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Acidic and alkaline precipitation in the Cilician Basin, north-eastern Mediterranean Sea

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Abstract

Samples from precipitation events collected at Erdemli during February 1996–June 1997 were analyzed to determine their particulate aluminium content, in addition to pH and conductivity measurements. Backward air mass trajectories corresponding to the rainy days were analyzed to determine potential source regions of acidic and alkaline constituents transported to the Cilician Basin. Approximately 28% of the rain samples were found to be acidic and the trajectories associated with half of the acid precipitation events were from the Mediterranean Basin and the Balkan Peninsula, while the other half were from the Anatolian mainland and local sources. Rain samples were found to be alkaline (58%), with their trajectories originating from North Africa and the Middle East. As a result of its $CaCO_3$ content, mineral dust from these arid regions significantly increased the pH of rainwater.

Keywords: Acid rain; Cilician Basin; Eastern Mediterranean; Mineral dust; Back trajectory

1. Introduction

Acid–base reactions taking place in the atmosphere between acidic and alkaline constituents and atmospheric water determine the final pH of rainwater. When gaseous acid precursors (NO_x and SO_x) or their oxidation products of HNO_3 and H_2SO_4 dissolve in atmospheric water, they supply H^+ ions to the medium (Likens et al., 1979), consequently acidity increases and acid precursors turn into NO_3^- and SO_4^{2-} anions. In the absence of pollutants leading to acid rain, precipitation of the clean atmosphere is slightly acidic (pH 5.6) resulting from equilibrium reactions between atmospheric CO_2 and rainwater (Charlson and Rodhe, 1982; Galloway et al., 1982; Pszenny et al., 1982). Organic acids can also con-

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tribute to the acidity of rainwater but this type of contribution was found to be insignificant in the western Mediterranean (Losno et al., 1991).

Temporal and spatial variation is high for atmospheric concentrations of acidic and alkaline constituents and consequently in the pH of rainwater. The highly variable character of pH has been identified in numerous studies, including sequential sampling of specific full rain events (Tuncel and Ungör, 1996; Chester et al., 1997). Scavenging processes of various constituents from the atmosphere and solubilization rate of ions in precipitation can control these variations. For example, it was demonstrated that the pH of the precipitation is strongly affected by the type of material scavenged from the atmosphere, e.g. Loye-Pilot et al. (1986) in the western Mediterranean, and Al-momani (1995) in the eastern Mediterranean. Precipitation samples from air masses scavenging 'urban dominated' black material from the atmosphere while sweeping through Western Europe had values in the range of 4.1–5.6, whereas the precipitation samples arriving with air masses sweeping over North Africa with high loads of red Saharan dust, had pH values as high as 6–7 as a result of calcite ($CaCO_3$) dissolution (Loye-Pilot et al., 1986; Loye-Pilot and Morelli, 1988; Avila et al., 1998).

In addition to aerosol calcite, gaseous ammonia (NH_3) is another important alkaline constituent present in the atmosphere which neutralizes the acidity of rainwater. Results of a study conducted near an industrial area of the western Anatolian region, Turkey, demonstrated that the main alkaline material responsible for the neutralization of the acidity was NH_3 from fertilizer used in the region (Al-momani et al., 1995b). On the other hand, several studies conducted in the Mediterranean (e.g. Mamane et al., 1987; Al-momani, 1995a in the eastern basin and Avila and Roda, 1991; Avila, 1996 in the western basin) revealed that the neutralization of the rainwater acidity is mainly due to $CaCO_3$ which originate either from airborne local soil or mineral dust transported from North African sources.

This paper focuses on the first long-term wet deposition monitoring programme conducted in the Cilician Basin of the eastern Mediterranean. In addition to pH and conductivity, particulate aluminium concentrations, often used as an indicator of mineral dust load (Prospero and Nees 1987; Kubilay et al., 2000) either in aerosols or the particulate fraction of precipitation, have been measured. Calculated air mass back trajectories corresponding to the rainy days were evaluated in conjunction with particulate aluminium, pH and conductivity measurements, in order to identify potential source regions of acidic and alkaline species and transformations which determine the final pH of the precipitation samples.

2. Materials and methods

2.1. Sampling station

The sampling station is located at the Institute of Marine Sciences, METU (36°33′54″ N and 34°15′18″ E) on the south-eastern Mediterranean coast of Turkey adjacent to the Cilician Basin. The two nearest urban centers are Erdemli (a small town with a population of 35 000) and Mersin (a big and industrialized city with more than 1 000 000 inhabitants) located 7 and 45 km east of the sampling site, respectively. Agricultural and tourist activity can be found in the close vicinity, while limited industrial activity such as petroleum refinery and soda production, non-ferrous metal (chromium), thermal power and fertilizer plants, pulp and paper production occurs along the coast at distances of more than 50 km to the east and west of the sampling tower.

2.2. Sampling procedure

A total of 87 samples from precipitation events have been collected between 5 February 1996 and 13 June 1997 by a Wet/Dry Sampler Analyzer, Model ARS 1000, MTX Italy, S.p.A., installed on a tower at a height of 22 m above sea level, located on the harbor jetty of the Institute of Marine Sciences. The system is comprised of two HDPE (high density polyethylene) buckets with 30 cm diameter; one for dry and the other for wet

deposition samples. A rain sensor detects the first few rain drops and activates a motor, opening the lid of the wet sampler. Due to practical difficulties of access to the sampling tower; night samples have been collected with buckets of the same size deployed at the roof of the Institute and kept there for the duration of rain. Sampling buckets, bottles and all glassware used in the laboratory have been soaked in 1 M HCl washing solution for 48 h and rinsed with distilled, deionized water several times prior to usage. Precipitation samples collected on an event basis were brought to the laboratory immediately following cessation of the rain. After measuring the volume of the samples they 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 different purposes of analysis.

2.3. pH and conductivity measurements

The pH was measured by a Microprocessor pH-meter (WTW-Model pH537, accuracy of 0.01 pH unit) which was calibrated by pH 6.94 and pH 3.97 standard buffer solutions before every measurement. The glass electrode was soaked in the sample container, while gently shaken, and the pH value was recorded only after the electrode became stable. The accuracy of the pH measurements has been tested by analyzing simulated acid rain samples prepared by the World Meteorological Organization (WMO) Precipitation Reference Laboratory (PRL) for inter-comparison. The analytical precision of pH measurements was found to be better than 5%.

Conductivity measurements have been performed with a Model 4070 Conductivity-Meter (Cole Palmer) which has a temperature range of −30 to +150°C and a conductivity range of 0–20 mS cm^{-1}. Precipitation was recorded at a sampling rate of 0.5 h by an Anderrea Meteorological Station installed at the roof of the Institute. Due to technical problems, conductivity measurements could be performed only in 41 of the precipitation samples. The pH and conductivity have been measured immediately after filtration. Further laboratory pH measurements indicated that these parameters were stable over several days.

