

## RAINWATER CHEMISTRY AT URBAN AND SUBURBAN AREAS IN GREATER CAIRO

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**ABSTRACT:** Rainwater samples were collected from urban (El-Maadi, Cairo) and suburban (Kafr Tohormos, Giza) areas in greater Cairo during the winter season (2003–2004), and were analyzed for major cations ( $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  and  $\text{NH}_4^+$ ) and anions ( $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$  and  $\text{HCO}_3^-$ ). The average concentrations of these ions in rainwater were found to follow the pattern  $\text{Ca}^{2+} > \text{SO}_4^{2-} > \text{Mg}^{2+} > \text{Cl}^- > \text{Na}^+ > \text{NH}_4^+ > \text{K}^+ > \text{NO}_3^- > \text{HCO}_3^-$  at the urban area, and  $\text{Ca}^{2+} > \text{SO}_4^{2-} > \text{Mg}^{2+} > \text{Cl}^- > \text{Na}^+ > \text{NH}_4^+ > \text{HCO}_3^- > \text{K}^+ > \text{NO}_3^-$  at the suburban area. The concentrations of  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{NO}_3^-$  at the urban area were significantly higher than those found at the suburban area. The ratios of different components with respect to sea water ratio, enrichment factors and sea salt fractions indicated that nearly all the  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$  and  $\text{K}^+$  and fractions of  $\text{Mg}^{2+}$  and  $\text{Cl}^-$  were of non-marine origin at both sites. The average values of pH were 6.94 at the urban area and 7.41 at the suburban area. Rainwater acidity at urban and suburban areas in greater Cairo appeared to decrease due to high loading of dust particles in the atmosphere, which are rich in alkaline species. The relationships between the acid ions  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  and the cations  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , and also between the various anion and cation combinations indicated that the acidity of precipitation is neutralized. Neutralization factors revealed that  $\text{Ca}^{2+}$  is the most dominant neutralization substance in both the urban and the suburban areas in greater Cairo atmosphere.

**KEY WORDS:** Rainwater; chemical composition; pH; urban and suburban areas; ion balance; ions; neutralization factors

### INTRODUCTION

Precipitation is known as the major sink for particulate matter and gaseous pollutants from the atmosphere. It plays a significant role in controlling the concentrations of air pollutants. Due to rapid economic development and consequent increase in energy consumption, emissions of acidic gases like  $\text{SO}_2$  and  $\text{NO}_x$  from fossil fuel combustion are increased. These gases are dissolved in clouds and produce sulfuric and nitric acids. Incorporation of sulfur and nitrogen oxides in wet deposition is particularly important as they are precursors of major acids ( $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ ) (Voldner et al., 1986; Ro et al., 1988; Dikaiakos et al., 1990; Minoura and Iwasaka, 1996). Because of its harmful effects on the ecosystem, acid precipitation and associated environmental problems have received more attention in the international

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community during the recent decades. Acid rain has a share of responsibility in forest decline (Casado et al., 1989), lake and soil acidification (Melack et al., 1985; Mosello et al., 1985), building deterioration (Camuffo, 1992) and marble deterioration (Cheng et al., 1987). Acidity of rainwater is determined by the presence of its acidic components like  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  and its alkaline components like  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . Emissions of alkaline substances can significantly influence precipitation acidity by neutralizing some fractions of the acids (Placet and Streets, 1987). Natural sources and human activities are the sources of alkaline substances in the atmosphere. Al-Momani et al. (1995) concluded that alkaline components in the atmosphere, such as  $\text{CaCO}_3$  generated by wind erosion from soil, and ammonia released from natural or/and agricultural and industrial activities, neutralize anthropogenic acids and control the acidity of precipitation. Rainwater in India is alkaline due to the contribution of soil derived particles in the atmosphere (Kulshrestha et al., 1990; Saxena et al., 1991; Kumar et al., 1993). Moreover, in India, the pH of rainwater has been observed to be very high, even at high  $\text{SO}_4^{2-}$  concentrations, due to the significant crustal interference (Khemani, 1993; Saxena et al., 1996; Kulshrestha, 1998).

Greater Cairo has a serious air pollution situation. It is one of the most polluted megacities in the world due to the emissions of about 52% of the industry in Egypt, about 40% of electricity generated from thermal power stations and more than 1.3 million vehicles running in Cairo streets (Nasralla, 2001). Temperature inversion during winter season leads to accumulation of  $\text{SO}_2$ ,  $\text{NO}_2$  and particulate matter in the atmosphere (Khoder, 1997; Hassan, 2000).  $\text{SO}_2$ ,  $\text{NO}_2$  and  $\text{NH}_3$  were detected at annual mean levels of 181, 167 and  $68 \mu\text{g m}^{-3}$  and 65, 74 and  $98 \mu\text{g m}^{-3}$  in the atmosphere of the Cairo city centre and the residential area (Faisal), respectively (Hassan, 2000). Moreover, Abd-El Aziz (2001) found that the annual mean levels of total suspended particulate matter were  $553.4 \mu\text{g m}^{-3}$  in the city centre and  $365.9 \mu\text{g m}^{-3}$  in the residential area (Dokki) in Cairo.

The chemical composition of wet precipitation varies from site to site and region to region due to the effect of local sources. Rainwater composition reflects the composition of the atmosphere through which it falls and helps us to evaluate and understand the relative contribution of the different sources of gases and suspended particulate matter. Therefore, the aim of the present study is to evaluate the chemical composition of rainwater at urban and suburban areas in greater Cairo, and to interpret the chemical characteristics of precipitation.

