CHEMICAL CHARACTERISTICS OF RAIN WATER AT AN URBAN SITE OF SOUTH WESTERN TURKEY

AHMET DEMIRAK*, AHMET BALCI, HAMDI KARAOĞLU and
BERRIN TOSMUR

Department of Chemistry, Faculty of Science and Arts, Mugla University, Mugla 48000, Turkey
(*author for correspondence, e-mail: ademirak@yahoo.com*)

Abstract. In this study, chemical composition of the rain water in Mugla was investigated from February to April 2002. Rain water samples were obtained from Mugla, a small city in south western Turkey. The Yatagan Power Plant is located 30 km northwest of Mugla city. The values of pH and the concentrations of major ions (Ca^{2+}, Na^+, K^+, SO_4^{2-}, NO_3^-, NH_4^+) in the rainwater samples were analyzed. The pH varied from 4.5 to 7.7 with an average of 6.9 which was in alkaline range considering 5.6 as the neutral pH of cloud water with atmospheric CO_2 equilibrium. In the total 30 rain events, only two events were observed in acidic range (<5.6) which occurred after continuous rains. The equivalent concentration of components followed the order: Ca^{2+} $>SO_4^{2-}$ $>NH_4^+>NO_3^->Na^+>K^+>H^+$. The volume-weighted mean (VWM) of the measured ionic sum is 371.62 μeq/l. The ratio of between sum cations and sum anions ($\sum$cations /$\sum$ anions) is 1.52 μeq/l. The alkaline components (Ca^{2+}, Na^+, K^+) contribute 52%, NH_4^+ 8%, whereas, the contribution from the acidic components is relatively small (40%). The low concentrations of H^+ found in rainwater samples from Mugla suggest that an important portion of H_2SO_4 and HNO_3 have been neutralized by alkaline particles in the atmosphere. The dust-rich local and surrounding limestone environment might have caused the high concentration of Ca^{2+} in Mugla area. The relatively high concentration of NH_4^+ observed at Mugla is suspected to be due to surrounding agricultural. The results obtained in this study are compared with those other studies conducted at various places in the world.

Keywords: acid rain, chemical composition, neutralization factor, air pollution, Turkey

1. Introduction

The issue of acid precipitation has received more and more attention in the international community for the last several decades because of its notable direct adverse effects on ecosystem and indirect effects on human health. It is primarily caused by a mixture of strong acids, H_2SO_4 and HNO_3, resulting from fossil fuel combustion so that it has been observed in many industrial regions, particularly in North America and Central Europe. The composition of wet deposition actually reflects the composition of the atmosphere through which it falls. Determination of composition of rain helps to evaluate the relative importance of the different sources for gases and particularly matter. Thus the research of chemistry composition of precipitation has been a primary focus of the field of acid deposition (Galloway *et al.*, 1983; Lacaux *et al.*, 1992; Smirnioudi and Siskos, 1992; Tuncel and Ungor,

1996; Gulsoy *et al.*, 1999; Lee *et al.*, 2000; Tuncer *et al.*, 2001; Topcu *et al.*, 2002; Hu *et al.*, 2003; Kulshrestha *et al.*, 2003; Basak and Alagha, 2004).

The natural acidity of rainwater is often taken to be pH 5.6, which is that of pure water in equilibrium with the global atmospheric concentration of CO_2 (330 ppm), and this pH value of 5.6 has been used as the demarcation line for acidic precipitation. However, CO_2 is not the only background trace constituent that is capable of influencing the pH of rainwater. The processes controlling the composition of rain are complex and influenced by both natural and anthropogenic sources. Rainwater pH values, in the absence of common basic compounds such as NH_3 and $CaCO_3$ may be expected to range from 4.5 to 5.6 due to natural sulfur compounds alone (Charlson and Rodhe, 1982; Gulsoy *et al.*, 1999; Okay *et al.*, 2002).

The pH of the precipitation is expected to be lower than 5.6 for the areas which are exposed to strong influence of SO_2 and NO_x gases, and free from any natural cleansing mechanism of the atmosphere. However, in regions where the atmosphere is highly loaded with one or more of the alkaline species, such as $CaCO_3$ and NH_3, acidity of the precipitation is through the aerosols containing Ca^{2+} and NH_4^+ ions (Gulsoy *et al.*, 1999).