2.4. Particulate aluminium measurements

Before the preparation of samples for particulate aluminium analysis, the color of the insoluble fraction of precipitation samples collected on 0.45-μm pore size membrane filters was identified

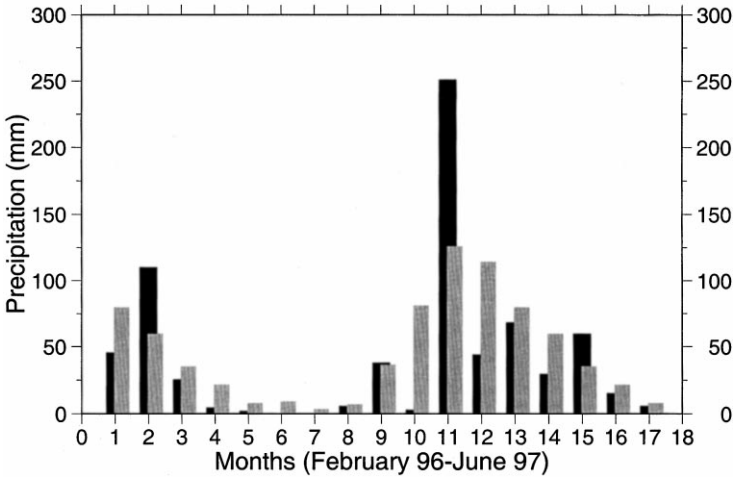

Fig. 1. Precipitation data for the sampling period of February 1996–June 1997 (dark columns) at Erdemli and the climatological mean precipitation of 30 years (1963–1994) for Mersin, obtained from the Turkish Meteorological Service (light columns).

and classified according to the standard soil color chart, based on the Munsell System.

Membrane filter samples have been digested according to the procedure given in UNEP (1995), using a microwave digestion oven (Questron Corporation, Q45 EnviroPrep Model) for particulate aluminium analysis. Digested samples were diluted to 50 ml volume by double distilled deionized water and then transferred into polyethylene bottles in order to preserve them at +4°C until analysis time. Particulate aluminium concentrations were determined directly with an atomic absorption spectrophotometer equipped with a deuterium (D2) lamp for background correction (GBC model 906 unit with a FS3000 flame attachment) by using an N_2O/acetylene flame. KNO_3 solution at a final concentration of 2000 mg l^{-1} K^+ was added to samples and standards to suppress ionization. Monthly field blanks were prepared by pouring 200 ml of double distilled-de-ionized water into the sampling bucket. The mean aluminium concentration of 14 field blanks submitted to the same treatment as the precipitation samples was found to be within the detection limit (defined as twice the standard deviation of the blank value). No detectable contamination was found in either the field or laboratory blanks. Since the concentration of the dissolved aluminium in rainwater samples were below the detection limit of the method (0.2 ppm), only particulate aluminium concentrations have been measured as an indicator of dust in the particulate fraction of the precipitation samples. The accuracy of the analytical procedure was tested by analyzing standard reference material light sandy soil (CRM 112) of Community Bureau of Reference Brussels (BCR). The overall analytical precision of the aluminium analysis was found to be 6%.

2.5. Air mass back trajectories

Three-dimensional, 3-day backward trajectories of air masses subjected to the scavenging by precipitation and arriving at the sampling point on 12:00 UT of the sampling day at levels of 900 and 850 hPa within the boundary layer and 700 and 500 hPa within the free troposphere were calculated for each rainy day. The trajectory model of the European Center for Medium-Range Weather Forecasts (ECMWF) in Reading, England was applied to three-dimensional analyzed wind fields available from the MARS archive of ECMWF. This model is similar to the method developed by Martin et al. (1987) and does not give any information about precipitation events during the travel of air masses.

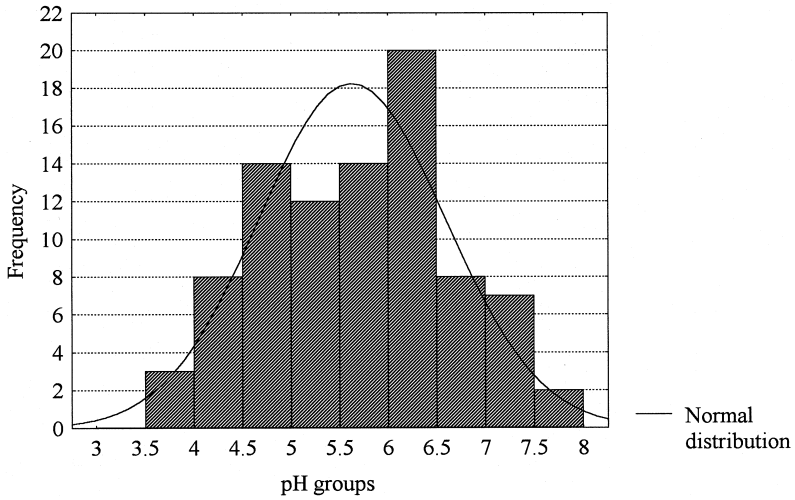

Fig. 2. Frequency distribution of measured pH values at Erdemli.

3. Results and discussion

3.1. Precipitation data

Precipitation data belonging to the sampling period of approximately 17 months (from 5 February 1996 to 13 June 1997) were compared with the mean precipitation of 30 years (1963–1994) obtained from the Turkish Meteorological Service, Mersin station, located 45 km east of the sampling station. Fig. 1 shows that wet deposition (dark columns) in Erdemli mainly occurred in the October–April period. Precipitation recorded at the Institute's meteorological station is in good agreement with the 30 years mean climatological rainfall in Mersin. Cumulative precipitation for the sampling period was 710 mm. Minimum and maximum event-based rainfall values were 0.2 and 87.6 mm, respectively.

3.2. Acidity and conductivity

The acidity in the precipitation samples was found to be highly variable. The minimum and maximum pH values were 3.5 and 7.6, respectively. For the entire sampling period, the mean pH of the precipitation, calculated from the volume weighted H^+ concentration, was found to be 4.95 while the arithmetic mean value and the standard deviation were 5.6 ± 0.9. This value is very close to the mean pH value reported for Antalya (5.17) (Al-momani et al., 1995a) approximately 500 km west of Erdemli. According to the frequency distribution of measured pH values presented in Fig. 2, approximately 28% of the samples had a pH of less than 5.0 and 3% of the samples had $pH < 4.0$, identified as highly acidic precipitation. Fifty-eight percent of the rain samples found to be alkaline, $pH > 5.5$ and 20% of the samples had $pH > 6.5$, identified as highly alkaline. Air mass back trajectories associated with the precipitation samples having high pH (alkaline) and low pH (acidic) values, classified according to their geographical source regions, are discussed in Sections 3.3 and 3.4, respectively.

A positive correlation was found between pH and the particulate aluminium fractions ($r = 0.42$). The coincidence of high particulate aluminium concentrations, representing increased atmospheric dust load, with high pH values of precipitation is attributed to the high calcite content of Saharan originated mineral dust. Independent mineralogical analyses of aeolian dust confirms the calcite content, e.g. in Corsica, western Mediterranean, the transported Saharan dust was found to contain 5–30% of calcite and some gypsum (Loye-Pilot et al., 1986). In the Cilician Basin, eastern Mediterranean, the calcite content

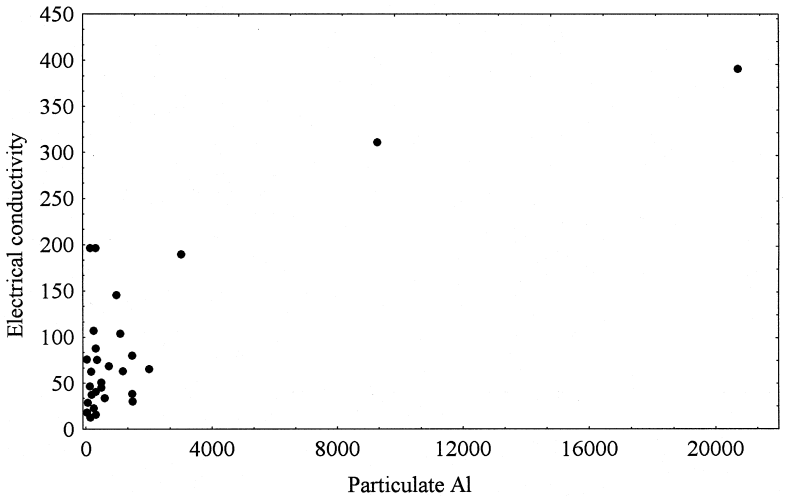

Fig. 3. The relation between the electrical conductivity ($\mu S\ cm^{-1}$) and particulate aluminium concentrations ($\mu g\ l^{-1}$) in Erdemli precipitation samples.

of aerosols was found to be 8–31% (Kubilay et al., 1997). The elevated pH in precipitation samples during the presence of high atmospheric dust loads is therefore attributed to wet scavenging of calcite from mineral dust.