## MATERIALS AND ANALYTICAL METHODS

### Sampling

Rainwater samples were collected at urban and suburban areas in greater Cairo. The urban area is represented by El-Maadi (at Cairo), it is located in the south of the city centre (Fig. 1). This site is approximately located near to a cement factory in the south and Mokattam plateau in the east. Moreover, the urban area is characterized

by heavy traffic and different human activities associated with some workshops and construction activities. On the other hand, the suburban area (Kafr Tohormos, Giza) is located southwest of the city centre (Fig. 1). It is located near to an agricultural region and characterized by low traffic density, low human activities and unpaved roads.

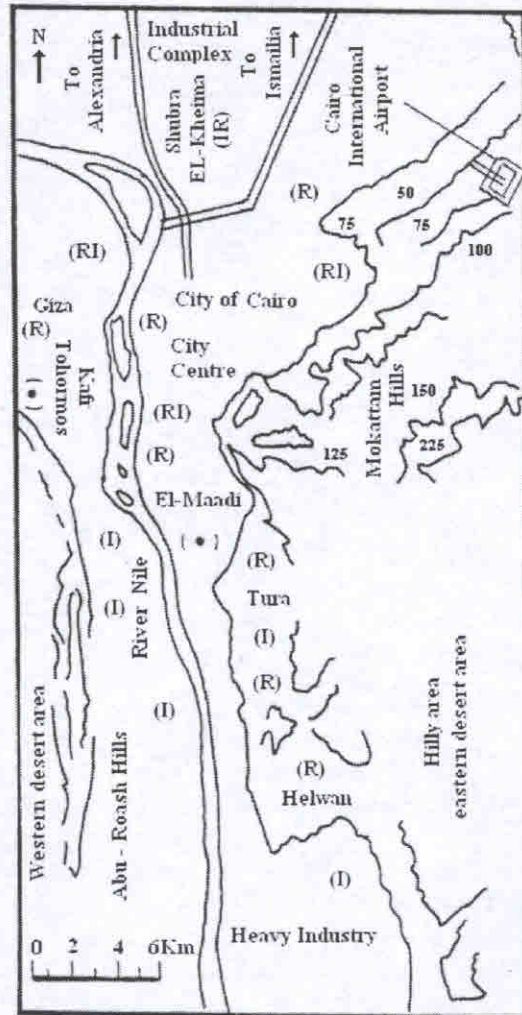


Fig. 1. Map of the greater Cairo area showing districts of residential (R), industrial (I) activities and the sampling sites (•)

Rainwater samples were collected from each site during the winter season (December 2003 to February 2004). Rainwater collectors (polyethylene bottles and funnels) were placed on the top of a four storey building about 10 m height from ground level on an event basis. The collectors were deployed as soon as the rain began and retrieved immediately after the rain stopped. In this way contamination of rain samples by dry deposition is avoided.

### Sample analysis

The pH of the samples was determined upon arrival at the laboratory, using a pH meter which was calibrated before and after each measurement. The concentration of  $H^+$  ion was calculated from the pH values.  $HCO_3^-$  concentration was calculated using a theoretical relation between the pH and  $HCO_3^-$  according to Parashar et al. (1996). After the pH measurement, the samples were filtrated through cellulose acetate membrane filter papers (0.2  $\mu m$  pore size) and divided into two fractions. The first fraction was stored under refrigeration in polyethylene bottles and used for  $Cl^-$ ,  $SO_4^{2-}$ ,  $NO_3^-$  and  $NH_4^+$  analysis, whereas the second fraction was acidified with 0.5 M  $HNO_3$  and used for  $Na^+$ ,  $K^+$ ,  $Ca^{2+}$  and  $Mg^{2+}$  analysis.

A dry deposition blank was collected using 50 ml deionized water by washing the funnel after 5 h to check the interference of dry deposition. Also, a blank sample of collector washing was collected after thorough washing of the funnel. Both blanks were analyzed for major anions and cations. All major ions were found below detection limits in both the blanks.

The  $Na^+$ ,  $K^+$ ,  $Ca^{2+}$  and  $Mg^{2+}$  were determined using atomic absorption spectrophotometer (flame AAS 3300, Perkin-Elmer, Norwalk, CT, USA), whereas  $Cl^-$ ,  $SO_4^{2-}$ ,  $NO_3^-$  and  $NH_4^+$  were measured according to Harrison and Perry (1986).  $NH_4^+$  was determined colorimetrically by catalysed indophenol blue method using spectrophotometer. Sulfate was determined by turbidimetric method using spectrophotometer. Nitrate was determined colorimetrically by hydrazine reduction-diazotization method using spectrophotometer. Chloride was determined colorimetrically by reaction of mercuric thiocyanate with chloride to liberate thiocyanate which was measured as ferric thiocyanate.

### Statistical analysis

The correlation coefficient ( $r$ ) and its level of significance were determined by using the alternative method of calculation according to Gregory (1963).

## RESULTS AND DISCUSSION

### Ion balance

The completeness of the measured species of each rainwater sample was checked by ion balance. The data were rejected if they did not meet the quality criteria, which allowed a 15% deviation of the ion balance (ratio sum cations/sum anions) (Melack et al., 1985). The average sum of anions ( $Cl^-$ ,  $NO_3^-$ ,  $SO_4^{2-}$ ,  $HCO_3^-$ ) were 1315 and 752  $\mu eq l^{-1}$ , whereas the average sum of cations ( $NH_4^+$ ,  $Ca^{2+}$ ,  $Na^+$ ,  $Mg^{2+}$  and  $K^+$ ) were 2969 and 1456  $\mu eq l^{-1}$  in rainwater at the urban and suburban areas, respectively (Table 1). The difference between the sum of cations and the sum of anions is an indicator for the completeness of the measured parameters. The anion deficiency in rainwater samples may be attributed to the exclusion of some anions.