The continental sources of $CaCO_3$ have been linked to the soil type. More than 90% of the emissions are attributed to 'open sources', while the remaining are attributed to the industrial and miscellaneous sources. Traffic on unpaved roads (67%), wind erosion (28%), and agricultural tilling (5%) can be named as the main open sources (National Acid Precipitation Assessment Program, 1987). Emissions from the livestock waste are the dominant source of the ammonia in the precipitation. In the USA, it constitutes 62% of the total ammonia emissions, compared with 81% in Europe (Buijsman *et al.*, 1987). Fossil fuel combustion, fertilizer production, vegetative decomposition including the combustion of agricultural waste such as straw and stubble, incineration, and waste water treatment are also sources of ammonia (Gulsoy *et al.*, 1999).

The aim of this study is to gain an initial understanding of the rain water chemistry, to identify possible sources that contribute to its chemical composition. The results obtained in this study are compared with those other studies conducted at various places in the world.

2. Materials and Methods

2.1. SAMPLING SITE

Mugla is an urban city in Turkey the south-western Turkey (Figure 1). It lies in south western Turkey (latitude 36°20′–37°31′N and longitude 21°14′–29°15′E) about 646 m above sea level and about 30 km away from the sea. Figure 1 shows the map of the sampling site. Mugla's average rainfall was 121 mm and the daily mean humidity was 73% with the temperature ranging from the minimum of −2°C
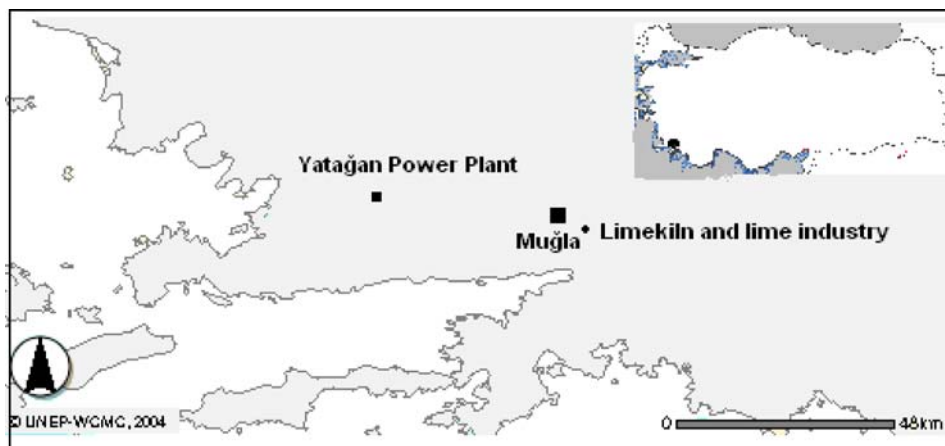
Figure 1. Map of study area.

to maximum of 38°C in the all year period. The population of city is low (43.845). The Yatagan Power Plant is located 30 km northwest of Mugla city. The annual average 18000 tons of coal is burned by houses for heating in Mugla. Yatagan Thermal Power Plant has a 360 MW energy capacity. There, 1500 tons of coal is burned daily (Demirak *et al.*, 2005). The large of the Mugla plain is covered by alluvium which is consist of limestone, clay, silt, sand and gravel (Akalan, 1988). The rain samples were collected at the terrace of a building in the city center. The height of the building is around 7 m. In the immediate vicinity of the site, there are other buildings. In this sampling site, there is heavy traffic. The limekiln and lime industry is located to the 2 km south of the sampling site.

2.2. SAMPLE COLLECTION

Precipitation samples were collected daily in high density polyethylene containers. Sample collection equipment used on an event basis were washed with 10% HCl and then rinsed with double distilled water (DDW). The containers were manually uncovered and rinsed with deonized water just before each rain event started. A total of 30 samples had sufficient volume for chemical analysis, which represented about 60% of the total rainfall during the study period. Upon arrival at the laboratory, pH were measured *in situ* using a "Hanna" water quality checker. The pH meter was calibrated before and after each measurement. The samples were filtered through 0.45 μm pore size membrane filters and then partitioned into separate aliquots. All the filtered samples were preserved at 4 °C in a refrigerator until subjected for ion analysis.

2.3. CHEMICAL ANALYSIS

The major anions (SO_4^{2-}, NH_4^+, NO_3^-) were analyzed by spectrophotometer using Dr Lange (CADAS 50S). The ammonium ion was determined by the Nessler Method. The concentration of sulphate ions was determined by the turbidimetric method basing on the formation of turbidity. Nitrate analyses were performed using the Cadmium Reduction Method (APHA-AWWA-WPCF, 1994). Na^+, K^+ and Ca^+ were measured by flame photometer (JENWAY PFP7). Blanks and standard samples were run to check accuracy.

