the other values. Among urban sites, the highest sulphate concentrations belong to the highly industrialized cities of İskenderun (353.0 μM) and İstanbul (242.3 μM) of which the mean values are approximately an order of magnitude higher than those for Mersin. Sulphate concentration in Mersin precipitation is similar to those found in Ankara, Menemen (a rural site of İzmir) and Singapore. The mean NO_3^- concentration in Mersin precipitation (28.5 μM) is quite lower than the values reported for big cities e.g., Ankara, İstanbul, Bordeaux, Madrid, Amman and Mexico City and similar to those found in Athens, Thessaloniki, Irbid and Singapore. Among the anthropogenic species only the mean NH_4^+ concentration of Mersin rain water is relatively higher than most of the

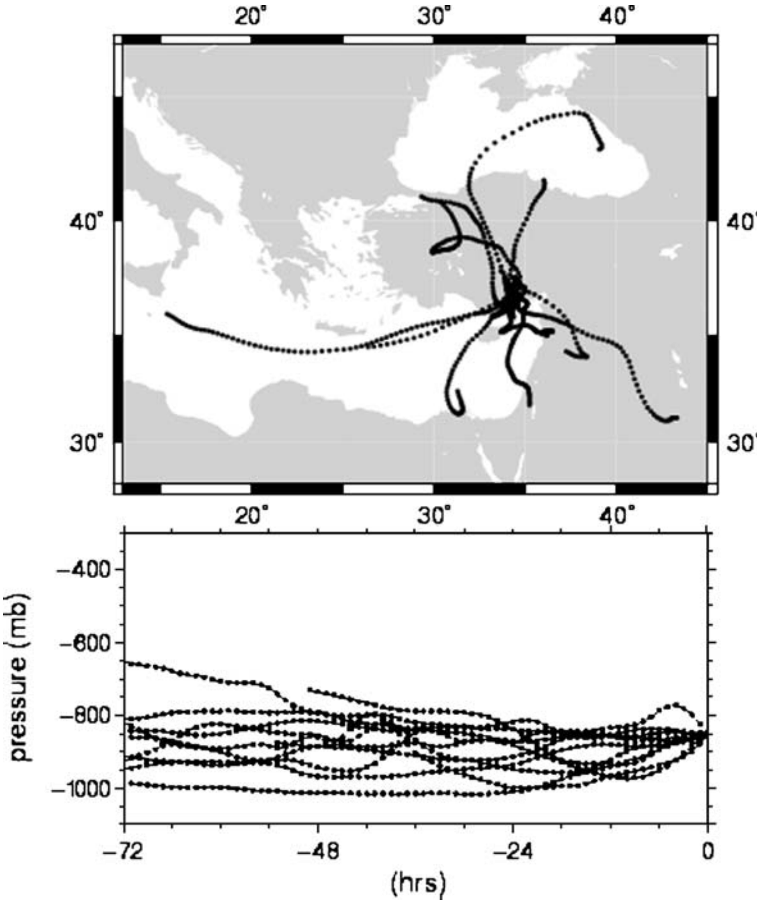

Fig. 7 Trajectories of air masses arriving at 850 hPa pressure level at Mersin, having mineral dust carrying capacity from Anatolian mainland and local sources. Trajectories are plotted for 11 events

data except the data from İstanbul and Mexico City. This result might be attributed to ammonium fertilizers extensively used in the region, especially during rainy days of the spring and early summer months. It has been reported that 40,850 tons of N (as ammonium solution, ammonium nitrate and ammonium sulphate) has been used in Mersin region during 2005 for agricultural purposes (Çevre Durum Raporu 2006).

4 Conclusions

Rainfall samples collected from four different stations during the December 2003–May 2005 period were analyzed to determine the chemical composition and describe general characteristics of Mersin precipitation. The mean airflow directions of the precipitation carrying air-masses were determined by the classification of trajectories for each barometric pressure levels and the prominent wind directions during rainy days within the planetary boundary layer were found to be SW and SE, which do not lead to transport towards the city from the industrial district located on the NE of the city.

