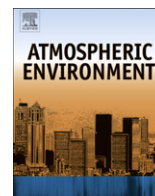




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Weekday/weekend differences in ambient aerosol level and chemical characteristics of water-soluble components in the city centre

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ABSTRACT

Weekday and weekend ambient aerosol samples were collected from the city centre of Cairo, namely “Ramsis” during the summer season of the year 2006, and have been analyzed for water-soluble ionic species. The average concentrations of the total suspended particulate matter (TSP) and their water-soluble components were higher during weekdays than on weekends, indicating that the decreased traffic density on weekends leads to a decrease in the levels of the TSP and their water-soluble ionic species. The average concentrations of the TSP were $454 \mu\text{g m}^{-3}$ on weekdays and $298 \mu\text{g m}^{-3}$ on weekends. The weekday/weekend concentration ratios were 1.52 for TSP, 1.27 for SO_4^{2-} , 1.64 for Cl^- , 1.54 for NO_3^- , 1.17 for NH_4^+ , 1.67 for Ca^{2+} , 1.83 for Na^+ , 1.75 for K^+ and 1.73 for Mg^{2+} . City centre of Cairo has high levels of the TSP and their water-soluble ionic species compared with many polluted cities in the world. Among all of the measured water-soluble components, SO_4^{2-} was the most abundant species followed by Ca^{2+} on weekdays and weekends. The average mass ratios of $\text{NO}_3^-/\text{SO}_4^{2-}$ in the TSP were 0.41 on weekdays and 0.34 on weekends, suggesting that the stationary source emissions were more predominant. The $\text{NH}_4^+/\text{SO}_4^{2-}$ molar ratios and its relation with the concentrations of TSP and Ca^{2+} during the weekdays and weekends indicate that the chemical form of sulfate and ammonium in aerosol particles varies with TSP and Ca^{2+} levels, and $\text{NH}_4^+/\text{SO}_4^{2-}$ molar ratios less than one, SO_4^{2-} in aerosol particles may be present as CaSO_4 and $(\text{NH}_4)_2\text{SO}_4 \cdot \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, whereas it is expected to be present as $(\text{NH}_4)_2\text{SO}_4$, $(\text{NH}_4)_2\text{SO}_4 \cdot \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and CaSO_4 at low levels of TSP and Ca^{2+} , and $\text{NH}_4^+/\text{SO}_4^{2-}$ molar ratios between 1 and 2. The mean pH values of the TSP were 7.65 on weekdays and 6.97 on weekends, indicating that aerosol particles brought a large amount of crustal species, and might alleviate the tendency of acidification. The relationships between the concentrations of acidic components (NO_3^- and SO_4^{2-}) and basic components (NH_4^+ , Ca^{2+} and Mg^{2+}) on weekdays and weekends indicate that the acidity of aerosol particles is neutralized. Ca^{2+} and NH_4^+ are the most dominant neutralization substances in Cairo atmosphere.

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1. Introduction

The rapid increase in the growth of population, lack of sufficient public facilities, urbanization and industrialization

processes, especially in developing countries, has led to uncontrolled growth and severe environmental deterioration. Ambient aerosol represents the most important one of air pollutant groups, since it plays a serious adverse role in the atmosphere. For example, aerosol particles and their ionic species have been observed to be responsible for the loss in visibility and for cloud formation (Sloane et al., 1991; Lee and Sequerira, 2002), and play a major role in acidification of precipitation and also affect climate (Charlson et al.,

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1992; Dockery and Pope, 1994). Ambient particulate matter may be the carrier of acidic or toxic species and may have detrimental effects on human health and ecosystems (Cheng et al., 1996). Human health endpoints associated with exposure to airborne particulate matter include increased mortality (Kunzli et al., 2000; Pope, 2000; Samet et al., 2000; Pope et al., 2002) and morbidity from respiratory and cardiopulmonary diseases (Ackermann-Lieblich et al., 1997; Sunyer, 2001).

Atmospheric aerosols are a complex mixture of anthropogenic and natural origin. They may be emitted directly or be formed in the atmosphere (Samura, 2001; Kemp, 2002). Main sources of natural atmospheric particles are volcanic activities, oceans and dust storms. Industrial activities, energy production, construction, urban waste treatment and vehicle exhausts constitute anthropogenic sources of particulate matter in the atmosphere (Sabbak, 1995; Bilos et al., 2001). Total suspended particulate matter (TSP) contains particles with aerodynamic diameter of approximately 100 μm or less (USEPA, 1999). Atmospheric aerosols are classified according to the size of particle into three modes: nuclei mode which is formed by condensation of gaseous and vapors, accumulation mode which consists of coagulation of small particles, gas-to-particle conversion and condensation vapors onto existing small particles, and coarse mode generates by bulk-to-particle conversion (Mouli et al., 2003). Atmospheric particles commonly occur in two distinct modes: the fine (<2.5 μm) mode and the coarse (2.5–10.0 μm) mode (USEPA, 1999). In urban environments, fine particles arise from anthropogenic sources, such as combustion processes including automobile exhaust and partially from gas-to-particle conversions, whereas coarse ones originate mainly from natural processes, such as wind action on land and sea surfaces (Reichhardt, 1995; Jonathan et al., 1997).

Atmospheric aerosols are an analytically matrix that contains water-soluble inorganic compounds, organic carbons, elemental carbon and metals. Among these components, water-soluble inorganic species, such as sulfate, nitrate, ammonium and chloride, are of great concern in urban air pollution problems; they control the degree of acidity of the aerosols and its effect on environmental acidification. Nitrate, sulfate and ammonium are the main compounds which defines the secondary aerosols. In the urban atmosphere, sulfate is contained in the fine mode particles, whereas the nitrate and chloride reveal a bi-modal size distribution (Kadowaki, 1976; Hara et al., 1983).