3. Results and Discussion

3.1. DATA SCREENING

A total of 30 rain water samples were collected from February to April 2002. Data quality of each rainwater sample was checked by ionic balance. The data was rejected if it could not meet the quality criteria, which allowed for a 10% deviation of the ion balance (ratio sum cations/sum anions) (Melack *et al.*, 1985). Consequently, three rain water samples were rejected. The linear correlation of sum cations on sum anions gave r^2 value of 0.826 (Figure 2) indicating that the quality of the data was good. All the correlation results presented in this communication were calculated using the standard statistical software.
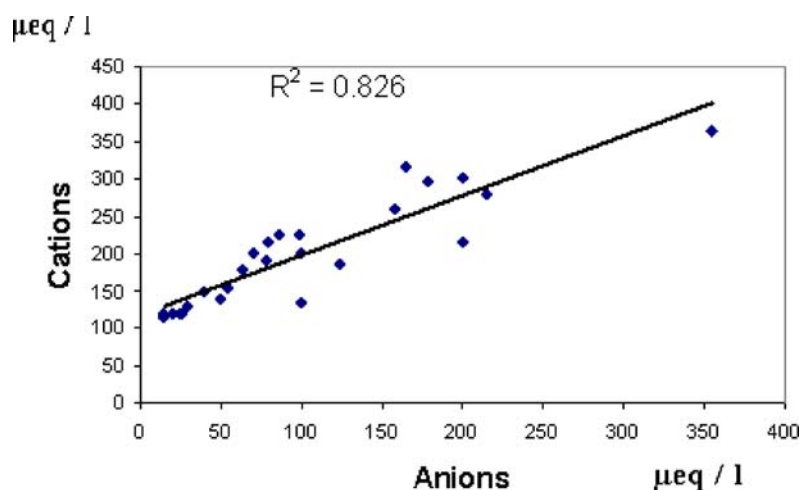

Figure 2. Sum of cations against sum of anions.

3.2. MAIN COMPOSITION OF RAINWATER

Volume weighted means and standard deviations of the measured parameters in the rain water samples of Mugla were summarized in Table I. Cloride was not included in table since the concentrations of cloride had not above the detection limit. Magnesium can not be measured by flame photometry. Geometric means and standart deviations were also included as most of parameters showed log-normal distribution.

The average pH of rainwater has been observed to be 6.9 which is in the alkaline range. Figure 3 shows the distribution of the pH in rain water samples. In total measured rain samples, 92% reflects the pH of rainwater to be in the alkaline range as compared to (5.6) pH of cloud water at equilibrium with atmospheric CO_2.

The concentration of major ionic species has the following order: $Ca^{2+} > SO_4^{2-} > NH_4^+ > NO_3^- > Na^+ > K^+ > H^+$. The high pH can be due to the influence of dust particles suspended in the atmosphere. These dust particles can be rich in calcium bicarbonate/carbonate which is a major buffering agent for acidity generated by sulphuric and nitric acids. The sum of major anions (SO_4^{2-} and NO_3^-) is 147 μeq/ l, while the sum of major cations (Ca^{2+}, NH_4^+, Na^+, K^+, H^+) is 225 μeq/l.

TABLE I
Chemical composition of rain water samples (μeq/l) in Mugla

	H^+	NO_3^-	SO_4^{2-}	Ca^{2+}	K^+	Na^+	NH_4^+	pH	$\sum{}^+/\sum{}^-$
AM	0.12	23	124	174	3.5	17	30	6.9	1.52
STD	9.09	16	80	86	3	9	20		
GM	0.09	17	92	106	3	16	50		
MIN	0.019	6	9	93	1	7	13	4.5	
MAX	31.6	48	307	280	8	30	48	7.7	
NS	27	27	27	27	27	27	27	27	

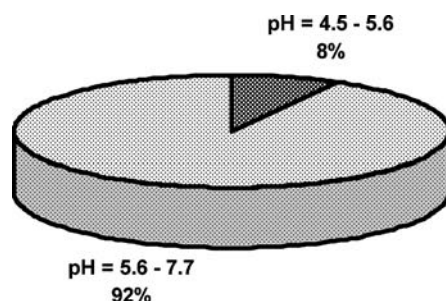AM, arithmetic mean (volume weighted); GM, geometric mean; STD, standard deviation; NS, number of samples.

Figure 3. pH distribution in rain water samples.