Electrical conductivity of the precipitation samples was found to be highly variable, within a range of 12.9–391.0 $\mu S\ cm^{-1}$. The geometric mean conductivity of the 41 precipitation samples was 51.4 $\mu S\ cm^{-1}$. The volume weighted mean particulate aluminium concentration of 84 precipitation samples was 1519 $\mu g\ l^{-1}$ (range: BDL–49 725 $\mu g\ l^{-1}$, G.M.: 412 $\mu g\ l^{-1}$). Precipitation samples with relatively high concentrations of particulate aluminium, hence mineral dust, had very high conductivity, most probably due to the high content of soluble solids, high ion adsorption capacity of mineral dust surfaces and adsorption–desorption processes taking place between the solid and liquid phases. The relationship between electrical conductivity and particulate aluminium concentration is presented in Fig. 3, representing a high positive correlation ($r = 0.81$) between the two parameters.

3.3. Mineral dust carrying air masses

Atmospheric dust in the eastern Mediterranean is highly variable in space and time (Ganor, 1994; Kubilay, 1996). The Cilician Basin, with a mean dust loading of $15.5 \pm 25\ \mu g\ m^{-3}$ (Kubilay et al., 2000), is a region where sporadic incursions of mineral dust from arid regions takes place. Often the dust transport is associated with a cyclone in North Africa during the spring (March–May) (Alpert et al., 1990). Dust storms, associated with cyclonic disturbances usually accompany outbreaks of rain near fronts as a result of which an abrupt decrease in the atmospheric dust load occurs after washout by rain (Kubilay et al., 1994).

Atmospheric aerosol samples collected either by meshes or by Hi-vol samplers during dust storms display a characteristic color of yellowish brown (10 YR 4/3) (Kubilay et al., 1997). Similar but somewhat lighter colors, light yellow–orange (10 YR 8/4) or dull yellow–orange (10 YR 7/4) have also been identified for the particulate fraction of the precipitation samples collected during

Table 1
Comparison of annual wet (particulate + dissolved) and annual total (wet + dry) deposition flux of aluminium (mg $m^{-2}\ year^{-1}$) with the data reported from various locations around the world

Location	Wet flux (part. + dissolved)	Total flux (wet + dry)
Maryland[a]	17.6[i]	–
North Sea[b]	61[i]	133
Miami, Florida[c]	101	–
Tour du Valat-NW Med.[d]	294[j]	918
Cap Ferrat-NW Med.[e]	94[k]	144
Cap Cavallo, NW Med.[f]	–	970
Antalya, E Mediterranean[g]	92	–
Erdemli, E Mediterranean[h]	870[l]	1382[m]

[a] Scudlark et al. (1994).
[b] Baeyens et al. (1990).
[c] Prospero and Nees (1987).
[d] Guieu et al. (1997)
[e] Migon (1988) (after Guieu et al., 1997).
[f] Bergametti (1987) (after Guieu et al., 1997).
[g] Al-momani (1995).
[h] Present work.
[i] Only the dissolved phase.
[j] Calculated from total deposition flux of Al, accepting percentage of dry deposition is 68%.
[k] Calculated from total deposition flux of Al, accepting percentage of dry deposition is 65%.
[l] Calculated from wet deposition flux of particulate Al, accepting the solubility of aluminium is 5%.
[m] Dry deposition flux accepted to be 36% of the total (wet + dry) deposition flux (Kubilay, 1996).

episodic dust events in the present study. Color identification along with particulate aluminium measurements of filter samples and air mass back trajectory analysis of the corresponding rainy days have revealed 12 such events, followed by rainfall during the entire sampling period and 18 precipitation samples have been collected during these outstanding events. Five of these transport events on 8–9 February 1996, 11 April 1996, 17 April 1996, 21 March 1997, and 13 April 1997 were remarkably intensive, subsequently collected precipitation samples with very high particulate aluminium concentrations of 49 725, 20 209, 14 185, 9271, 20 690 $\mu g\ l^{-1}$ and high pH values of 7.6, 6.7, 6.0, 7.6 and 7.2, respectively. Electrical conductivity of the precipitation samples collected on the last two dates had the highest values of 311.0 and 391.0 $\mu S\ cm^{-1}$, respectively. Unusually high electrical conductivity measured in precipitation samples during dust transport events with high ionic concentrations, suggests that the elevated pH values results from neutralization of their acidity, rather than the absence of acidic constituents in precipitation.

Wet deposition flux of the particulate aluminium (F_w, $mg\ m^{-2}$) was calculated using the relationship $F_w = C_w\ P$, where C_w is the particulate aluminium concentration in precipitation and,