In urban areas, road traffic density and different anthropogenic activities vary substantially between weekdays and weekends. The difference between aerosol concentration levels and their chemical composition on weekdays and weekends allows us to differentiate the contribution of different sources, especially road vehicles, to the atmospheric load. Recent studies are focusing on the “weekend effect”, to compare between the particulate matter concentration levels on weekdays and weekends (Morawska et al., 2002; Blanchard and Tanenbaum, 2003; Motallebi et al., 2003; Qin et al., 2004). In Cairo, there is a lack of information on the atmospheric aerosol concentration level and the chemical characteristics of water-

soluble ionic species on weekdays and weekends. Therefore, monitoring aerosol concentration and the related chemical composition on weekdays and weekends is very important to evaluate the impact of road traffic and different anthropogenic activities on the ambient air quality of Cairo.

The aim of this study was to investigate the differences in aerosol concentration levels and chemical characteristics of water-soluble components between weekdays and weekends in the city centre of Cairo.

2. Materials and methods

2.1. Sampling site and periods

Cairo is characterized by the presence of Mokattam hills to the east and southeast, then desert area extending west and east, besides the Shoubra-El Kheima industrial area in the north and Helwan industrial area in the south of Cairo city (Fig. 1). Cairo is known as a city of heavy air pollution.

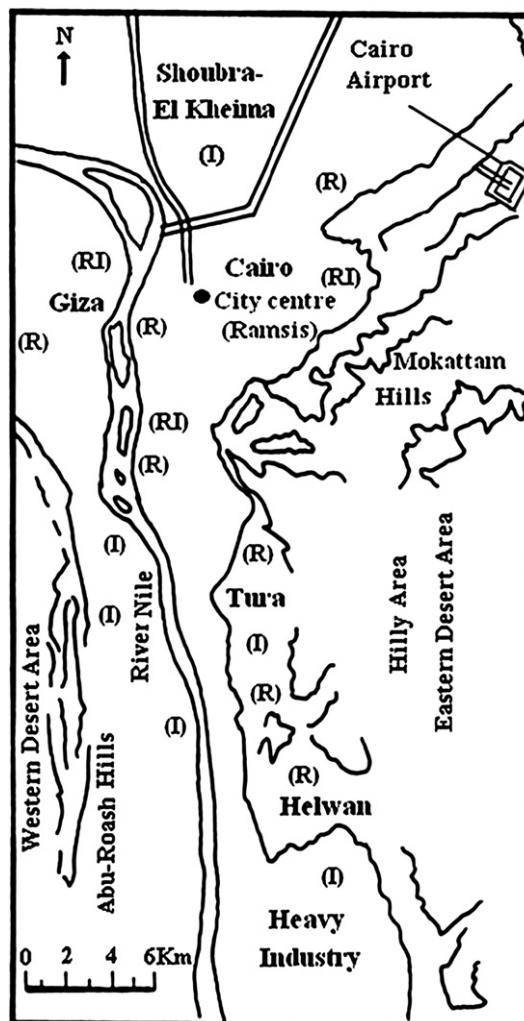


Fig. 1. Map of the greater Cairo areas showing districts of residential (R), industrial (I), residential industrial (RI) activities and the sampling site (•).

Industrial activities, heavy traffic density and the surrounding hills and desert are the main sources of suspended particulate matter in Cairo. The climate is typically Mediterranean, cold, moist and rainy winters and high temperature, high solar radiation, clear sky and dry summers. The higher photochemical reactions during the summer season due to the higher solar radiation intensity and temperature lead to an increase in the oxidation and conversion of nitrogen dioxide to nitrate and sulfur dioxide to sulfate in the atmosphere of Cairo (Khoder, 2002).

The sampling site is located in the city centre of Cairo (Ramsis), it is the busiest commercial and heaviest traffic area in Greater Cairo and most of air pollutant emissions in the vicinity of measurement site arise from traffic activities (Fig. 1). Twenty four daily (24 h) ambient aerosol samples were collected during the summer season of the year 2006 (June, July and August, i.e. 12 weeks). The samples were collected twice per week (every weekend (Friday), i.e. 12 samples and in any one of the weekdays chosen between Saturday through Thursday, i.e. 12 samples). Sampling was carried out at a height of approximately 6 m above the ground level.

2.2. Sampling and analysis

High volume air sampler, operated at a flow rate of $1.13 \text{ m}^3 \text{ min}^{-1}$, was used for the total suspended particulate (TSP) sample collection. Glass fiber filters were used to collect TSP samples. Glass fiber filter was carefully equilibrated in desiccator before and after sampling to eliminate the effect of humidity, which results in the change of weight due to the hygroscopic nature of the glass fiber filter. Mass of the TSP collected on each filter was determined by the difference in weight before and after sampling, then, the TSP concentration in air was calculated from the volume of air filtered. Field blanks were collected through putting another set of glass fiber filters in the sampling site for the same duration with the same steps without operating the high volume air sampler.

For the analysis of water-soluble components, one-quarter portion of the particulate loaded the glass fiber filters was extracted by distilled water and then filtered through a filter paper (Whatman No. 42). The water-soluble fraction was completed to a known volume, then its pH value was measured, its Na^+ , K^+ , Ca^{2+} and Mg^{2+} content were analyzed by atomic absorption spectrophotometer, 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. The mass of each water-soluble components in one-quarter portion of the particulate loaded the glass fiber filters were calculated and multiplied by four to give the total mass collected on the glass fiber filters, then the air concentration of each components ($\mu\text{g m}^{-3}$) were calculated. Based on the average

volume of air filtered, the detection limits for Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , NO_3^- and NH_4^+ were 5, 5, 3, 3, 245, 245, 2.5 and 5 ng m^{-3} , respectively. The precision, estimated from the standard deviation of repeat measurements of standards, was less than 5% for the measured ionic species. Filter blanks and field blanks were also prepared in the same manner and analyzed for both the inorganic species. Filter blanks values were found to be below the detection limits. The field blanks values were subtracted from sample determinations.

3. Results and discussion

3.1. Mass concentration of TSP in the city centre of Cairo

Weekday and weekend mass concentrations of aerosols and their related water-soluble components concentrations are given in Table 1. The average concentration of the TSP was higher during weekdays than during weekends, and the difference in mean concentration was statistically significant ($p < 0.001$). The concentrations of the TSP ranged from 300 to $580 \mu\text{g m}^{-3}$ (with an average of $454 \mu\text{g m}^{-3}$) on weekdays and from 245 to $357 \mu\text{g m}^{-3}$ (with an average of $298 \mu\text{g m}^{-3}$) on weekends. The weekdays/weekends concentration ratio of the TSP was 1.52 (Fig. 2). The TSP concentration on weekends compared with the concentration of the weekdays was reduced by 34.36%.