From these values a cation excess of 78 μeq/l is observed. The significant anion deficiency in rain water samples may be due to the exclusion of some anions. The main anions which may cause the imbalance are bicarbonate, organic ions (formate and acetate) and NO_2^-, PO_4^{3-} and Br^-. The role of HCO_3^- becomes very important due to the highly alkaline nature of soil in Mugla (Akalan, 1988). Since no direct method is available for the measurement of HCO_3^-, the concentration of HCO_3^- has been estimated from the theoretical relation between pH and HCO_3^- When pH is above 5.6 and the sample is in equilibrium with atmospheric carbon dioxide, the concentration of HCO_3^- is calculated as follows (Kulshrestha $et\ al.$, 2003):

$$[HCO_3^-] = 10^{-11,2+pH}$$

The above equation could under estimate the concentrations of HCO_3^-. At very high pH, the HCO_3^- concentrations so calculated are too high and do not match the ion balance (Kulshrestha $et\ al.$, 2003).

The percentage contribution of each ion towards the total deposition is shown in Figure 4(a). Calcium makes the highest contribution to both total ion concentration ($\sim$47%), and to total cation concentration ($\sim$77%). This may be due to dust particles activities in the region. Contribution of proton is very low (around 0.1%). The alkaline components (Ca^{2+}, Na^+, K^+) contribute 52%, NH_4^+ 8%, whereas, the contribution from the acidic components is relatively small accounting to 40% (Figure 4b).The dust-rich local and surrounding limestone environment might have caused the high concentrations of Ca^{2+} in Mugla. In addition, Mugla is a city in the coastal Mediterranean. Mediterranean sites are under the influence Saharan dust including high concentration of Ca^{2+} (Basak and Alagha, 2004).

Acidity of the precipitation is mostly dependent on sulfate and nitrate which are the measure of acid concentrations.

The relatively high NH_4^+ and SO_4^{2-} concentrations suggest the effect of local anthropogenic emissions. The high average concentration of SO_4^{2-} is due to local pollution over the city.

3.3. NEUTRALIZATION FACTORS

Calcium and ammonium are known as the principal neutralizing agents of the acidity. The main source of the calcium is the soil with high $CaCO_3$ content, and the source of the ammonium is the ammonium based fertilizers. The role of NH_4^+ and Ca^{2+} has been validated by calculating neutralization factors as follows (Kulshrestha $et\ al.$, 2003):

$$NF_{Ca} = Ca^{2+}/NO_3^- + SO_4^{2-}$$
$$NF_{NH4} = NH_4^+/NO_3^- + SO_4^2$$
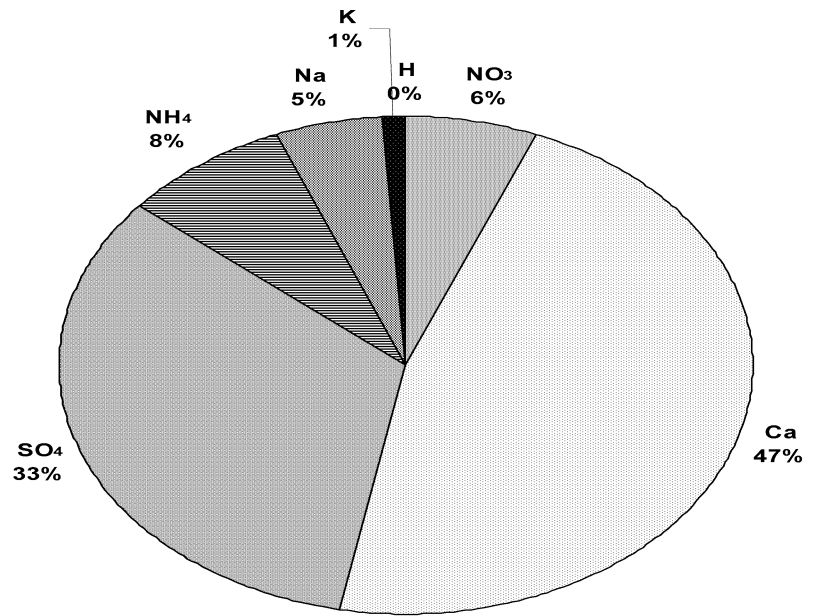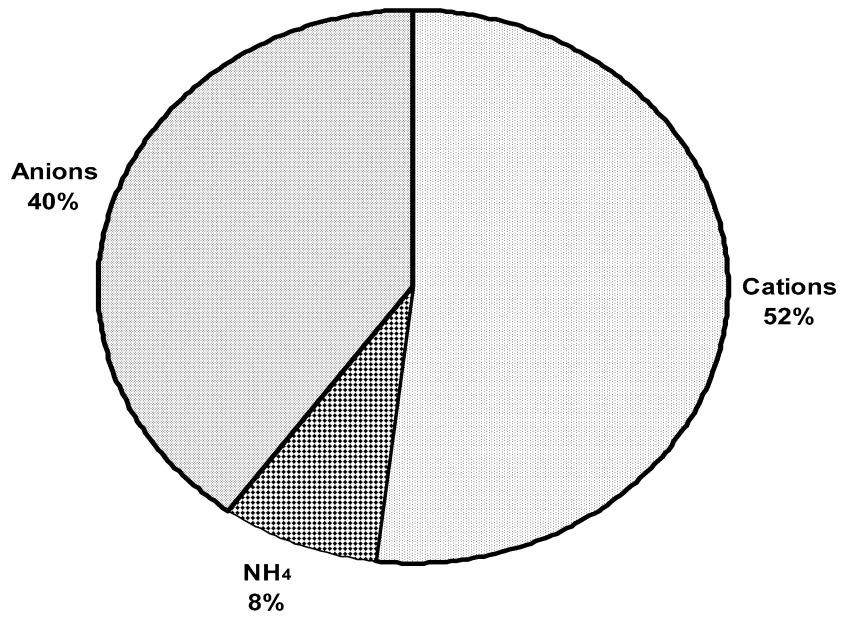
Figure 4. (a) Percentage contribution of each ion towards the total deposition. (b) Percentage contribution of cations, NH_4, and anions.