The main anions which may cause the imbalance are organic ions (formate and acetate),  $F^-$ ,  $NO_2^-$ ,  $PO_4^{3-}$  and  $Br^-$ .

**TABLE 1. Minimum, maximum and mean concentrations of chemical components ( $\mu\text{eq l}^{-1}$ ) and pH in rainwater at urban and suburban areas**

	Urban			Suburban		
	Range	Mean	SD	Range	Mean	SD
$Cl^-$	184.00 – 685.00	423.50	153.80	114.00 – 463.40	250.00	110.92
$NO_3^-$	39.70 – 154.80	86.00	37.11	33.10 – 97.90	55.00	22.10
$SO_4^{2-}$	376.50 – 1298.50	750.00	320.95	152.00 – 504.40	285.00	118.12
$HCO_3^-$	28.00 – 100.00	55.00	27.50	79.40 – 282.00	162.00	57.17
$NH_4^+$	121.00 – 475.60	274.00	128.37	89.40 – 339.40	178.50	85.07
$Ca^{2+}$	867.00 – 2858.00	1736.00	668.88	360.50 – 1475.50	781.50	355.97
$Na^+$	216.90 – 531.70	336.50	113.03	83.00 – 326.90	181.00	82.22
$Mg^{2+}$	259.00 – 808.00	484.00	172.83	138.30 – 432.90	257.60	92.99
$K^+$	78.20 – 225.40	138.00	49.56	23.60 – 118.90	57.50	29.64
$H^+$	0.06 – 0.22	0.12	0.06	0.02 – 0.08	0.04	0.02
pH	6.65 – 7.20	6.94	0.21	7.10 – 7.65	7.41	0.17

Notes:  $H^+$  and  $HCO_3^-$  are derived from pH; SD: Standard deviation

### Chemical composition of the rainwater

The minimum, maximum and mean concentrations of the main chemical components of rainwater samples together with pH at the two sampling sites are summarized in *Table 1*. It is clear that, the most abundant components in rainwater at both sites were  $Ca^{2+}$  and  $Mg^{2+}$  for cations, and  $SO_4^{2-}$  and  $Cl^-$  for anions. Meanwhile,  $Ca^{2+}$  was the dominant species in rainwater at both sites. Generally, the following sequence was displayed with regard to the average concentrations of ions:  $Ca^{2+} > SO_4^{2-} > Mg^{2+} > Cl^- > Na^+ > NH_4^+ > K^+ > NO_3^- > HCO_3^-$  at the urban area, and  $Ca^{2+} > SO_4^{2-} > Mg^{2+} > Cl^- > Na^+ > NH_4^+ > HCO_3^- > K^+ > NO_3^-$  at the suburban area (*Table 1*). In this connection, it may be mentioned that calcium was the dominant cation and  $SO_4^{2-}$  the dominant anion in wet deposition at Erzurum, Turkey and Tirupati (Bayeraktar and Turalioglu, 2005; Mouli et al., 2005).

The chemical composition of rainwater depends on local sources emitting gases and particulate matter. This is due to the direct input of these pollutants in rainwater. The concentrations of  $Ca^{2+}$ ,  $SO_4^{2-}$ ,  $Mg^{2+}$ ,  $Cl^-$ ,  $Na^+$ ,  $K^+$ ,  $NO_3^-$  and  $H^+$  at the urban area were significantly ( $p < 0.05$ ) higher than those found at the suburban area (*Table 1*). However, there was no significant difference between the concentrations of  $NH_4^+$  at the two sites.  $Ca^{2+}$  concentrations in rainwater ranged from 867 to 2858  $\mu\text{eq l}^{-1}$  (with a mean value of 1736  $\mu\text{eq l}^{-1}$ ) at the urban area, and 360.5 to 1475.5  $\mu\text{eq l}^{-1}$  (with a mean value of 781.5  $\mu\text{eq l}^{-1}$ ) at the suburban area (*Table 1*). Our results are lower than those found in Riyadh, Saudi Arabia, which were ranged from 1440 to

4350  $\mu\text{eq l}^{-1}$  (with a mean value of 2528  $\mu\text{eq l}^{-1}$ ) (Alabdula'aly and Khan, 2000). In the present study, the observed high  $\text{Ca}^{2+}$  concentrations may be due to the high emission of  $\text{Ca}^{2+}$  from both anthropogenic and natural sources. These sources include human activities such as construction activities. Cement factory in Tura in the south of the urban area may also bring additional  $\text{Ca}^{2+}$  through transport phenomenon by the southerly winds which are relatively predominant during the winter season. Moreover, dust transported by winds from Mokattam plateau, which is rich by calcite (Sowelim, 1983), leads to an increase in the levels of  $\text{Ca}^{2+}$  in the atmosphere of the urban area. Calcium carbonate constitutes the major components of dust at Mokattam area. The surface soil of Mokattam plateau contains 29.12% carbonates (Sowelim, 1983; Moharram and Sowelim, 1980).

Most of the sulfate in the rainwater can be attributed to the emission of  $\text{SO}_2$  gas and the collection of particulate sulfate. The high formation of  $\text{H}_2\text{SO}_4$  from the oxidation of  $\text{SO}_2$  gas emitted by the heavy traffic leads to an increase in the concentration of sulfate in rainwater. The concentrations of sulfate in rainwater ranged from 376.5 to 1298.5  $\mu\text{eq l}^{-1}$  (with a mean value of 750  $\mu\text{eq l}^{-1}$ ) at the urban area, and 152 to 504.4  $\mu\text{eq l}^{-1}$  (with a mean value of 285  $\mu\text{eq l}^{-1}$ ) at the suburban area (*Table 1*). Our results of the urban area are in agreement with Shakour (1992) who found that the concentration of sulfate in rainwater was 729  $\mu\text{eq l}^{-1}$  in a residential area (New Maadi) near to a cement factory in Cairo. Alabdula'aly and Khan (2000) found that the average concentration of sulfate was 685.4  $\mu\text{eq l}^{-1}$  in rainwater at Riyadh, Saudi Arabia. In the present study, the observed high concentrations of sulfate found in the samples from the urban site may be due to heavy traffic which leads to an increased concentration of sulfate. City centre in the north and the cement factory in the south of the urban area may also bring additional particulate sulfate through transport phenomenon by winds. Moreover, natural particulate sulfate is introduced into the atmosphere of the urban area through the erosion of Mokattam hills, which contain some gypsum deposits.