In the study area, TSP is mainly emitted from anthropogenic and natural sources. These sources include heavy traffic density, constructional activities, dust transported by winds from Shoubra-El Kheima industrial area in the north and Helwan industrial area in the south and natural dust transported by winds from Mokattam hills located in the east and southeast of centre of Cairo city.

The decreased TSP concentrations observed on weekends in the present study could be easily attributed to the decreased traffic density due to the official days-off of government institutions, schools and colleges. The effect of decreased traffic density during weekends did not only cause low exhaust particulate emissions, but also reduced emissions generated from tyre wears and re-suspension of street dust. In addition, the reduced emissions of nitrogen oxides (NO_x) from the traffic sources on weekends lead to a decrease in the formation of secondary aerosols (Almeida et al., 2005), which is consistent with the observation of other investigators that attributed the decrease in aerosol concentration on weekend days to the decrease in traffic density (Latha and Highwood, 2006; Lough et al., 2006; Lonati et al., 2006; Karar et al., 2006). However, although the TSP mean concentrations are lower during weekend days than during working days compared with other urban areas, the weekends TSP levels are high indicating that the emissions were not only derived from local source but some of them are transported from other sources around centre of the city.

The TSP mean concentrations on weekdays and weekends exceeded the annual average of the Egyptian Ambient Air Quality Standard ($90 \mu\text{g m}^{-3}$) (EEAA, 1995). Moreover, the daily concentrations of the TSP on weekdays and on weekends exceeded the Egyptian Ambient Air Quality

Table 1

Weekday and weekend mass concentrations ($\mu\text{g m}^{-3}$) of aerosols and their related water-soluble components in the city centre of Cairo

	Weekdays					Weekends				
	Minimum	Maximum	Median	Mean	SD	Minimum	Maximum	Median	Mean	SD
TSP	300	580	455	454	93.80	245	357	300	298	36.80
SO ₄ ²⁻	19.50	45.66	32.72	32.75	9.38	14.50	36.26	25.32	25.71	8.21
Cl ⁻	7.85	22.50	14.72	14.47	4.36	5.39	12.48	8.96	8.81	1.93
NO ₃ ⁻	7.23	20.43	13.47	13.40	3.85	5.71	11.98	8.75	8.71	2.03
NH ₄ ⁺	5.90	7.74	6.88	6.88	0.6	4.9	6.61	6.08	5.86	0.57
Ca ²⁺	9.70	31.58	18.53	18.53	6.45	7.32	15.15	11.16	11.12	2.63
Na ⁺	2.41	9.08	6.38	6.26	1.80	1.90	4.92	3.48	3.42	0.91
K ⁺	1.52	4.68	3.07	3.06	0.8	1.04	2.41	1.75	1.75	0.42
Mg ²⁺	1.31	3.79	2.53	2.51	0.65	0.80	2.18	1.48	1.45	0.36

SD: standard deviation.

Standard ($230 \mu\text{g m}^{-3}$) for 24-h during 100% of the investigated days during the period of study. Therefore, from these results, one can state that the Cairo's city centre is heavily polluted by particulate matter, compared with other similar urban centres.

3.2. Concentrations and distribution of water-soluble ions in TSP

Airborne concentrations of water-soluble inorganic ions in the TSP depend on many processes such as upwind chemical reactions, removal by wet and dry deposition, and variability in source regions. In the present study, the average concentrations of the water-soluble inorganic components were higher during weekdays than on weekends (Table 1). Statistically significant differences ($p < 0.01$) were found only between the mean concentrations of Cl⁻, NO₃⁻, NH₄⁺, Ca²⁺, Na⁺, K⁺, and Mg²⁺ on weekdays and weekends. The weekday/weekend concentration ratios were 1.27 for SO₄²⁻, 1.64 for Cl⁻, 1.54 for NO₃⁻, 1.17 for NH₄⁺, 1.67 for Ca²⁺, 1.83 for Na⁺, 1.75 for K⁺ and 1.73 for Mg²⁺ (Fig. 2). The higher concentrations of water-soluble inorganic components observed on weekdays than those observed on weekends were due to the higher weekday concentrations of the TSP.

Sulfur and nitrogen oxides introduced into the atmosphere are oxidized to sulfuric acid and nitric acid, which in turn form particulate sulfate and nitrate. Therefore, the

higher emissions of sulfur and nitrogen oxides during working days, due to higher traffic density, lead to an increase in the particulate sulfate and nitrate. The higher concentrations of crustal–mineral components on weekdays than on weekends resulted from the influence of local and regional anthropogenic activities on the generation of crustal–mineral dust, such as re-suspension of street dust by traffic and different anthropogenic activities, such as industrial processes and building construction.

Among all the water-soluble ions determined in the present study, SO₄²⁻ is the most abundant chemical components on weekdays and weekends. SO₄²⁻ accounts for about 33.47% and 38.47% of the total mass of ions, 54.02% and 59.47% of the total anion mass and 7.21% and 8.63% of the TSP concentration on weekdays and weekends, respectively (Figs. 3 and 4). From all of the other seven inorganic species, Ca²⁺ has the highest concentration and accounts for about 18.93% and 16.64% of the total mass of ions, 49.76% and 47.12% of the total cation mass and 4.08% and 3.73% of the TSP concentration on weekdays and weekends, respectively (Figs. 3 and 4). The sum mass concentration of SO₄²⁻, NO₃⁻, Ca²⁺ and NH₄⁺ accounts for about 73.12 and 76.91% of the total mass ions and 15.76% and 17.25% of the TSP concentration on weekdays and weekends, respectively. The sum mass concentration of the eight ions accounts for about 21.55% and 22.44% of the TSP concentration on weekdays and weekends, respectively. Lower mass concentrations were observed for all the