For the above calculations, equivalent concentrations of Ca^{2+} and NH_4^+ have been used. The values of neutralization factor (NF) for Ca^{2+} and NH_4^+ were 1.18 and 0.20, respectively. This feature suggests that major neutralization has occured due to Ca^{2+}. On the other hand, Ca^{2+} aerosols seem to be a major component for neutralization of rainwater acidity at most of Turkey sites (Tuncel and Ungor, 1996; Gulsoy et al., 1999; Topcu et al., 2002; Okay et al., 2002; Basak and Alagha, 2004).

3.4. COMPARISON WITH THE LITERATURE

Average ion concentrations for the precipitation of Mugla associated with the literature data from other urban regions in the world are presented in Table II. The SO_4^{2-} concentration (124 μeq/l) was found to be very high when compared with those in the literature for similar sampling sites on the urban. High SO_4^{2-} concentrations are due to strong SO_2 emissions. Mugla can be considered with its poor air quality due to emmisions from central heating and Yatagan Power Plant. The SO_2 and SO_4^{2-} mixture has an average lifetime of 2 to 6 days in atmosphere during which time it may travel up to 4000 km from its sources (O'Neill, 1993). Therefore, we consider that Yatagan Power Plant can be effective on level SO_4^{2-} concentrations in rain water. The SO_2 concentrations reported by the Public Health Institute were exceeds 400 μg/m^3 in Mugla in the heating season 2001–2002. The nitrate concentration (23 μeq/l) was also found to be higher than forest area (Silent Valley) and no point of pollution area but less than other cities (Table II). During the day, however, NO_3 is rapidly broken down by visible light via two possible pathways:

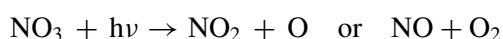$$NO_3 + h\nu \rightarrow NO_2 + O \quad \text{or} \quad NO + O_2$$

TABLE II
Comparision of measured ion concentrations (μeq/l) in Mugla with other sites

	H^+	NO_3^-	SO_4^{2-}	Ca^{2+}	K^+	Na^+	NH_4^+	pH
This study	0.12	23	124	174	3.5	17	30	6.9
Ankara (Tuncel and Ungor, 1995)	3.7	62	150	210	19	21	12	6.1
Athens (Dikaiakos et al., 1989)	4	94.2	100	137	67.7	14.5	21.9	6.1
İstanbul (Basak and Alagha, 2004)		33.4	115.2	285	57.4	75.2	12.8	4.81
Antalya (Okay et al., 2002)		70	113	140	12.1	450	50	5.17
Gopalpura (Satsangi et al., 1998)		42.6	15.4	134.3	2.5	19.4	43.4	
Silent Valey (Rao et al., 1995)		21	20	43	4	46	3	
Dayalbagh (Saxena et al., 1996)		17.6	28.4	83.9	7.7	54.8	12.7	
Rize (Balcı et al., 2001)		71	33					6.9