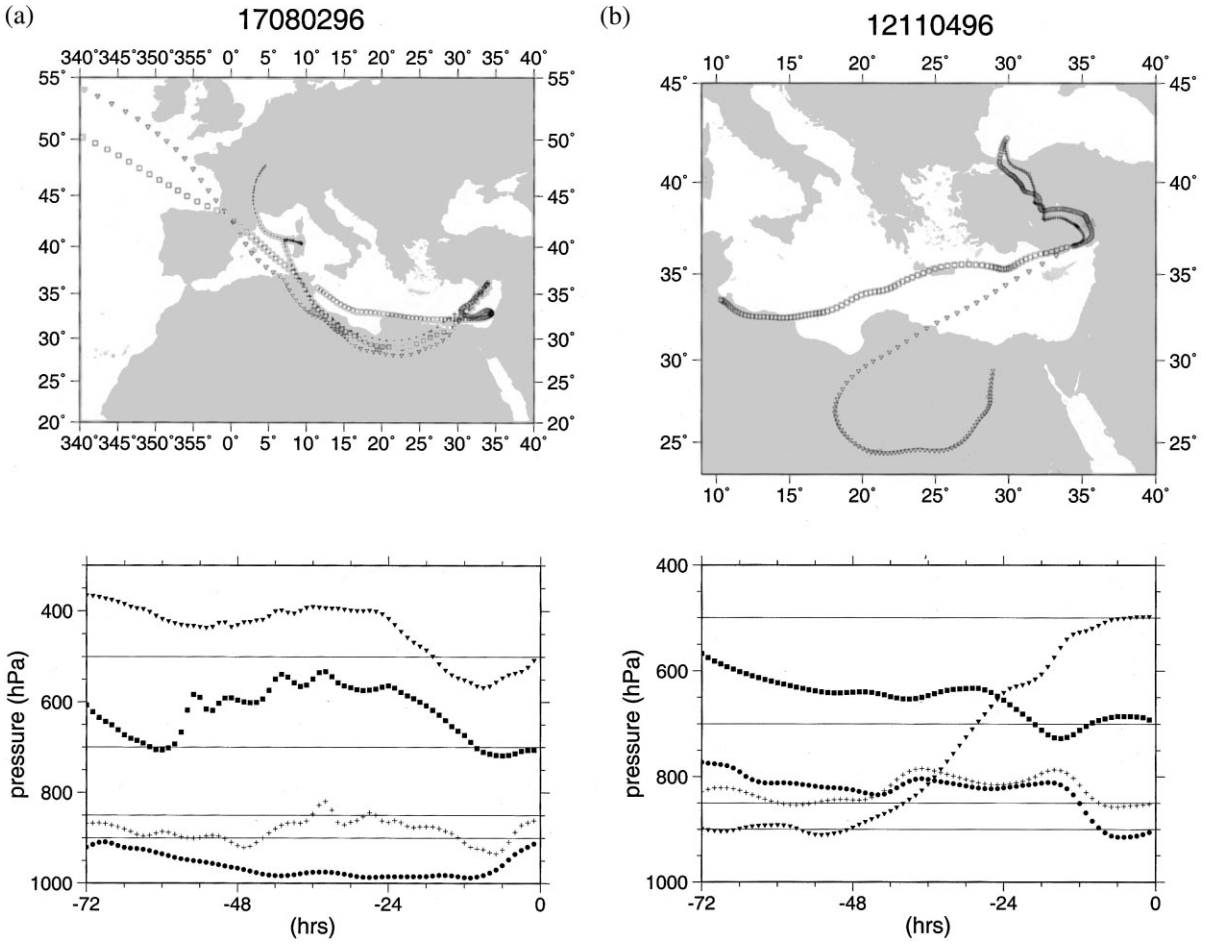

Fig. 4. Air mass back trajectories arriving to the sampling station at four different barometric pressures for the most outstanding cases of mineral dust transportation: (a) 8–9 February 1996; (b) 11 April 1996; (c) 17 April 1996; (d) 21 March 1997; and (e) 13 April 1997.

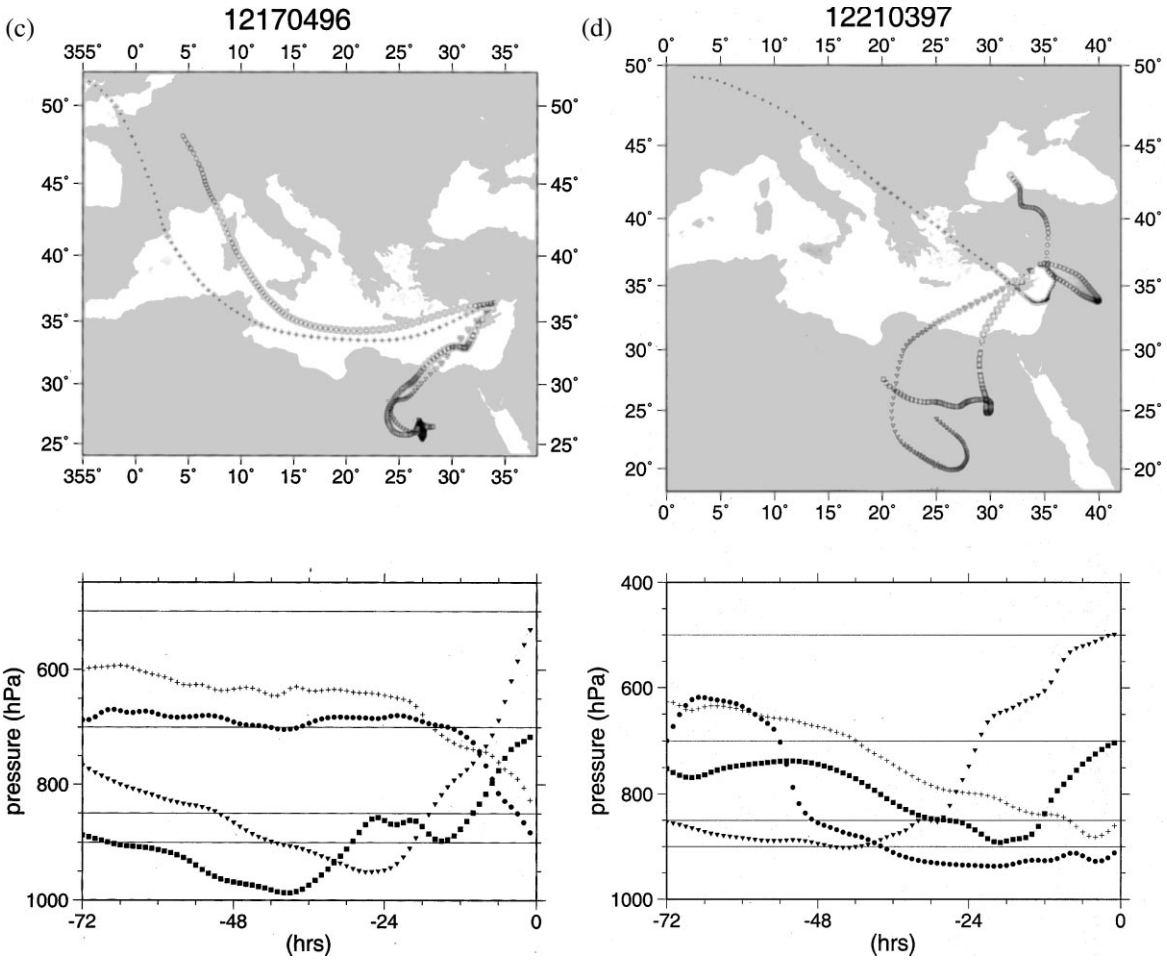

Fig. 4. (*Continued*)

P is the rainfall. The total wet deposition flux of particulate aluminium was found to be 1118 mg m^{-2} during the sampling period. This value corresponds to an annual flux of 829 mg m^{-2} (942 mg m^{-2} real flux for the February 1996–1997 period). On average, the solubility of aluminium is reported to be $< 20\%$ in the Mediterranean region (Guieu et al., 1997). The calculated total (particulate + dissolved) wet deposition flux for Erdemli was based on an assumption of 5% solubility. Even though this solubility ratio is the lowest recorded mean value for aluminium solubility in rainwater (Prospero and Nees, 1987), the annual total wet deposition flux of aluminium obtained at Erdemli is far greater than the values reported from stations around the world (Table 1).

Approximately 90% of the transport events occur between March and October, with the most intense cases taking place between March and May (Kubilay et al., 2000). Pressure vs. time plots in the lower panels of Fig. 4a–e for each back trajectory display vertical motions which can be used to characterize the prevailing meteorological conditions during the dust transport events (Martin et al., 1987). Trajectories in Fig. 4a–e confirm that the air masses arriving at the upper barometric levels (500 or 700 hPa) had originated from the Sahara, and exhibited ascending motion, while the trajectories arriving at the lower baro-

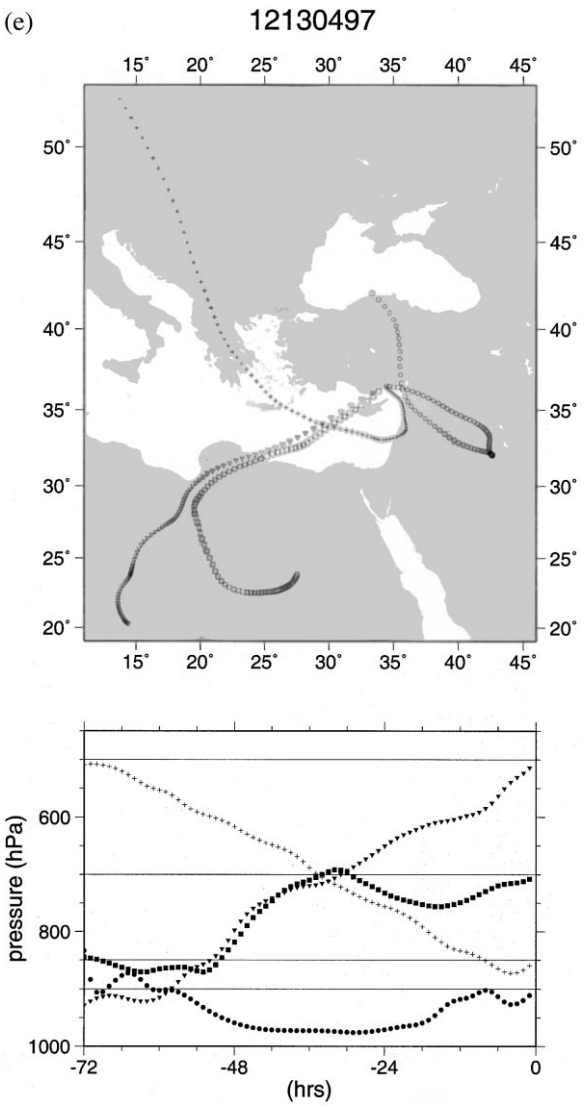

Fig. 4. (*Continued*)

metric levels (850 or 900 hPa) displayed descending motion. This type of airflow pattern is typical of frontal systems associated with the unsettled weather (Reiff et al., 1986; Martin et al., 1990), which reinforces dust transport (Kubilay, 1999). The air mass back trajectory on 8 February 1996 was computed for 17:00 UT, since storm conditions developed at that time near the sampling station, and the sample was taken about the same time.