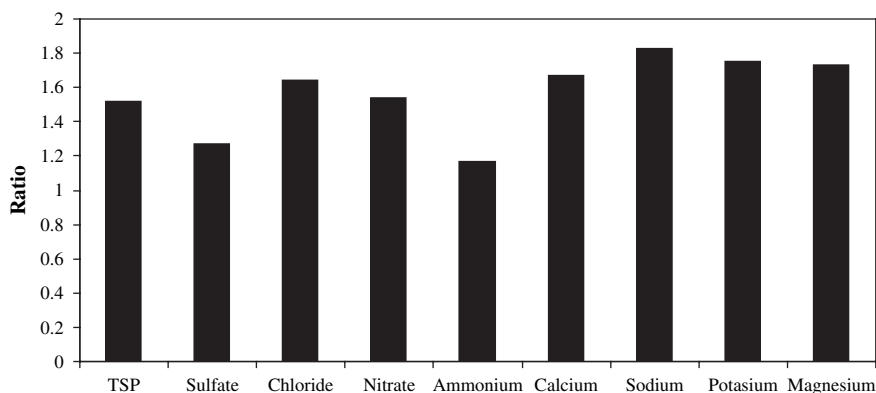


Fig. 2. Weekday/weekend concentration ratios of the TSP and their related water-soluble components in the city centre of Cairo.

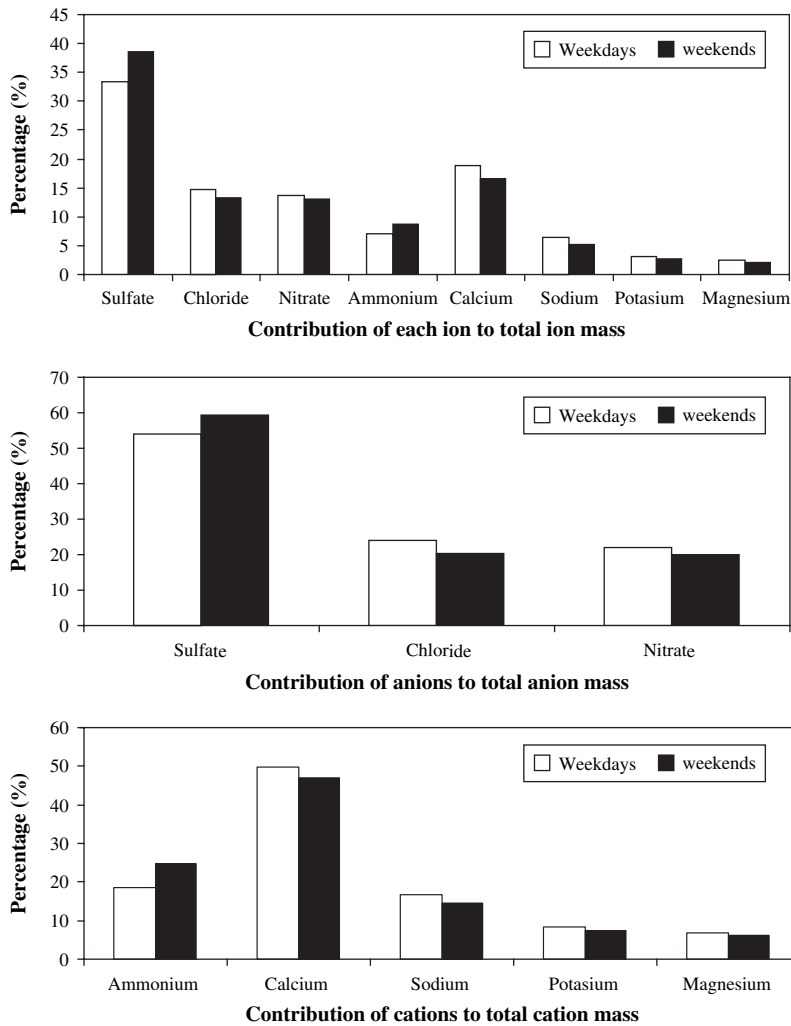


Fig. 3. The contribution of ions to total cation/anion and total ion mass in the TSP during the weekdays and weekends.

water-soluble inorganic ions on weekends relative to those found on weekdays (Table 1), while the mass percentages of SO_4^{2-} and NH_4^+ in the TSP were relatively higher on weekends (Fig. 4).

TSP is a mixture of fine and coarse particles. The fine aerosol particles have a longer residence time than the coarse particles in the atmosphere. Therefore, the relatively higher percentage of SO_4^{2-} and NH_4^+ in the TSP on weekends

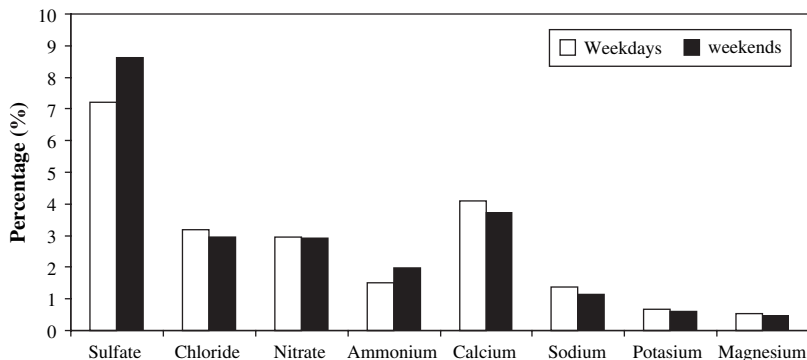


Fig. 4. Percentage of water-soluble components in the TSP during the weekdays and weekends.

relative to those on weekdays may be attributed to the existence and association between SO_4^{2-} and NH_4^+ in the fine aerosol particles. Consistent with the observation of previous investigators, sulfate and ammonium were the most abundant in fine particles, whereas nitrate and sodium were found in both fine and coarse particles (Cabada et al., 2004; Wang et al., 2006a).