The relative importance of each pathway depends on the wavelength of the radiations involved. Because of the instability of NO_3 toward light, highest concentrations are observed at night. Even ay night, however, NO_3 can be consumed by reaction with NO, or excess NO_2.

$$NO + NO_3 \rightarrow 2NO_2$$
$$NO_2 + NO_3 \leftrightarrow N_2O_5$$
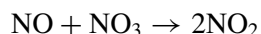
The dinitrogen pentoxide (N_2O_5) can react with water, forming nitric acid.

$$N_2O_5 + H_2O \rightarrow 2HNO_3$$
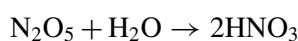
For this reason, the detectable levels of NO_3 are observed if the relative humidity is over 50%. In drier air, the lifetime of NO_3 is of the order of minutes (Conell, 1997). Therefore, in the areas which are far away from sea can be low concentrations of NO_3^-. The concentrations of NO_3^- are very high in coastal areas such as Rize, Antalya and Athens (Table II).

If sulfate and nitrate ions in the precipitation were completely in the form of H_2SO_4 and HNO_3, the average pH of the precipitation would be as low as 3. However, acidity of the precipitation caused by anthropogenic sources may be neutralized by calcium and ammonium cations as expressed in the other studies conducted in Turkey (Al-Momani et al., 1995; Tuncel and Ungor, 1996; Gulsoy et al., 1999).

The average SO_4^{2-} is observed to be higher than NO_3^-. These observations are similar to that reported at other Turkey sites (Al-Momani et al., 1995; Tuncel and Ungör, 1996; Basak and Alagha, 2004). The concentrations of Na^+ and K^+ has been found to be same in rural and urban areas when our results are compared with that of Rao et al. (1995) and Satsangi et al. (1998). But these values are observed to be less than other Turkey sites (Table II).

The average ammonia ion is observed to be higher than several sites. In a rural area, a high concentration of NH_4^+ is usually an indication of agricultural activities. Ammonia release from the soil to the atmosphere can be low. This shows the importance of the fertilization can be effective on the NH_4^+ concentration found in a rural atmosphere during the period studied here.

3.5. RATIOS

In order to understand the relative contribution of nitric acid to total acid rain formation in the region studied, the ratios $H^+/(NO_3^- + SO_4^{2-})$ and NO_3^- (NO_3^- + SO_4^{2-}) have been calculated and the results are shown in Table III. In the first ratio, the value is very low. Average $H^+/(NO_3^- + SO_4^{2-})$ ratio at our site is 0.008 indicating that approximately 99% of the acidity in rain is neutralized at study period. Although neutralization of rainwater acidity have also been reported in the

TABLE III
The ratios of H^+, NO_3^- and SO_4^{2-} concentrations

Ratio	
$H^+/(NO_3^- + SO_4^{2-})$	0.008
$NO_3^-/(NO_3^- + SO_4^{2-})$	0.156
NO_3^-/SO_4^{2-}	0.185

samples collected at the Mediterranean, Black Sea and Aegean coasts of Turkey, neutralization of approximately 95% of rainwater acidity at the Central Anatolia is significantly higher than 60% neutralization reported in other studies (Tuncer *et al.*, 2001). The second ratio $[NO_3^-/(NO_3^- + SO_4^{2-})]$ is found as 0.156. This shows that about 15.6% of the total nitrates and sulfates in the rain samples are due to nitrates. It can be assumed that approximately 74.4% of the acid rain is caused by the acidification with sulfuric acid formed from SO_2 and 15.6% with nitric acid coming from nitrogen oxides. On the other hand, the ratio of nitrate concentration to sulfate concentration in precipitation is found as 0.185 (Table III). It is indicated that there are less NO_3^- ions per each SO_4^{2-} ion in the samples. Takahashi and Fujita (2000) explained the relative contribution of H_2SO_4 and HNO_3 to the acidity of precipitation using the ratio of NO_3^- concentration to SO_4^{2-} concentration. Based on previous discussions, following mechanism can be proposed for neutralization of acidity in rain arriving to the Anatolian plateau. There is extensive transport of pollutants including acids from sources in Europe and northwestern parts of Turkey to the plateau. Approximately 60–70% of the transported acidity is in the form of H_2SO_4 and 30–40% is in the form of HNO_3. More than 90% of the acids transported to the Central Anatolia are neutralized both during transport from their source regions to the receptor site and locally at the region (Tuncer *et al.*, 2001).