Classifying the back trajectories according to geographical sources for the 18 precipitation samples corresponding to 12 dust transport events, has shown that all of the air masses moving within the free troposphere (500 and 700 hPa) had originated from North Africa without exception. Approximately half of the trajectories moving within the boundary layer partly swept over the Middle East (Arabian Peninsula and Syria) sources of mineral dust, while the other half have moved over various (non-desert) regions making it difficult to identify sources when they were trapped within the planetary boundary layer. The air masses having mineral dust carrying capacity from both North Africa (at 500 hPa) and from the Middle East (Arabian Peninsula and Syria) (at 900 hPa) are displayed in Fig. 5a,b, respectively. The 18 precipitation samples which had either light or dull yellow–orange color on membrane filters, had volume weighted mean pH and particulate aluminium concentration of 6.56 (range: 6.0–7.6) and 11 705 $\mu g\ l^{-1}$ (range: 1463–49 725 $\mu g\ l^{-1}$), respectively. These values are considerably higher than the volume weighted mean pH (4.95) and particulate aluminium concentration (1519 $\mu g\ l^{-1}$) values for the entire set of samples. The geometric mean conductivity of the same samples was 133.4 $\mu S\ cm^{-1}$, which is approximately 2.5 times higher than the overall geometric mean (51.4 $\mu S\ cm^{-1}$).

3.4. Acid rain carrying air masses

Within the collection of 87 precipitation samples, 25 had pH < 5.0 corresponding to acid rain conditions. The air mass back trajectories arriving at 850 and 900 hPa levels for these 25 events have been classified geographically to identify potential source regions. Three major sources can be identified:

- South-eastern Europe and the Mediterranean Basin (9 samples, Fig. 6a);
- Balkan Peninsula (4 samples, Fig. 6b); and the
- Anatolian mainland, local sources (11 samples, Fig. 6c)

All of the air masses arriving at the pressure level of 900 hPa (Fig. 6a), follow long routes

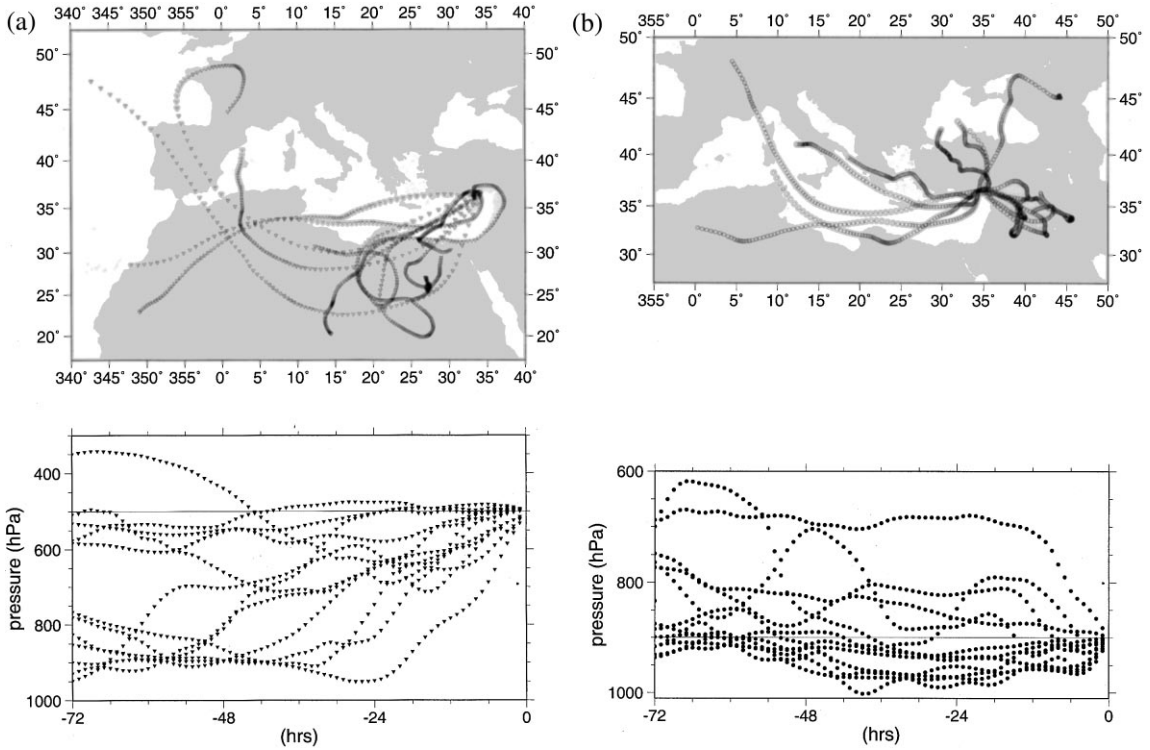

Fig. 5. The air masses arriving at Erdemli, having mineral dust carrying capacity from North Africa at 500 hPa (a) and from the Middle East (Arabian Peninsula and Syria) at 900 hPa (b).

which pass over southern Europe, including industrialized countries such as Italy. In addition to possible industrial sources, volcanoes in the Mediterranean Basin, particularly near Italy, are known to be the most important natural sources of atmospheric sulfuric acidity (Jaeschke et al., 1982). Air masses passing over the coastal areas of the Mediterranean Basin, along the South European or North African coasts have a possibility of transporting natural or anthropogenic acidic constituents to the Cilician Basin. Only four samples of acidic precipitation correspond to 900 hPa trajectories originating from the Balkan Peninsula, whereas only approximately half of them display descending motion (Fig. 6b). Stagnant conditions appear to be responsible for the accumulation of acidic constituents emitted from local sources. Approximately 10 samples of precipitation were associated with trajectories at 900 hPa crossing over the Anatolian mainland and identifying local sources (Fig. 6c). Most of these trajectories exhibit isobaric motion following relatively shorter routes than the trajectories originated from the two former potential source regions.

A review of the potential source regions for pollutants resulting in acid rain in the Cilician Basin reveals that the long range transport from the Balkan Peninsula or Central Europe has a minor effect compared to the other remote (South-eastern Europe and the Mediterranean Basin) and local (Anatolian mainland) sources.