3.3. Comparison of TSP and their water-soluble components levels in the city centre of Cairo with other cities in the world

The mass concentrations of the TSP and the related ionic species on weekdays and weekends in the city centre of Cairo were compared with those found in different locations over the world (Gao et al., 1996; Kocak et al., 1997; Li et al., 1997; Fang et al., 2002; Kim et al., 2002; Mouli et al., 2003; Xiao and Liu, 2004; Wang et al., 2006b; Wen and Fang, 2007 and Hegde et al., 2007). As shown in Table 2, it could be seen clearly that the TSP mean concentrations on weekdays and weekends in Cairo city centre were much higher when compared with those reported in other cities over the world. The average SO_4^{2-} concentrations in Cairo city centre on weekdays and weekends were much higher than those found in other cities except those found in Guangzhou, China and Taichung Harbor, Taiwan. This is due to the heavy traffic and other anthropogenic and natural sources around the city centre of Cairo. Shoubra El-Khema industrial area in the north and the Helwan industrial area with its huge cement factories located in the south, in addition to the erosion of Mokattam hills in the east of the city centre of Cairo, which contains some gypsum deposits; lead to an increase in the particulate sulfate in the atmosphere of the city centre of Cairo.

Generally, soil is considered to be the main source of Ca^{2+} , Mg^{2+} and K^+ . The average Ca^{2+} concentrations on weekdays and weekends in Cairo city centre were higher than those found in other cities (Table 2), which may be due to the dust transported from Mokattam hills, which is rich by calcite (Sowelim, 1983), and Ca^{2+} emitted from cement industry by the winds. Weekdays K^+ concentration in the city centre of Cairo was much higher than those found in other cities, whereas the weekends concentration is higher than those found in most of other cities except that found in

Guangzhou, China. The average concentrations of Mg^{2+} and Na^+ on weekdays and weekends were much higher than those found in most of the other cities except those found in Taichung Harbor and WcChi Traffic, Taiwan. Weekdays Cl^- concentration in the city centre of Cairo was much higher than those found in other cities. In Cairo city centre, weekdays concentration of NO_3^- was relatively lower than that found in Shanghai, China and higher than those found in other cities. Weekdays concentrations of NH_4^+ in Cairo city centre was higher than those found in most other cities except those found in Guangzhou, China and Taichung Harbor and WcChi Traffic, Taiwan. Generally, the mass concentration of the TSP and the related ionic species is more serious in Cairo city centre and at high range among the comparable cities over the world.

3.4. Source identification by $\text{NO}_3^-/\text{SO}_4^{2-}$ ratio

Nitrogen oxides emissions from mobile sources are an important contributor to particulate NO_3^- in the atmosphere. Therefore, the mass ratio of $\text{NO}_3^-/\text{SO}_4^{2-}$ has been used as an indicator of the relative importance of stationary vs. mobile sources of sulfur and nitrogen in the atmosphere (Arimoto et al., 1996; Yao et al., 2002; Xiao and Liu, 2004). Arimoto et al. (1996) ascribed high $\text{NO}_3^-/\text{SO}_4^{2-}$ mass ratio to the predominance of mobile source over stationary source of pollutants.

In the present study, the average mass ratios of $\text{NO}_3^-/\text{SO}_4^{2-}$ were 0.41 on weekdays and 0.34 on weekends. The relatively higher mass ratio of $\text{NO}_3^-/\text{SO}_4^{2-}$ on weekdays relative to that on weekends may be due to the higher traffic density on weekdays. Generally, the mass ratio of $\text{NO}_3^-/\text{SO}_4^{2-}$ in the TSP was lower than 1 in the city centre of Cairo, suggesting that the stationary source emissions are more predominant. The average mass ratio of $\text{NO}_3^-/\text{SO}_4^{2-}$ on weekdays was relatively similar to that found in Shanghai (0.43; Yao et al., 2002). During weekends, the mass ratio is relatively similar to that found in Qingdao (0.35; Hu et al., 2002). The mass ratios of $\text{NO}_3^-/\text{SO}_4^{2-}$ in the TSP at the city centre of Cairo during weekdays and weekends were higher than those reported in Taiwan (0.2; Fang et al., 2002) and Guiyang (0.13; Xiao and Liu, 2004), whereas they were lower than those found in Beijing

Table 2

Mass concentrations ($\mu\text{g m}^{-3}$) of aerosols and their related water-soluble inorganic ions at different sites all over the world

Site	Mass	SO_4^{2-}	Cl^-	NO_3^-	NH_4^+	Ca^{2+}	Na^+	K^+	Mg^{2+}	Reference
City centre of Cairo, Egypt (Weekdays)	454	32.75	14.47	13.40	6.88	18.53	6.26	3.06	2.51	Present study
City centre of Cairo, Egypt (Weekends)	298	25.71	8.81	8.71	5.86	11.12	3.42	1.75	1.45	Present study
Shanghai, China	230.50	17.83	8.06	14.19	5.68	6.98	1.90	1.13	0.67	Wang et al. (2006b)
Guangzhou, China	223.00	43.68	5.13	9.59	8.49	6.71	1.65	2.47	0.58	Gao et al. (1996)
Tirupati, South India	55.64	2.48	0.23	0.84	0.77	0.38	0.75	0.21	0.05	Mouli et al. (2003)
Guiyang, China	153.60	22.34	0.89	3.03	3.81	5.29	NR	NR	0.60	Xiao and Liu (2004)
Taiwan	172.00	12.60	3.73	6.00	5.82	1.83	2.79	0.81	0.82	Fang et al. (2002)
Dalian, China	91.40	11.70	3.14	9.14	3.01	NR	2.20	NR	0.37	Li et al. (1997)
Xiamen, China	182.00	18.19	1.78	3.87	1.34	8.11	0.87	0.66	0.50	Gao et al. (1996)
Cheju, Korea	NR	3.41	2.09	1.97	0.76	0.11	1.40	0.17	0.03	Kim et al. (2002)
Erdeмли, Turkey	NR	7.50	4.63	3.34	2.22	2.66	2.87	0.30	0.44	Kocak et al. (1997)
Taichung Harbor, Taiwan	NR	26.76	9.21	9.40	11.85	10.50	6.62	NR	3.85	Wen and Fang (2007)
WuChi Traffic, Taiwan	NR	23.31	7.10	10.07	8.17	10.44	6.05	NR	3.51	Wen and Fang (2007)
Mangalora, India	53.00	1.70	1.40	0.31	0.64	0.33	1.20	0.16	0.10	Hegde et al. (2007)

Bold indicates the relatively higher values. NR: not reported.