The presence of nitrate and ammonium ions in rainwater is due to direct input of gaseous nitric acid and ammonia in addition to the collection of particulate nitrate and ammonium. The average concentrations of nitrate and ammonium ions in rainwater were 86  $\mu\text{eq l}^{-1}$  and 274  $\mu\text{eq l}^{-1}$  at the urban area, whereas they were 55  $\mu\text{eq l}^{-1}$  and 178.5  $\mu\text{eq l}^{-1}$  at the suburban area, respectively (*Table 1*). The relatively high concentrations of nitrate and ammonium ions in rainwater at the urban area may be attributed to the high traffic density and human activities associated with workshops and construction of new buildings and roads, besides the effect of pollutants coming from the city centre.

The  $\text{Mg}^{2+}$  levels in the rainwater are affected by both dust and sea salt particles in the atmosphere. The concentration of  $\text{Mg}^{2+}$  is dominated by crustal sources in stations far from the sea; however it is determined by a marine source at sampling sites close to the sea (Crawley and Sievering, 1986). The mean concentrations of  $\text{Mg}^{2+}$  in rainwater were 484  $\mu\text{eq l}^{-1}$  and 257.6  $\mu\text{eq l}^{-1}$  at the urban and suburban areas, respectively (*Table 1*). The highest concentration of  $\text{Mg}^{2+}$  at the urban area is attributed to the transportation of  $\text{Mg}^{2+}$  particles from Mokattam hills by wind. Shakour (1982) concluded that Mokattam hills are an important source of  $\text{Mg}^{2+}$  in

Cairo atmosphere, since these hills contain some dolomite ( $\text{Ca}(\text{Mg}(\text{CO}_3)_2)$ ). In the present study, a fraction of  $\text{Cl}^-$  which is emitted by the cement industry and Mokattam hills leads to an increase of  $\text{Cl}^-$  in rainwater at the urban area in comparison to the suburban area.

In the present study, the mean concentrations of  $\text{HCO}_3^-$  in rainwater were  $55 \mu\text{eq l}^{-1}$  at the urban area, and  $162 \mu\text{eq l}^{-1}$  at the suburban area (Table 1). Since no direct method is available for the measurements of  $\text{HCO}_3^-$  ion, its concentration was calculated using a theoretical relation between the pH and  $\text{HCO}_3^-$ . When pH is above 5.6 and the sample is in equilibrium with atmospheric carbon dioxide, the concentration of  $\text{HCO}_3^-$  is calculated using the formula (Parashar et al., 1996):

$$\text{HCO}_3^- = 10^{-11.2+\text{PH}}$$

The contributions of each ion to the average cation/anion ratio and to the total ion mass in rainwater at the urban and suburban areas are presented graphically in Figs. 2 and 3, respectively.  $\text{Ca}^{2+}$  is clearly dominated in rainwater of both sites. It accounts for 40.53% and 35.39% of the total mass of ions and 58.48% and 53.67% of the total mass of measured cations at the urban and suburban areas, respectively (Figs. 2 and 3). Among the anions,  $\text{SO}_4^{2-}$  ion had the highest contribution and accounted for approximately 57.06% and 37.9% of the total anion mass at the urban and suburban areas, respectively. The  $\text{Cl}^-$  ion concentration was the highest after  $\text{SO}_4^{2-}$  and accounted for approximately 32.22% and 33.24% of the total anion mass at the urban and suburban areas, respectively. The  $\text{NO}_3^-$  ion appears to have a small contribution compared to  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  in both total ion and total anion masses at both sites. Among cations, the  $\text{Mg}^{2+}$  ion had the greatest contribution after  $\text{Ca}^{2+}$  and accounted for approximately 16.30% and 17.69% of the total cation masses at the urban and suburban areas, respectively.  $\text{K}^+$  and  $\text{H}^+$  ions had the least contribution to all cations at the both sites, the two ions accounted together for approximately 4.65% and 3.95% of the total cation masses at the urban and suburban areas, respectively.

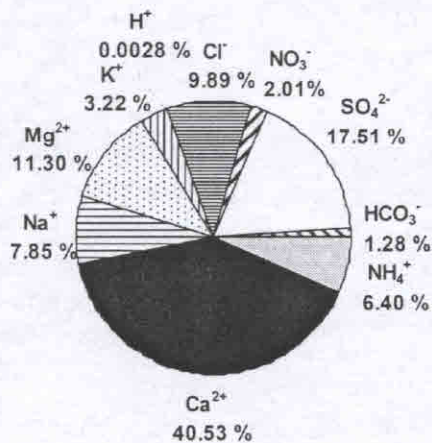
### Sea salt contribution

To estimate the marine and non-marine contributions to the rainwater at both sites, different ratios like sea salt fractions (SSF), non-sea salt fraction (NSSF) and enrichment factors (EF) have been calculated using  $\text{Na}^+$  as the reference element assuming that all  $\text{Na}^+$  is of marine origin (Keene et al., 1986; Kulshrestha et al., 1996). Enrichment factor (EF) of different species with respect to  $\text{Na}^+$  was calculated by the following equation (Kulshrestha et al., 1996):