3.6. CORRELATION

Table IV shows the linear regression correlation among the ions present in precipitation. Most of the well correlated pairs have common sources or occur in precipitation as a result of atmospheric chemistry. We considered the correlation as good if the value is $r^2 > 0.6$ and if the r^2 value is $0.4 < r^2 < 0.6$ we considered the correlation as marginal. The SO_4^{2-} shows good correlation Ca^{2+} and NH_4^+. It is very interesting to see that SO_4^{2-} has been observed to be well correlated with Ca^{2+} as well as NH_4^+. Ca^{2+} is a major earth crust component while NH_4^+ mainly comes from anthropogenic activities. Association of SO_4^{2-} with both Ca^{2+} and NH_4^+ suggests its origin from crustal as well as anthropogenic sources. The possibility of SO_4^{2-} association with Ca^{2+} is in the form of $CaSO_4$ due to the gypsiferous nature of the crust. In addition, dry deposition of SO_2/H_2SO_4 on dust particles during dry weather conditions can also contribute significant $CaSO_4$ (Kulshrestha *et al.*, 2003).

TABLE IV

The linear regression correlation among the ions present in precipitation

	H^+	K^+	Na^+	Ca^{2+}	NH_4^+	NO_3^-	SO_4^{2-}
H^+	1.						
K^+	0.22	1					
Na^+	0.01	0.08	1				
Ca^{2+}	0.56	0.30	0.16	1			
NH_4^+	0.50	0.33	0.13	0.47	1		
NO_3^-	0.06	0.15	0.41	0.12	0.12	1	
SO_4^{2-}	0.39	0.56	0.30	0.67	0.67	0.22	1

The SO_4^{2-} and NO_3^- are probably well correlated because of the similarity in their behavior in precipitation and co-emission of their precursors SO_2 and NO_x. But the correlation between SO_4^{2-} and NO_3^- is not good in this study. The linear regression coefficient between them in this study is 0.22. The lack of a good correlation might due to different oxidation mechanisms other than photochemical processes for these parameters. NH_4^+ and SO_4^{2-} were correlated higher than that with NO_3^-.

4. Conclusion

- The pH of rainwater at this site varied from 4.5 to 7.7 with an average of 6.9 which is in the alkaline range.
- The levels of concentration of components were similar to those at other Turkey sites.
- SO_4^{2-} has been observed to be well correlated with Ca^{2+} as well as NH_4^+. Association of SO_4^{2-} with both Ca^{2+} and NH_4^+ suggests its origin from crustal as well as anthropogenic sources.
- Ca^{2+}·seem to be a major component for neutralization of rainwater acidity.
- This study indicated that the chemistry of dry deposition of SO_2 is a very important phenomenon. High SO_4^{2-} concentrations are due to strong SO_2 emissions. Mugla can be considered with its poor air quality due to emmisions from heating and Yatagan Power Plant. The low concentrations of H^+ found in rainwater samples from Mugla suggest that an important portion of H_2SO_4 and HNO_3 have been neutralized by alkaline particles in the atmosphere.
- The dust-rich local and surrounding limestone environment might have caused the high concentration of Ca^{2+} in Mugla area. The relatively high concentration of NH_4^+ observed at Mugla is suspected to be due to surrounding agricultural activity.

Acknowledgments

References

Akalan, I.: 1988, *Soil Knowledge (in Turkish)*. Ankara University, Agricultural Faculty Pb. No: 1058–309 pp. 47–73.

Al-Momani, I. F., Ataman, O. Y., Anwari, M. A., Tuncel, S., Köse, C. and Tuncel, G.: 1995, 'Chemical composition of precipitation near an industrial area at Izmir, Turkey', *Atmospheric Environment* **29**(10), 1131–1143.

APHA-AWWA-WPCF: 1994, *Standard Methods for the Examination of Water and Wastewater*, American Public Health Association, Washington, DC, 15th edn., 2.

Balcı, A., Demirak, A. and Tabak, F.: 2001, 'Investigation of the some chemical properties of the rains in Rize (in Turkish)', *Journal of Ecology* **40**, 17–19.

Basak, B. and Alagha, O.: 2004, 'The chemical composition of rain water over Büyükçekmece Lake, Istanbul', *Atmospheric Research* **71**, 275–288.

Buijsman, E., Mass, H. F. M. and Asman, W. A. H.: 1987, 'Anthropogenic ammonium emission in Europe', *Atmospheric Environment* **21**, 1009–1022.

Charlson, R. J. and Rodhe, H.: 1982, 'Factors controlling the acidity of natural rainwater', *Nature* **295**, 683–685.