Gray (10 Y 6/1; 10 Y 5/1), grayish white (N 7/0) or light gray (5 Y 7/1) colors have been detected in the particulate fractions of the acidic precipitation, depending on the volume of the collected samples. The volume weighted mean particulate aluminium concentration of 25 acidic precipitation samples was 301 $\mu g\ l^{-1}$ (range: BDL–3021 $\mu g\ l^{-1}$). This value is considerably lower than the overall volume weighted mean particulate aluminium concentration (1519 $\mu g\ l^{-1}$). Even though trace metal solubility is ex-

pected to be a function of pH (Losno et al., 1988; Chester et al., 1997), this low concentration of particulate aluminium in acidic precipitation samples cannot be attributed to low pH. Aluminium is poorly soluble in rainwater although its solubility depends on the type of aerosol scavenged from the air. On average, 5% solubility of aluminium was found in precipitation samples containing mineral dust in Florida (Prospero and Nees, 1987) and 17% solubility was found in precipitation samples containing urban-rich aerosols at Cap Ferrat in the western Mediterranean (Chester et al., 1997). Additionally, the effect of pH on the aluminium solubility was found to be negligible due to its occurrence in alumino-silicate mineralogical structure (Kaya and Tuncel, 1997). Therefore, we can safely conclude that the acidity of the precipitation samples combined with low aluminium concentrations has to do with the source regions of the air masses with the trajectories crossing over non-desert areas, resulting in limited dust carrying, hence acid neutralizing capacity. The geometric mean of the conductivity of the same samples was found to be 43.1 $\mu S\ cm^{-1}$, which is not much different from the overall geometric mean of electrical conductivity (51.4 $\mu S\ cm^{-1}$), probably indicating the existence of acid forming ions in the precipitation.

The lowest pH values of 3.6, 3.5 and 3.9 were measured in the precipitation samples, collected

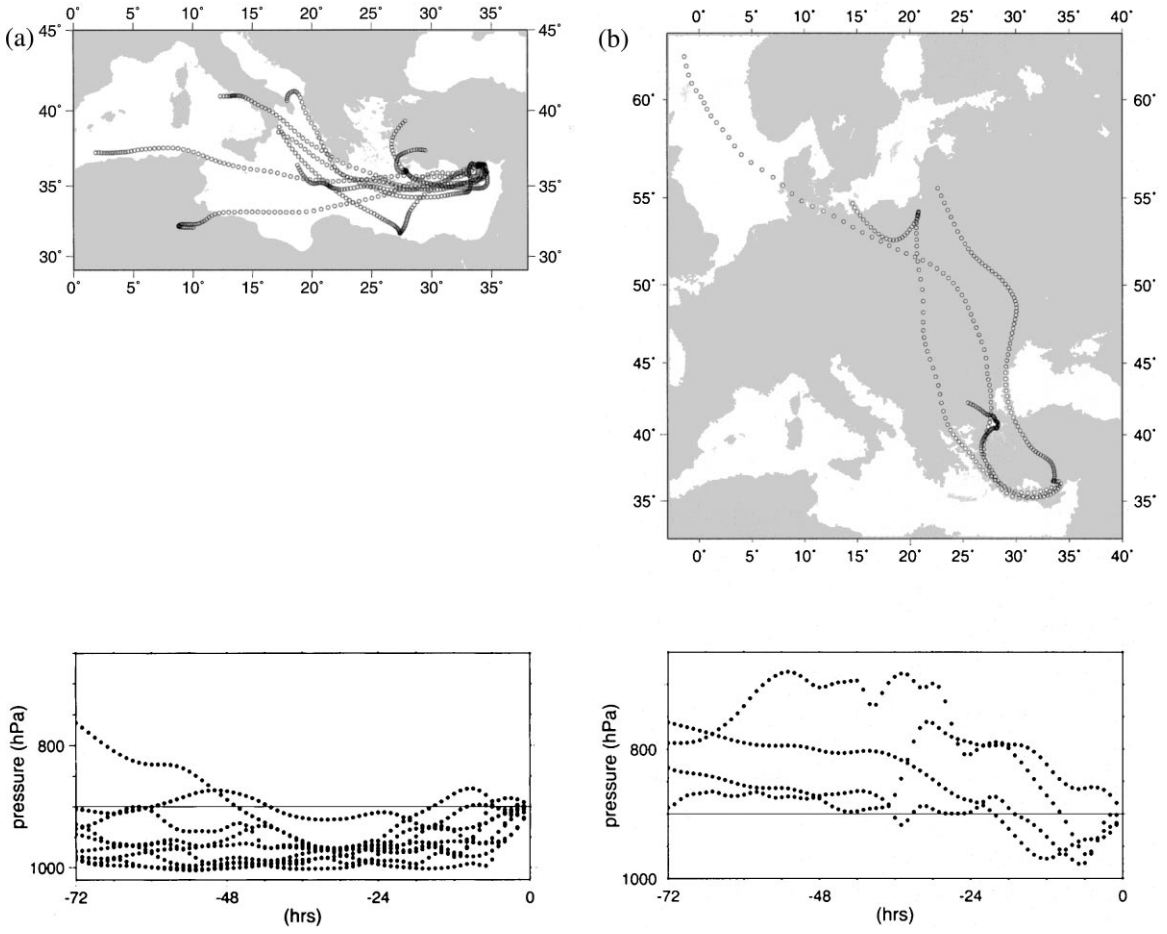

Fig. 6. Potential geographic source regions of air masses arriving at Erdemli and carrying acid precipitation from: (a) South-eastern Europe and the Mediterranean Basin; (b) Balkan Peninsula; and (c) Anatolian mainland and local sources.

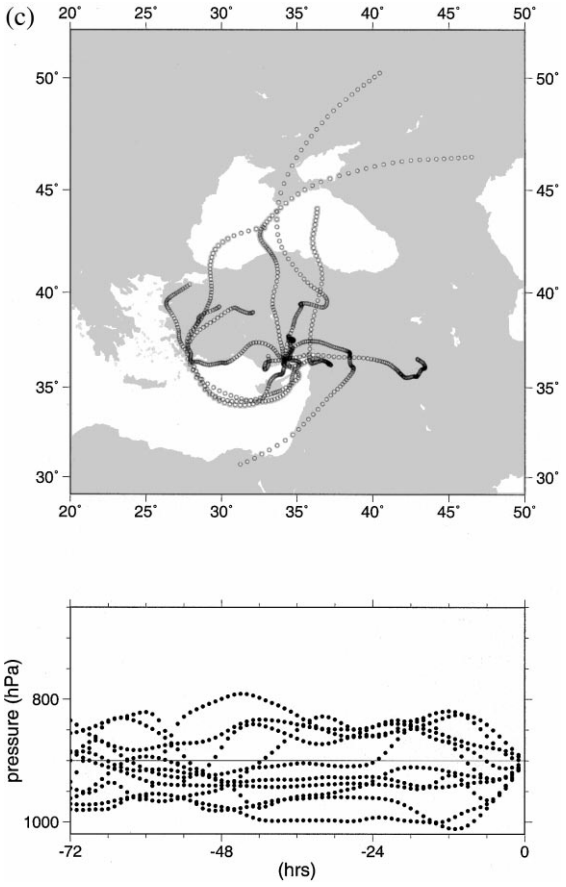

Fig. 6. (*Continued*)

on 5 March 1996, 26 March 1996 and 25 May 1997, following the air mass back trajectories presented in Fig. 7a–c, respectively. The lower panel in Fig. 7a shows that the lower air masses (850, 900 hPa) followed almost isobaric motion, so that they could be expected to have a high pollutant carrying capacity, possibly being trapped within the boundary layer. On 25 May 1997, the air mass trajectories arriving at the higher pressure levels of 500 and 700 hPa originated from the mid-Atlantic and Central European regions, respectively. These trajectories were not included in Fig. 7c because they indicated descending motion, and therefore, would have small pollutant carrying capacity. Again the air masses arriving at the lower pressure level of 850 and 900 hPa swept over the local region, isobarically. The slow motion, indicated by short trajectories, could have favoured the accumulation of pollutants emitted to the local atmosphere, resulting in a very low value of pH (3.9) in the subsequent precipitation. The high conductivity (104.3 μS cm^{-1}) measured in this particular sample is also consistent with its low pH.