The results show that precipitation is typically of alkaline character with volume weighted mean pH of 6.2. Dominant ions are calcium and bicarbonate owing to the natural influence of calcareous mineral dust over the region; sulphate, chloride and ammonium concentrations are also notable. Mainly calcite content (and thus Ca^{2+} ions) of atmospheric dust particles and secondly NH_4^+ ions were found to be the major components responsible for neutralization of Mersin precipitation. NH_4^+, SO_4^{2-} and NO_3^- ions, evaluated as anthropogenic species, were found to contribute approximately by 33% to the total ionic

Table 6 Comparison of VWM and standard deviation of rainfall (mm), pH, conductivity (μS cm^{-1}), major ionic concentrations (μeq l^{-1}) and formaldehyde (μM) associated with normal versus red rain events

Parameter	Red rain (*n*: 96)	Normal rain (*n*: 150)
Rainfall (mm)	635	2,034
pH	7.21	6.10
H^+	0.061 (0.017)	0.786 (0.220)
Conductivity[a]	121.4 (2.6)	26.2 (2.8)
HCO_3^-	601.6 (338.4)	37.6 4.9)
Cl^-	150.0 (51.7)	36.7 (3.4)
NO_3^-	45.8 (5.9)	22.6 (1.9)
SO_4^{2-}	122.5 (17.7)	60.0 (5.0)
NH_4^+	78.3 (12.4)	45.2 (3.5)
Na^+	110.3 (26.0)	26.1 (3.4)
K^+	10.9 (1.6)	3.0 (0.4)
Mg^{2+}	82.4 (27.8)	16.8 (4.1)
Ca^{2+}	480.6 (69.8)	114.3 (12.4)
HCHO	1.93 (0.27)	1.08 (0.10)

Standard deviations of the VWM values were calculated using the formula of Galloway et al. (1984) and presented in parentheses.

[a] Conductivity is in μS cm^{-1} unit. Geometric mean of the data and its standard deviation is presented in the table.

budget of precipitation. Formaldehyde concentrations along with the concentration of all measured chemical species were found to be a function of the precipitation volume. Spatial variations, particularly in the concentration of anthropogenic species, are evident. The difference between the VWM concentrations of ammonium, sulphate, nitrate and formaldehyde among the central and suburban stations were statistically significant. Relatively higher concentrations of these anthropogenic parameters at central stations, which are closer to the industrial zone of the city, emphasize the effects of human activities e.g., dense traffic and population.

Totally, 96 red rain samples have been collected during the entire sampling period. The comparison of the VWM concentrations of the measured parameters associated with normal versus red rain events revealed that red rain is quite a rich source of all major ions and formaldehyde. We can conclude that mineral dust particles act as a host for all these measured species in the Mersin atmosphere. When compared with rainwater data reported from other urban stations, the Mersin atmosphere does not appear to be heavily loaded particularly with anthropogenic species of SO_4^{2-}, NO_3^- and HCHO. Relatively higher levels of NH_4^+ in Mersin precipitation might be attributed to the agricultural fertilizers. Mersin atmosphere appears mostly to be under the influence of natural sources (such as mineral dust and marine sources), while the contribution from anthropogenic sources are considerably smaller than those reported for big settlements around the world.

Table 7 Comparison of the VWM concentrations (μM) of some major ions in Mersin precipitation with previous data obtained from big settlements in Turkey and around the world

Location	pH	SO_4^{2-}	NO_3^-	Ca^{2+}	NH_4^+	Reference
Mersin	6.2	37.9	28.5	96.4	53.6	This study
İskenderun	7.1	353.0	40.3	250.0	-	Örnektekin and Çakmaklı 2003
Ankara	6.1	75.0	61.0	105.0	19.0	Tuncel and Ungör 1996
Ankara	4.2	26.6	35.5	57.4	66.7	Kaya and Tuncel 1997
Menemen, İzmir	5.6	33.0	23.0	40.5	43.0	Al Momani et al. 1995b
İstanbul	6.2	242.3	124.0	90.0	150.0	Gülsoy et al. 1999
Gebze	6.3	130.1	42.9	115.5	39.4	Akkoyunlu et al. 2001
Athens	5.4	50.0	23.6	68.5	21.9	Dikaiakos et al. 1990
Thessaloniki	5.9	80.0	27.0	128.5	58.0	Samara and Tsitouridou 2000
Bordeaux, France	5.2	44.8	62.9	22.5	–	Beysens et al. 2006
Madrid	6.5	126.0	45.0	195.0	44.0	Hontoria et al. 2003
Irbid, Jordan	6.0	50.1	25.9	65.7	36.9	Al Momani et al. 2000
Amman, Jordan	6.2	124.4	46.9	147.0	48.6	Jaradat et al. 1999
Eshidiya, Jordan	6.6	121.5	63.7	192.1	43.0	Al-Khashman 2005
Singapore	4.2	41.7	22.3	8.0	19.1	Hu et al. 2003
Mexico City	4.6	65.5	41.5	35.3	93.5	Baez et al. 1997

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