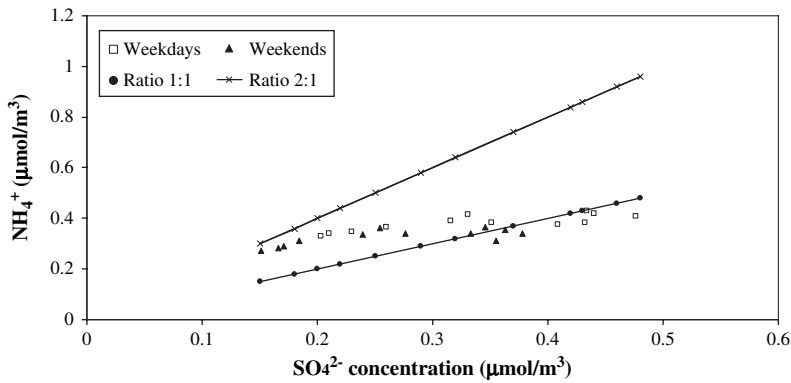


Fig. 5. Scatter plot of NH_4^+ and SO_4^{2-} concentration during the weekdays and weekends. Note: Ratios of 1:1 and 2:1 indicate the theoretical molar $\text{NH}_4^+/\text{SO}_4^{2-}$ ratio of NH_4HSO_4 and $(\text{NH}_4)_2\text{SO}_4$, respectively.

during 2001–2003 (0.71; Wang et al., 2005), Shanghai (0.83; Wang et al., 2006b), Beijing during 1999–2000 (0.58; Yao et al., 2002).

3.5. Relationship of $\text{NH}_4^+/\text{SO}_4^{2-}$ molar ratio with TSP and water-soluble Ca^{2+} level

From the concentration value of ionic species in the TSP and the ratios of these concentrations, we can get some information about the relationship of different ions and estimate the chemical form of ionic species. In the present study, the $\text{NH}_4^+/\text{SO}_4^{2-}$ molar ratios ranged from 0.85 to 1.62 on weekdays and from 0.87 to 1.80 on weekends. Fig. 5 shows the scatter plot of NH_4^+ and SO_4^{2-} data. From this figure, it can be noticed that with reference to the theoretical molar ratio of 1:1 for NH_4HSO_4 and 2:1 for $(\text{NH}_4)_2\text{SO}_4$, the weekdays and weekends data point out a fall in two regions and hence can be classified in two groups. The first group contains samples with $\text{NH}_4^+/\text{SO}_4^{2-}$ molar ratios ranges from 1.00 to 1.62 on weekdays and from 1.00 to 1.80 on weekends, scattering between 1:1 and 2:1 theoretical lines in Fig. 5. This case cannot be accounted for by the existence of NH_4HSO_4 or $(\text{NH}_4)_2\text{SO}_4$ alone, but probably by both. The simplified hypothesis for the existence of NH_4HSO_4 is assumed for a $\text{NH}_4^+/\text{SO}_4^{2-}$

molar ratio of one. Querol et al. (1998) proposed the presence of $(\text{NH}_4)_2\text{SO}_4 \cdot \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ for $\text{NH}_4^+/\text{SO}_4^{2-}$ molar ratio close to one, based on the XRD (X-ray diffraction) observation. The laboratory experimental simulation results indicate that in the presence of calcium carbonate, $(\text{NH}_4)_2\text{SO}_4$ can be converted to $(\text{NH}_4)_2\text{SO}_4 \cdot \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and further to CaSO_4 within 2–6 days (Mori et al., 1998). Duan et al. (2003) reported that the $\text{NH}_4^+/\text{SO}_4^{2-}$ molar ratio between 1:1 and 2:1 theoretical lines indicate the presence of sulfate in aerosol particles as $(\text{NH}_4)_2\text{SO}_4$, $(\text{NH}_4)_2\text{SO}_4 \cdot \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and CaSO_4 . In the present study, the second group consists of weekdays and weekends samples whose $\text{NH}_4^+/\text{SO}_4^{2-}$ molar ratios are less than one, which deviate from and scatter below the 1:1 theoretical line, indicating that sulfate may present as CaSO_4 and $(\text{NH}_4)_2\text{SO}_4 \cdot \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Consistent with the observation of previous investigator, the $\text{NH}_4^+/\text{SO}_4^{2-}$ molar ratios less than one could be explained by the combination of sulfate with calcium to form CaSO_4 and with ammonium and calcium to form $(\text{NH}_4)_2\text{SO}_4 \cdot \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (Duan et al., 2003).

The relationship between the TSP levels and $\text{NH}_4^+/\text{SO}_4^{2-}$ molar ratios during weekdays and weekends is represented graphically in Fig. 6. From this figure, it can be noticed that, significant negative correlation coefficients ($p < 0.001$)

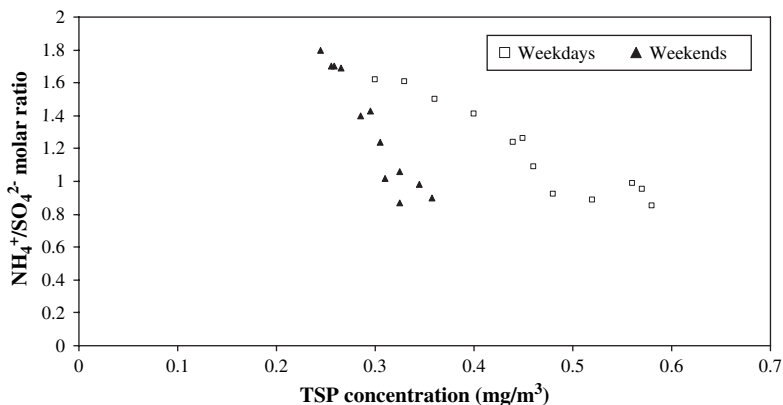


Fig. 6. Relationship between the TSP concentration and $\text{NH}_4^+/\text{SO}_4^{2-}$ molar ratio during the weekdays and weekends.