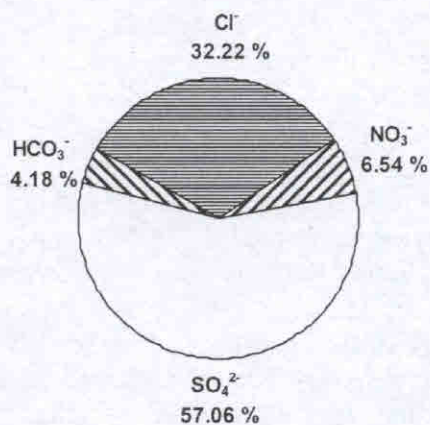
$$EF = \frac{X / \text{Na}^+_{\text{rain}}}{X / \text{Na}^+_{\text{seawater}}}$$

where  $X$  is the chemical component of interest.

Contribution of each ion to total ion mass



Contribution of anions to total anion mass



Contribution of cations to total cation mass

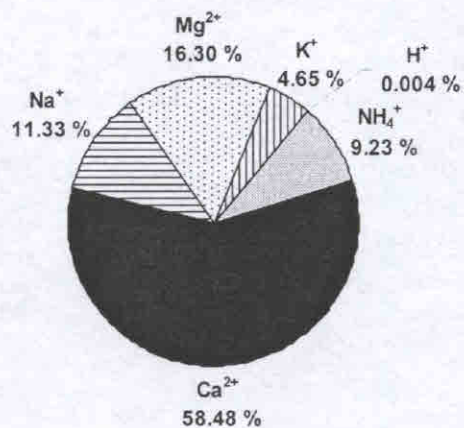
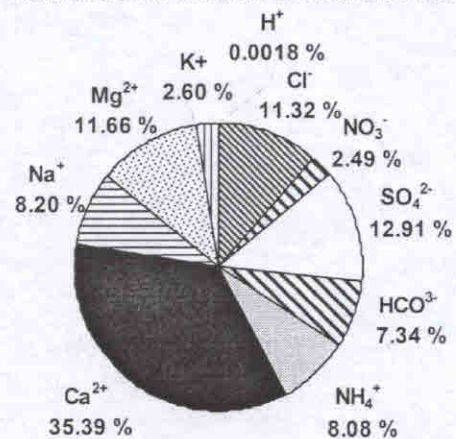


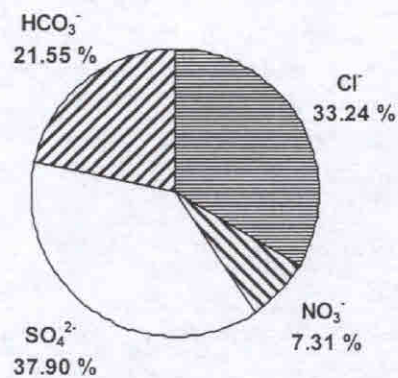
Fig. 2. Contribution of ions to the total cation/anion and the total ion mass in rain-water at the urban area



Contribution of each ion to total ion mass



Contribution of anions to total anion mass



Contribution of cations to total cation mass

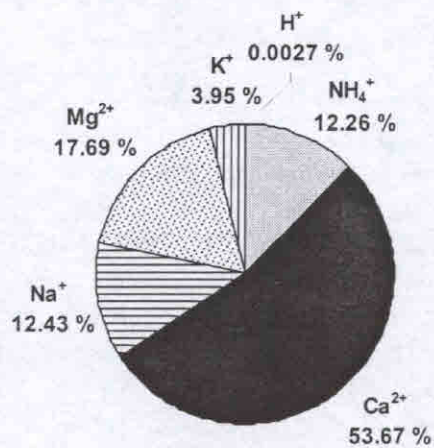


Fig. 3. Contribution of ions to the total cation/anion and the total ion mass in rain-water at the suburban area

The sea salt fraction (SSF) and the non sea salt fraction (NSSF) of the different components in rain water were calculated by the following equations (Kulshrestha et al., 1996):

$$\%SSF = \frac{100(Na^+) \left( X/Na^+ \right)_{sea}}{X}$$

where  $X$  is the component of interest

$$\%NSSF = 100 - SSF$$

The ratios of  $Cl^-$ ,  $SO_4^{2-}$ ,  $Mg^{2+}$ ,  $K^+$  and  $Ca^{2+}$  with respect to  $Na^+$  in the sea water and rainwater collected from urban and suburban areas are summarized in *Tables 2* and *3*, respectively. It can be observed that the ratios in rainwater were 1.26 and 1.38 for  $Cl^-$ , 2.23 and 1.57 for  $SO_4^{2-}$ , 1.44 and 1.42 for  $Mg^{2+}$ , 0.41 and 0.32 for  $K^+$  and 5.16 and 4.32 for  $Ca^{2+}$  at the urban and suburban areas, respectively. The ratios of  $SO_4^{2-}$ ,  $Mg^{2+}$ ,  $K^+$  and  $Ca^{2+}$  with respect to  $Na^+$  in rainwater were found to be higher at both sites than that reported for sea water ratios. These indicate the incorporation of non-marine constituents in rain water through the contribution of local sources (anthropogenic and natural). Our results are in agreement with Kulshrestha et al., (1996 and 2003) and Satsangi et al., (1998) who suggested that high ratios of  $SO_4^{2-}$ ,  $Mg^{2+}$ ,  $K^+$  and  $Ca^{2+}$  with respect to  $Na^+$  in rainwater are due to non-marine origins for these components.