3.5. A case study verifying the instant effect of a directional change of transport on the acidity of the precipitation

Considerably different values have been measured in two subsequently collected precipitation samples on 21 and 22 March 1997. On 21 March 1997, unsettled weather conditions have prevailed over the sampling region and rain started at approximately 21:00 h and continued until 07:00 h the next morning, 22 March 1997. The analysis of this sample (A) was performed as soon as the rain ceased. After a short break the rain started again and this time it lasted intermittently the whole day with variable wet deposition rates. The second sample (B) has been collected between 09:00 h and 22:00 h on 22 March 1997 and analyzed at night, following the final cessation of the rain. The results obtained from the analyses of precipitation samples of A and B are presented in Table 2. In order to explain significantly different values observed in subsequently collected precipitation samples, air mass trajectories have been calculated according to arrival times of 12210397, 21210397, 09220397 and 12220397 (the numbers represent UT time, day, month and year in order) concurrent with the sampling of precipitation, respectively presented in Fig. 8a–d. The computed air mass trajectories arriving at Erdemli on 21 March at 12:00 UT (Fig. 8a) suggest very different origins of the air masses according to the final barometric levels. The lower level air masses have moved over the Anatolian mainland (900 hPa) and European countries (850 hPa) while the upper (700 and 500 hPa) levels have Northeast African origin. The vertical components of the upper level trajectories reveal a notable upward motion, showing the transport of mineral dust by a cyclonic system. Unsettled weather conditions accompanying this cyclonic system re-

sulted in rain commencing at 21:00 UT on the night of 21 March and resulted in a washout of dust from the local atmosphere. The computed air mass trajectories arriving at Erdemli on 21 March at 21:00 UT (Fig. 8b), at the time of commencement of the first rain (sample A) shows that the air masses at four different pressure levels had already changed their directions, becoming mainly of European origin. The vertical components of the air mass trajectories all reveal descending motion corresponding to anticyclonic motion likely to create stagnant conditions and most probably to allow accumulation of mineral dust in the local atmosphere. As a result, the collected rainwater (sample A) exhibited typical characteristics of Saharan dust with abnormal pH (7.6), very high particulate aluminium concentration (9278 $\mu g\, l^{-1}$) and electrical conductivity (311 $\mu S\ cm^{-1}$) (Table 2). The appearance of the particulate matter collected on a 0.45-μm diameter membrane filter was also unusual with its distinctly yellowish red color. In contrast to this observation, the air masses washed out to yield the subsequent precipitation sample (Sample B) have moved almost isobarically over the potential source regions of acid precipitation (Fig. 8c,d), consequently having a low pH (4.5) and very low particulate aluminium concentration (48 $\mu g\, l^{-1}$), representing more than two orders of magnitude decrease in particulate aluminium compared to the previous sample (Table 2). This case study showing distinct characteristics for two subsequent precipitation events demonstrates the effects of synoptic meteorology, leading to rapid

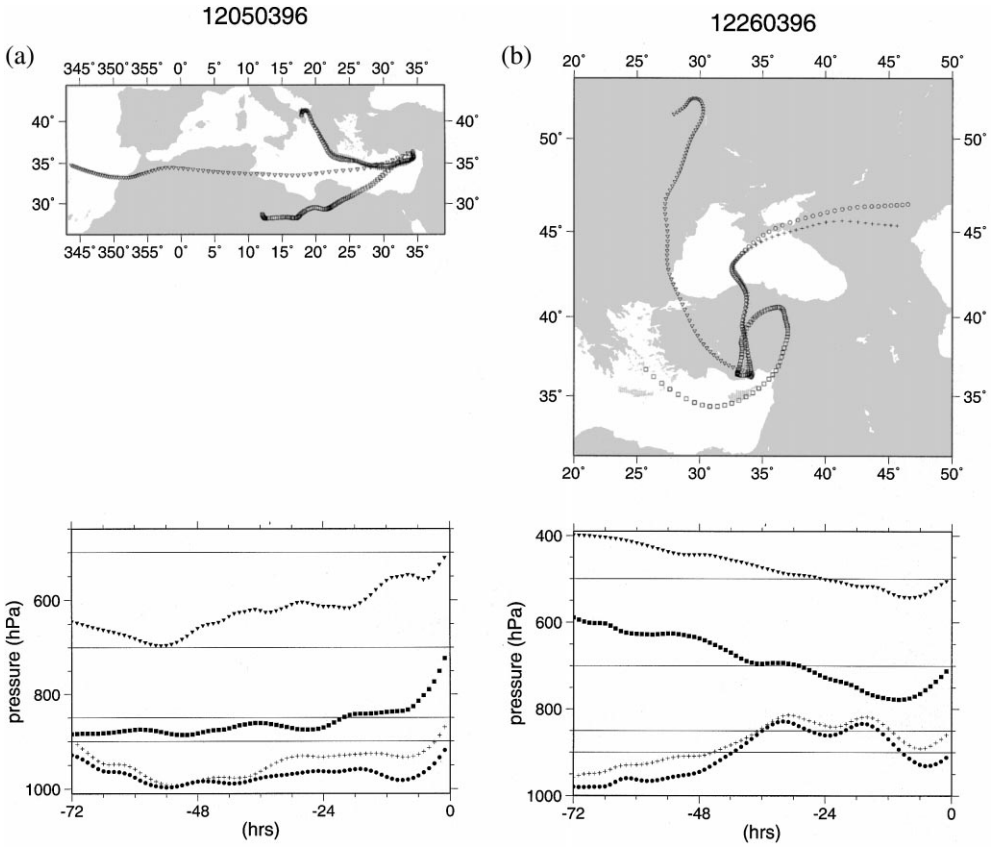

Fig. 7. The air mass back trajectories arriving at Erdemli carrying precipitation with the lowest pH values (a) 5 March 1996; (b) 26 March 1996; (c) 25 May 1997.

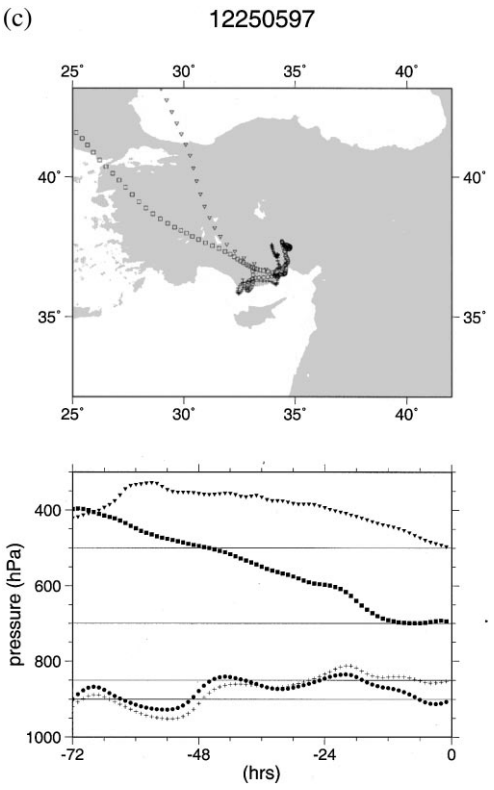

Fig. 7. (*Continued*)

changes in transport direction and associated changes in the geographic origin of air masses, resulting in widely different properties of precipitated water. This experience implies that collection of samples should be guided by dynamical considerations as well as general ones. In any of the research programmes conducted on precipitation events, the collection of samples has to be performed on an event basis rather than on a daily basis.