Conell, D. W.: 1997, *Basic Concepts of Environmental Chemistry*. ISBN 0-87371-998-0 Lewis Publishers New York, pp 368.

Demirak, A., Balcı, A., Dalman, Ö. and Tüfekçi, M.: 2005, 'Chemical Investigation of water resources around the Yatagan Power Plant of Turkey', *Water, Air and Soil Pollution* **162**, 171–181.

Dikaiakos S. G., Tsitouris, C. G., Siskos, P. A., Melissos, D. A. and Hastos, P.: 1989, 'Rain water composition in Athens, Greece', *Atmospheric Environment* **24B**, 171–176.

Galloway, J. N., Knap, A. H. and Church, T. M.: 1983, 'The composition of western Atlantic precipitation using ship board collectors', *Journal of Geophysical Research* **88**, 10859–10864.

Gulsoy, G., Tayanç, M. and Ertürk, F.: 1999, 'Chemical analysis of the major ions in the precipitation of Istanbul, Turkey', *Environmental Pollution* **105**, 273–280.

Hu, G. P., Balasubramanian, R. and Wu, C. D.: 2003, 'Chemical characterization of rainwater at Singapore', *Chemosphere* **51**, 747–755.

Kulshrestha, U. C., Kulshrestha, J. M., Sekar, R., Sastry, G. S. R. and Vairamani, M.: 2003, 'Chemical characteristics of rain water at an urban site of south-central India', *Atmospheric Environment* **37**, 3019–3026.

Lacaux, J. P., Delmas, R., Kouadio, G., Cros, B. and Andreae, M. O.: 1992, 'Precipitation chemistry in the Mayombe forest of equatorial Africa', *Journal of Geophysical Research* **97**, 6195–6206.

Lee, B. K., Hong, S. H. and Lee, D. S.: 2000, 'Chemical composition of precipitation and wet deposition of major ions on the Korean peninsula', *Atmospheric Environment* **34**, 563–575.

Melack, J. M., Stoddard, J. I. and Ochs, C. A.: 1985, 'Major ion chemistry and sensitivity to acid precipitation of Sierra Nevada Lakes', *Water Resource Research* **21**, 27–32.

National Acid Precipitation Assessment Program,: 1987, C. N. Herrick, J. L. Kulp (Eds.), Interim Assessment: the Causes and Effects of Acid Deposition, Vol. II. US Government Printing Office,Washington, DC.

Okay, C., Akkoyunlu, B. O. and Tayanç, M.: 2002, 'Composition of wet deposition in Kaynarca', *Turkey Environmental Pollution* **118**, 401–410.

O'Neill, P.: 1993, *Environmental Chemistry*. ISBN 0 412 48490 0 Published by Chapman & Hall, 2–6 Boundary Row, London SE1 8HN, UK, pp. 121

Rao, P. S. P., Momin, G. A., Safai, P. D., Pillai, A. G. and Khemani, L. T.: 1995, 'Rainwater and throughfall chemistry in the Silent Valley forest in south India', *Atmospheric Environment* **29**(16), 2025–2029.

Satsangi, S. G., Lakhani, A., Khari, P., Singh, S. P., Kumari, K. M. and Srivastava, S.S.: 1998, 'Composition of rain water at semi-arid rural site in India', *Atmospheric Environment* **32**, 3783–3793.

Saxena, A., Kulshrestha, U. C., Kumar, N., Kumari, K. M. and Srivastava, S. S.: 1996, 'Characterization of precipitation at Agra', *Atmospheric Environment* **30**(20), 3405–3412.

Smirnioudi, V. N. and Siskos, P. A.: 1992, 'Chemical composition of wet and dust deposition in Athens, Greece, in relation to meteorological conditions', *Atmospheric Environment* **26B**, 483–490.

Takahashi, A. and Fujita, S.: 2000, 'Long-term trends in nitrate to non-sea salt sulfate ratio in precipitation collected in western Japon', *Atmospheric Environment* **34**, 4551–4555.

Topcu, S., Incecik, S. and Atimtay, A. T.: 2002, 'Chemical composition of rain water at EMEP station in Ankara, Turkey', *Atmospheric Research* **65**, 77–92.

Tuncel, G. S. and Ungor, S.: 1996 'Rain water chemistry in Ankara, Turkey', *Atmospheric Environment* **30**, 2721–2727.

Tuncer, B., Bayar, B., Yeşilyurt, C. and Tuncel, G.: 2001, 'Ionic composition of precipitation at the central Anatolia (Turkey)', *Atmospheric Environment* **35**, 5989–6002.