**TABLE 2. Comparison of sea water ratios with rainwater components at the urban area**

	$Cl^-/Na^+$	$SO_4^{2-}/Na^+$	$Mg^{2+}/Na^+$	$K^+/Na^+$	$Ca^{2+}/Na^+$
Sea water ratio*	1.16	0.125	0.227	0.0218	0.0439
Rainwater ratio	1.26	2.230	1.440	0.4100	5.1600
EF	1.09	17.840	6.340	18.8100	117.5400
SSF, %	92.17	5.600	15.780	5.3100	0.8500
NSSF, %	7.83	94.400	84.220	94.6900	99.1500

\* Values taken from Kulshrestha et al. (1996)

EF: Enrichment factor; SSF: Sea salt fraction; NSSF: Non-sea salt fraction

In the present study, enrichment factor (EF) values at both sites are presented in *Tables 2* and *3*. It is clear that,  $SO_4^{2-}$ ,  $K^+$  and  $Ca^{2+}$  are enriched with respect to the sea water indicating the significant influence of local sources at both study areas. However,  $Cl^-$  and  $Mg^{2+}$  are slightly enriched. This indicates that some of the rainwater samples were affected by the sea salts.

The sea salt fraction (SSF) and the non-sea salt fraction (NSSF) of the different components of rainwater at the urban and the suburban areas are summarized in *Tables 2* and *3*, respectively. The NSSF were 7.83% and 16.02% for  $Cl^-$ , 94.4% and 92.06% for  $SO_4^{2-}$ , 84.22% and 84.05% for  $Mg^{2+}$ , 94.69% and 93.14% for  $K^+$  and

99.15% and 98.99% for  $\text{Ca}^{2+}$  at the urban and suburban areas, respectively. These results indicated that nearly all the  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$  and  $\text{K}^+$ , and fractions of  $\text{Mg}^{2+}$  and  $\text{Cl}^-$  were of non-marine origins. Thus, it can be surmised that the rainwater composition at both sites in Cairo is predominantly influenced by the local sources.

**TABLE 3. Comparison of sea water ratios with rainwater components at the suburban area**

	$\text{Cl}^-/\text{Na}^+$	$\text{SO}_4^{2-}/\text{Na}^+$	$\text{Mg}^{2+}/\text{Na}^+$	$\text{K}^+/\text{Na}^+$	$\text{Ca}^{2+}/\text{Na}^+$
Sea water ratio*	1.16	0.125	0.227	0.0218	0.0439
Rainwater ratio	1.38	1.570	1.420	0.3200	4.3200
EF	1.19	12.560	6.260	14.6800	98.4100
SSF,%	83.98	7.940	15.950	6.8600	1.0100
NSSF,%	16.02	92.060	84.050	93.1400	98.9900

\* Values taken from Kulshrestha et al. (1996)

EF: Enrichment factor; SSF: Sea salt fraction; NSSF: Non-sea salt fraction

### Acid neutralization

The pH of rainwater is determined by the nature and relative proportions of acids and bases. Acidic pH of the rainwater indicates the presence of strong acids, whereas neutral or alkaline pH values reveal the neutralization of acids by ammonia gas and the carbonates of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  contained in dust particles suspended in the atmosphere. The pH of rainwater in a clean atmosphere is usually around 5.6, owing to carbonate buffer as a result of  $\text{CO}_2$  dissolved in rain droplets (Charlson and Rodhe, 1982). In the present study, pH values of the rainwater ranged from 6.65 to 7.20 (with a mean value of 6.94) at the urban area, and 7.10 to 7.65 (with a mean value of 7.41) at the suburban area (Table 1), all indicating that the acidity of rainwater is decreased as compared with the reference level of 5.6 (Charlson and Rodhe, 1982). This is due to the high concentration of suspended particulate matter in the city atmosphere. These dust particles are usually rich in alkaline species. The contribution of the alkaline components ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  and  $\text{K}^+$ ) were 62.90% and 57.85%, those of  $\text{NH}_4^+$  were 6.40% and 8.08%, whereas the contribution of the acidic components were relatively small, accounting to ~ 30.69% and 34.06% of the total ion mass at the urban and suburban areas, respectively (Figs. 2 and 3). The average pH of the wet deposition was 6.60 at Erzurum in Turkey, due to extensive neutralization of the acidity (Bayraktar and Turalioglu, 2005). In the Petra region in Jordan, the higher pH of the wet precipitation was due to the dust in the atmosphere containing a large fraction of calcite (Al-Khashman, 2005). In the present study, the pH values of the rainwater were nearly similar to those found in many countries, such as in India (ranged from 6–7), Saudi Arabia (7.41), southern Nigeria (ranged from 6.42–7.06), west Africa (6.70), Jordan (6.85), Tirupati (6.78), northern India (7.05) and Erzurum, Turkey (6.60) (Ayodele, 1995; Parashar et al., 1996; Kulshrestha, 1998; Uzomah and Sangodoyin, 2000; Alabdula'aly and Khan, 2000; Al-

Khashman, 2005; Bayraktar and Turalioglu, 2005; Mouli et al., 2005; Al Obaidy and Joshi, 2006). On the other hand, our results are much higher than those found in Singapore (4.20), southern China (4.70), Japan (4.80), northern China (5.80), south Brazil (5.40), Tokyo metropolitan area (4.23–4.62), northwestern Greece (5.13–5.99), southwestern China (4.53) and Mexico city (4.95) (Hara et al., 1990; Hara et al., 1995; Wang and Wang, 1996; Hu et al., 2003; Migliavacca et al., 2004; Okuda et al., 2005; Báez et al., 2006; Han and Liu, 2006; Tsitouridou and Anatolaki, 2007).