4. Conclusions

The results obtained from this study suggest that the pH of the precipitation samples, particularly collected from the Cilician Basin, could be explained essentially by taking into consideration the analyses of air mass back trajectories and the local emissions are significantly effective on the composition of precipitation. Approximately 28% of the rain samples were found to be acidic and the trajectories associated with half of the acid precipitation events were from the Mediterranean Basin and Balkan Peninsula, while the other half were from the Anatolian mainland and the local sources. The most distinctive contribution to the rainwater composition from remote sources is the mineral dust, with its high capacity for neutralizing rainwater acidity, particularly observed in precipitation events associated with frontal passages. Rain samples were found to be alkaline (58%), with the trajectories from North Africa and the Middle East. Mineral dust from these arid regions with its high $CaCO_3$ content significantly increased the pH of rainwater. A singular case study has verified the instant effect of change in the direction of the air masses on the acidity of the precipitation in the subsequently collected samples. This unique event validated the importance of our sampling protocol which has been performed on an event basis. Calculated wet deposition flux of the particulate aluminium (mg m^{-2}) for Erdemli was found to be the highest value among reported values from various stations around the world. It has been confirmed that the eastern Mediterranean atmo-

Table 2
The distinction in the measured parameters in subsequently collected precipitation samples upon the instant change in the direction of the corresponding air masses

Sample	A	B
Precipitation (mm)	6.21	8.48
Color of filter	Dull yellow–orange (10 YR 7/4)	Gray (10 Y 5/1)
pH	7.6	4.5
Conductivity (μS cm^{-1})	311.0	66.3
Particulate Al (μg l^{-1})	9278	48.1

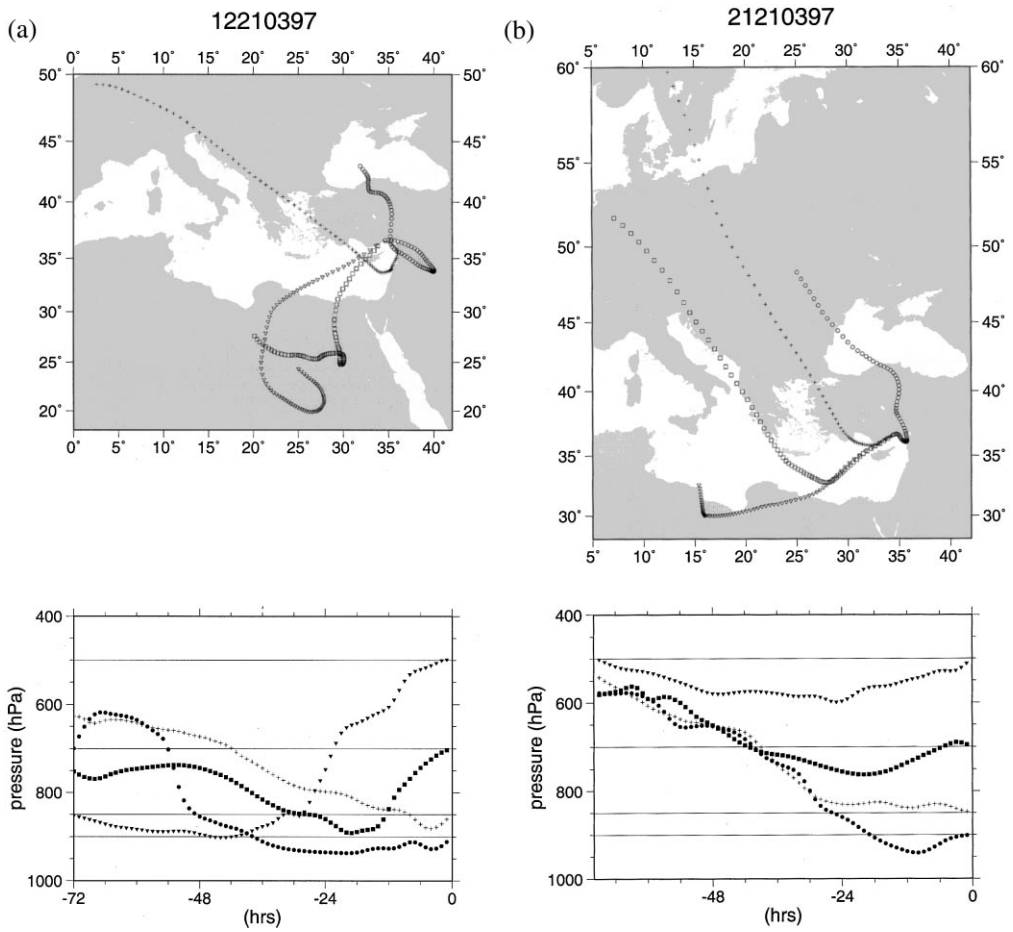

Fig. 8. Air mass back trajectories calculated according to different arriving times of (a) 12210397, (b) 21210397, (c) 09220397, (d) 12220397, concurrent to the sampling duration of the consecutively collected precipitation samples.

sphere is heavily loaded by mineral dust sporadically transported from arid regions. The region and particularly the Cilician Basin can be considered suitable locations to assess the potential impact of desert dust, especially in terms of trace element–biota interactions through biogeochemical processes ensuing deposition, expected to take place in the sea or land.

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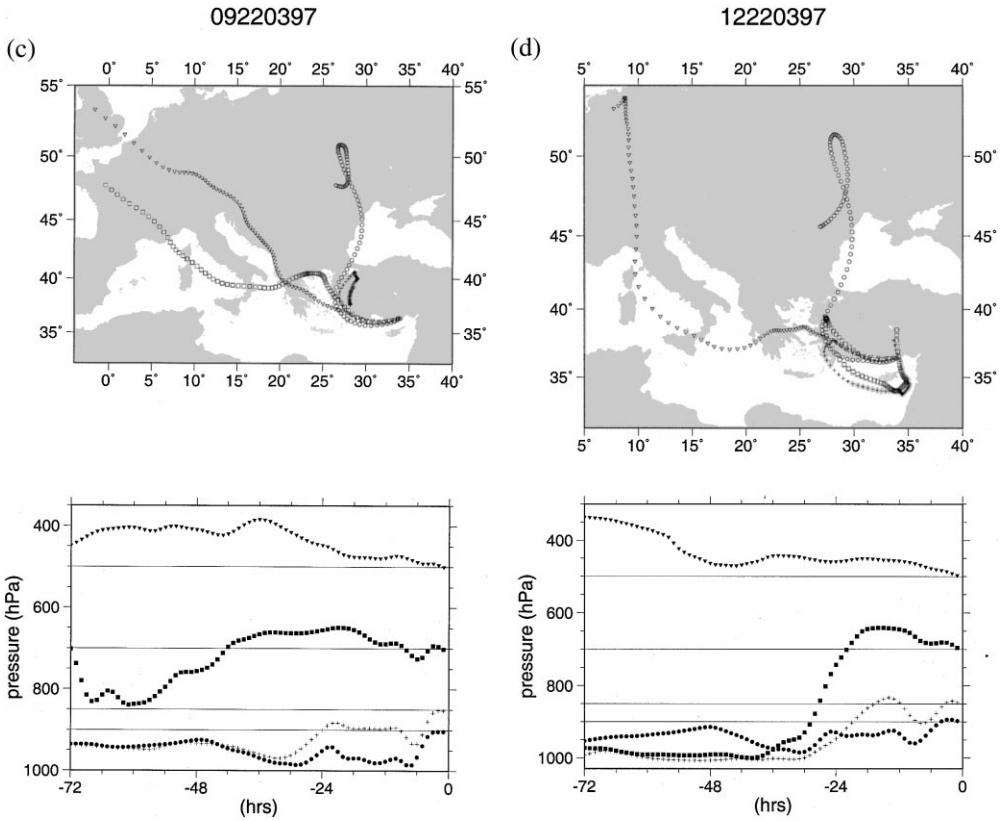

Fig. 8. (*Continued*)

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