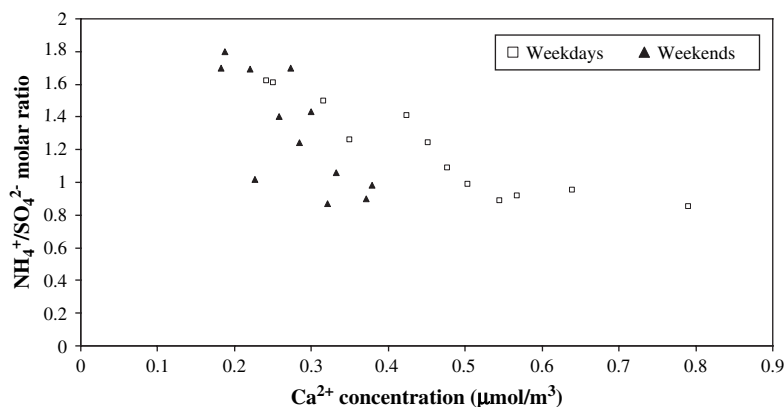


Fig. 7. Relationship between water-soluble calcium concentration and $\text{NH}_4^+/\text{SO}_4^{2-}$ molar ratio during the weekdays and weekends.

were found between the concentration of the TSP and $\text{NH}_4^+/\text{SO}_4^{2-}$ molar ratio ($r = -0.95$ on weekdays and $r = -0.96$ on weekends). This result indicates that at higher TSP level the importance of $(\text{NH}_4)_2\text{SO}_4$ in TSP is reduced, whereas other chemical forms of sulfate, such as $(\text{NH}_4)_2\text{SO}_4 \cdot \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and CaSO_4 are shown up.

Fig. 7 illustrates the relationship between the concentration of water-soluble calcium and $\text{NH}_4^+/\text{SO}_4^{2-}$ molar ratio during weekdays and weekends. Significant negative correlation coefficients were found between the concentration of water-soluble calcium and $\text{NH}_4^+/\text{SO}_4^{2-}$ molar ratio ($r = -0.91$, $p < 0.001$ on weekdays and $r = -0.77$, $p < 0.01$ on weekends). These negative correlation coefficients indicate that sulfates other than $(\text{NH}_4)_2\text{SO}_4$, such as $(\text{NH}_4)_2\text{SO}_4 \cdot \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and CaSO_4 , are present at higher water-soluble calcium levels. These results are in agreement with Duan et al. (2003) who concluded that the negative correlation between $\text{NH}_4^+/\text{SO}_4^{2-}$ molar ratio with the concentrations of the TSP and water-soluble calcium in aerosol particles indicates that the importance of $(\text{NH}_4)_2\text{SO}_4$ is reduced, whereas other sulfates, such as $(\text{NH}_4)_2\text{SO}_4 \cdot \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and CaSO_4 are shown up.

3.6. Correlation between ionic species in TSP

Correlation coefficients between the ionic concentrations of the TSP during weekdays and weekends are presented in Table 3. Significant positive correlation coefficients were found between the concentrations of Ca^{2+} and SO_4^{2-} , Mg^{2+} and SO_4^{2-} , and Na^+ and SO_4^{2-} on weekdays and weekends. These relationships could be explained by the reaction of H_2SO_4 , results from the oxidation of atmospheric SO_2 , with alkaline components of aerosols rich in Ca^{2+} , Mg^{2+} and Na^+ . SO_2 or H_2SO_4 can react with aqueous carbonates such as dissolved CaCO_3 and MgCO_3 on soil particles to form a coarse mode sulfate (De Bock et al., 1994). Buttler (1988) found conversion rates of CaCO_3 to CaSO_4 of up to 20% per day from ambient SO_2 at a rural site in the USA.

The concentration of SO_4^{2-} was also found to be significantly positively correlated with NH_4^+ concentration during both weekdays and weekends (Table 3), suggesting neutralization by ammonia gas. The significant positive

correlation coefficients between each other of SO_4^{2-} , Ca^{2+} and NH_4^+ concentrations indicate that the forms of $(\text{NH}_4)_2\text{SO}_4$ and/or NH_4HSO_4 and CaSO_4 are existed in the TSP. Strong positive correlation coefficient between SO_4^{2-} and NH_4^+ concentration indicate that SO_4^{2-} is present as $(\text{NH}_4)_2\text{SO}_4$ and/or NH_4HSO_4 (Almeida et al., 2006).

In the present study, insignificant positive correlation coefficients were found between NH_4^+ and NO_3^- , whereas significant positive correlation coefficients were found between Ca^{2+} and NO_3^- , Mg^{2+} and NO_3^- , and Na^+ and NO_3^- concentrations during weekdays and weekends (Table 3). In Cairo, the summer season is characterized by high temperature. Therefore, the fine mode nitrate (NH_4NO_3) is volatilized and forms gaseous nitric acid and ammonia gas. A portion of the nitric acid which is volatilized from the fine mode nitrate particles is adsorbed by the coarse particles with alkaline components of mineral aerosols, and form the coarse mode nitrate through the gas-to-particle reaction, such as $\text{Ca}(\text{NO}_3)_2$, $\text{Mg}(\text{NO}_3)_2$ and NaNO_3 . Nitrate mainly

Table 3

Correlation coefficients between the ionic concentrations of the TSP during the weekdays and weekends in the city centre of Cairo

	SO_4^{2-}	Cl^-	NO_3^-	NH_4^+	Ca^{2+}	Na^+	K^+	Mg^{2+}
Weekdays								
SO_4^{2-}	1							
Cl^-	0.66 ^a	1						
NO_3^-	0.64 ^a	0.69 ^a	1					
NH_4^+	0.82 ^b	0.58	0.46	1				
Ca^{2+}	0.92 ^c	0.68 ^a	0.80 ^b	0.67 ^a	1			
Na^+	0.75 ^b	0.80 ^b	0.86 ^b	0.56	0.87 ^c	1		
K^+	0.73 ^a	0.54	0.4	0.61 ^a	0.63 ^a	0.63 ^a	1	
Mg^{2+}	0.86 ^b	0.82 ^b	0.76 ^b	0.72 ^a	0.91 ^c	0.89 ^c	0.72 ^a	1
Weekends								
SO_4^{2-}	1							
Cl^-	0.70 ^a	1						
NO_3^-	0.55	0.49	1					
NH_4^+	0.74 ^a	0.45	0.36	1				
Ca^{2+}	0.81 ^b	0.70 ^a	0.70 ^a	0.69 ^a	1			
Na^+	0.75 ^b	0.61 ^a	0.49	0.64 ^a	0.91 ^c	1		
K^+	0.75 ^b	0.25	0.47	0.70 ^a	0.71 ^a	0.69 ^a	1	
Mg^{2+}	0.68 ^a	0.46	0.85 ^b	0.47	0.74 ^a	0.75 ^b	0.53	1

^a Significant ($p < 0.05$).