The correlation between ions in rainwater indicates the likely sources of pollutants and suggests the chemical reactions in the atmosphere. *Tables 4* and *5* show the correlation coefficients among main ions in rainwater collected from urban and suburban areas, respectively. Strong correlation was found between  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  ( $r = 0.87$ ) at the suburban site (*Table 5*), indicating the co-emission of their precursors  $\text{NO}_x$  and  $\text{SO}_2$  and their origin from similar sources. However, the lack of a strong correlation between  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  ( $r = 0.77$ ) at the urban area (*Table 4*) may be due to the effect of different sources other than traffic such as cement factory, gypsum erosion, terrestrial origin and Mokattam hills.  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  were more closely correlated ( $r = 0.87$ ) than  $\text{NH}_4^+$  with  $\text{NO}_3^-$  ( $r = 0.70$ ) at the urban site (*Table 4*). These correlations indicate that  $\text{NH}_4^+$  is largely associated with  $\text{SO}_4^{2-}$  and also suggest that the majority of  $\text{NH}_4^+$  in the atmosphere of urban area may occur as  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NH}_4\text{HSO}_4$ . Sulfate derived from anthropogenic sources is often associated with  $\text{NH}_4^+$  forming  $(\text{NH}_4)_2\text{SO}_4$  (Jain et al., 2000). The existence of  $(\text{NH}_4)_2\text{SO}_4$  in rainwater has been reported by various researchers (e.g. Mahadevan et al., 1989; Khemani, 1993; Saxena et al., 1996). It is suggested that the use of fertilizers like  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NH}_4\text{NO}_3$  in the agricultural area near to the suburban area may be implicated as a source of  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NH}_4\text{NO}_3$  aerosols, and can be incorporated in the precipitation. This is confirmed by the strong relationships between  $\text{NH}_4^+$  and both  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  at the suburban area.

**TABLE 4. Correlation coefficient between measured parameters in rainwater at the urban area**

	$\text{Cl}^-$	$\text{NO}_3^-$	$\text{SO}_4^{2-}$	$\text{H}^+$	$\text{Na}^+$	$\text{K}^+$	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$	$\text{NH}_4^+$
$\text{Cl}^-$	1								
$\text{NO}_3^-$	0.72 <sup>a</sup>	1							
$\text{SO}_4^{2-}$	0.60	0.77 <sup>b</sup>	1						
$\text{H}^+$	-0.32	0.29	0.21	1					
$\text{Na}^+$	0.76 <sup>b</sup>	0.97 <sup>c</sup>	0.74 <sup>a</sup>	0.03	1				
$\text{K}^+$	0.75 <sup>a</sup>	0.74 <sup>a</sup>	0.95 <sup>c</sup>	-0.01	0.79 <sup>b</sup>	1			
$\text{Ca}^{2+}$	0.65 <sup>a</sup>	0.79 <sup>b</sup>	0.97 <sup>c</sup>	0.16	0.80 <sup>b</sup>	0.88 <sup>c</sup>	1		
$\text{Mg}^{2+}$	0.86 <sup>c</sup>	0.91 <sup>c</sup>	0.64 <sup>a</sup>	-0.12	0.91 <sup>c</sup>	0.72 <sup>a</sup>	0.66 <sup>a</sup>	1	
$\text{NH}_4^+$	0.28	0.70 <sup>a</sup>	0.87 <sup>c</sup>	0.54	0.63 <sup>a</sup>	0.72 <sup>a</sup>	0.78 <sup>b</sup>	0.56	1

<sup>a</sup> Significant ( $p < 0.05$ ); <sup>b</sup> Significant ( $p < 0.01$ ); <sup>c</sup> Significant ( $p < 0.001$ )

In the present study, fractions of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  in rainwater at both sites may be derived as primary pollutant from roadside dust, natural dust, soil and dust resulting from agricultural activities or may be associated with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  after the reaction of  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  acids with alkaline compounds which are rich in  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  and carried into the atmosphere by wind blown dust. This is corroborated by correlation between  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$  and  $\text{NO}_3^-$ ,  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$ ,  $\text{Mg}^{2+}$  and  $\text{NO}_3^-$  at both sites (Tables 4 and 5). These relationships indicate that the acidity in rainwater is neutralized by the alkaline species in the atmosphere, and  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  ions in rainwater occurred mostly in neutralized forms. This is confirmed by the weak correlations between  $\text{H}^+$  and  $\text{SO}_4^{2-}$ ,  $\text{H}^+$  and  $\text{NO}_3^-$  at both sites (Tables 4 and 5). These results are in agreement with those reported by Kawaja and Husain (1990) who concluded that the higher correlation coefficients between  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$  and  $\text{NO}_3^-$  indicate that their cocurrence in precipitation is mostly as  $\text{CaSO}_4$  and  $\text{Ca}(\text{NO}_3)_2$ . The correlation between  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  (Tables 4 and 5) may be due to the common occurrence of these species in dust.

**TABLE 5. Correlation coefficient between measured parameters in rainwater at the suburban area**

	$\text{Cl}^-$	$\text{NO}_3^-$	$\text{SO}_4^{2-}$	$\text{H}^+$	$\text{Na}^+$	$\text{K}^+$	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$	$\text{NH}_4^+$
$\text{Cl}^-$	1								
$\text{NO}_3^-$	0.51	1							
$\text{SO}_4^{2-}$	0.50	0.87 <sup>c</sup>	1						
$\text{H}^+$	0.01	0.03	0.20	1					
$\text{Na}^+$	0.66 <sup>a</sup>	0.96 <sup>c</sup>	0.86 <sup>c</sup>	-0.05	1				
$\text{K}^+$	0.78 <sup>b</sup>	0.42	0.49	-0.31	0.38	1			
$\text{Ca}^{2+}$	0.86 <sup>c</sup>	0.75 <sup>a</sup>	0.84 <sup>b</sup>	0.03	0.73 <sup>a</sup>	0.61	1		
$\text{Mg}^{2+}$	0.49	0.91 <sup>c</sup>	0.86 <sup>c</sup>	0.16	0.95 <sup>c</sup>	0.41	0.63 <sup>a</sup>	1	
$\text{NH}_4^+$	0.10	0.82 <sup>b</sup>	0.85 <sup>b</sup>	0.15	0.76 <sup>b</sup>	0.25	0.36	0.84 <sup>b</sup>	1

<sup>a</sup> Significant ( $p < 0.05$ ); <sup>b</sup> Significant ( $p < 0.01$ ); <sup>c</sup> Significant ( $p < 0.001$ ).

The rainwater acidity at Cairo was decreased even at high levels of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ . If all of the measured  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  in rainwater were in the form of free acids ( $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ ), this would produce lower pH values. Therefore, the high pH values were not due to the lack of acidity, but they indicated the high neutralization of the acidity by alkaline substances. These alkaline substances neutralize the acidity of rainwater before being deposited on the ground surface. High concentrations of  $\text{NH}_3$  and dust containing  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in the atmosphere of Cairo lead to increase the neutralization of acidity of rainwater. This is confirmed by the relationships between the acidic ions  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  and the major cations  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  (Tables 4 and 5) and also between the various anion and cation combinations. Significant positive correlations ( $p < 0.001$ ) were found between cation combinations ( $\text{NH}_4^+ + \text{Ca}^{2+} + \text{Mg}^{2+}$ ) and  $\text{SO}_4^{2-}$  ( $r = 0.95$  and  $0.92$  at the urban and suburban areas,

respectively) and between cation combinations and  $\text{NO}_3^-$  ( $r=0.87$  and  $0.89$  at both sites, respectively). Moreover, cation combinations were significantly correlated ( $p<0.001$ ) with the anion combinations ( $\text{SO}_4^{2-} + \text{NO}_3^-$ ) ( $r = 0.97$  and  $0.93$  at both sites, respectively). These correlations indicate that the acidity of precipitation is neutralized, and  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  play significant role in the neutralization of acidity in rainwater in Cairo. These alkaline species act as a neutralizing agent/buffer. The correlations also suggested that  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  react with  $\text{NH}_3$ , calcite and dolomite to form their salts of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ . The suspended particulate matter which is rich in carbonate/ bicarbonate of calcium, buffers the acidity of rainwater (Khemani, 1993; Kulshrestha et al., 1996). Such neutralization is frequently reported and attributed to  $\text{NH}_3$  and/or  $\text{CaCO}_3$  (Vong, 1990). Rainwater acidity can be neutralized by soil components like  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{NH}_4^+$  (Mouli et al., 2005)

Neutralization factors (NF) were calculated to evaluate the relative neutralization of rainwater by  $\text{NH}_3$ , calcite and dolomite. Neutralization factors (NF) were calculated using the following equations (Possanzini et al., 1988; Saxena et al., 1996):

$$NF_{\text{NH}_4^+} = \frac{[\text{NH}_4^+]}{2[\text{SO}_4^{2-}] + [\text{NO}_3^-]}$$

$$NF_{\text{Ca}^{2+}} = \frac{[\text{Ca}^{2+}]}{[\text{SO}_4^{2-}] + 2[\text{NO}_3^-]}$$

$$NF_{\text{Mg}^{2+}} = \frac{[\text{Mg}^{2+}]}{[\text{SO}_4^{2-}] + 2[\text{NO}_3^-]}$$

Neutralization factors (NF) were 0.17 and 0.28 for  $\text{NH}_4^+$ , 1.88 and 1.98 for  $\text{Ca}^{2+}$  and 0.52 and 0.65 for  $\text{Mg}^{2+}$  at the urban and suburban areas, respectively. The values of neutralization factors revealed that calcite is the most dominant neutralization substance and it plays a significant role in neutralizing a large fraction of the available acid in the atmosphere of Cairo. The NF for  $\text{NH}_4^+$  was less than the NF for both  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  and the acid neutralization is brought about by crustal ions, particularly calcium at urban site in Tirupati (Mouli et al., 2005). The quantification of the neutralization effect of the alkaline ions showed the prevalent role of  $\text{Ca}^{2+}$  followed by  $\text{NH}_4^+$ ,  $\text{Na}^+$  and  $\text{Mg}^{2+}$  (Tsitouridou and Anatolaki, 2007).

## SUMMARY

This study presents the results and interpretations of the chemical analysis of rainwater at two different geographical areas in greater Cairo. The chemical composition of rainwater depended on local sources. Calcium, sulfate, magnesium and chloride were the major ions in rain water at the urban and suburban areas.  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$

and  $K^+$  were of non-marine origins. The average values of pH were 6.94 at the urban area and 7.41 at the suburban area. The rainwater acidity at Cairo was decreased even at high levels of  $SO_4^{2-}$  and  $NO_3^-$ . The high pH values could not be attributed to the lack of acidity, but due to a high neutralization of the acidity of rainwater by alkaline components (ammonia gas and the carbonates of  $Ca^{2+}$  and  $Mg^{2+}$  that are contained in the suspended dust). This finding was confirmed by the positive relationships between cations and anions in the rainwater. The study indicates that the acidity of precipitation is neutralized, and suggests that  $H_2SO_4$  and  $HNO_3$  acids react with  $NH_3$ , calcite and dolomite to form their salts. Calcite is the most dominant neutralization substance in the atmosphere of Cairo, and to a lesser degree dolomite. The two types of rocks are distributed and quarried in the high ground bordering the greater Cairo from north to south and used in the cement industry.

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