^b Significant ($p < 0.01$).

^c Significant ($p < 0.001$).

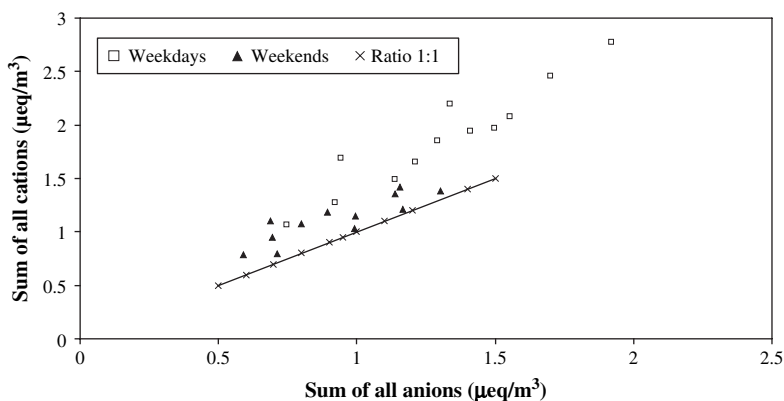


Fig. 8. Comparison between the sum of all cations and that of all anions in equivalent value during the weekdays and weekends.

exists in coarse particles together with alkaline ions, such as calcium and potassium (Hayami and Carmichael, 1998; Wu and Okada, 1994). The correlation among NO_3^- , Mg^{2+} and Ca^{2+} suggests a nitrate salt formation on coarse particle (Bourotte et al., 2007).

Lack of strong positive correlation coefficients were found between SO_4^{2-} and NO_3^- concentrations ($r=0.64$ on weekdays and $r=0.55$ on weekends, Table 3). This may be attributed to the effect of different sources of SO_4^{2-} other than traffic sources, such as Shoubra-El Kheima industrial area in the north, Mokattam hills in the east and southeast, and cement factories in the south of Cairo city centre.

3.7. The acidity of TSP

3.7.1. Equivalent concentrations of total cations and anions

The ratios of the sum of the equivalent concentration ($\mu\text{eq m}^{-3}$) of cations to anions in the TSP on weekdays and weekends were calculated. The ratios calculated from all the measured ionic species on weekdays samples ranged from 1.31 to 1.79 (with an average of 1.43). For weekend samples, the ratios ranged from 1.10 to 1.59 (with an average of 1.23). The comparison between the sum of the equivalent concentrations of all cations and that of all anions in the TSP on weekdays and weekends are represented in Fig. 8. As it can be seen, linear relationships are obvious, with significant positive correlation coefficients ($p < 0.001$) between the sum of the equivalent concentrations of all cations and that of all anions ($r=0.95$ on weekdays and $r=0.87$ on weekends), in parallel with the theoretical line of 1:1. The deviation to the upper side of the theoretical line indicates a deficiency of anions, since bicarbonate, organic ions (formate and acetate), F^- , NO_2^- , PO_4^{3-} and Br^- were not determined in the present study.

3.7.2. pH

The pH of the TSP filtrate is a parameter to directly denote the acidity of the atmospheric particulate matter. The mean pH value of the TSP in the city centre of Cairo was 7.65 on weekdays and 6.97 on weekends. This means that

the mean value of pH of the TSP during weekends was slightly less than that on weekdays, suggesting that the acidity of water-soluble fraction on weekends was slightly stronger than that on weekdays. Compared with the blank value of 5.65, aerosol particles in the atmosphere of the city centre of Cairo brought a large amount of crustal species, and might alleviate the tendency of acidification of the atmospheric particulate matter during both weekdays and weekends.

3.7.3. Neutralization factors

In order to know the neutralization of acidic components of aerosol by crustal components and ammonia, neutralization factors (NF) for NH_4^+ , Ca^{2+} and Mg^{2+} have been calculated using the following formula (Saxena et al., 1996):

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

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

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

In weekday and weekend TSP samples, the order of NF is $\text{Ca}^{2+} > \text{NH}_4^+ > \text{Mg}^{2+}$ (Table 4). This feature suggests that the major neutralization of acidic components of aerosols in the atmosphere of the city center of Cairo during weekdays and weekends had occurred by Ca^{2+} and NH_4^+ .

Table 4
Neutralization factors for NH_4^+ , Ca^{2+} and Mg^{2+}

	NH_4^+	Ca^{2+}	Mg^{2+}
Weekdays	0.24	0.83	0.18
Weekends	0.27	0.68	0.14

4. Conclusion

Weekday/weekend differences in ambient aerosol concentration level and chemical characteristics of water-soluble components during the summer season of the year 2006 in the city centre of Cairo (Ramsis) have been discussed in this work. Daily concentrations of the TSP ranged from 300 to 580 $\mu\text{g m}^{-3}$ (with an average of 454 $\mu\text{g m}^{-3}$) on weekdays and from 245 to 357 $\mu\text{g m}^{-3}$ (with an average of 298 $\mu\text{g m}^{-3}$) on weekends. The daily concentrations of the TSP on weekdays and weekends exceeded the Egyptian Ambient Air Quality Standard for 24-h during 100% of the investigated days during the period of study. The average concentrations of water-soluble inorganic components were higher during weekdays than on weekends. Among all of the measured water-soluble components, SO_4^{2-} was the most abundant species followed by Ca^{2+} on both weekdays and weekends. The average mass ratios of $\text{NO}_3^-/\text{SO}_4^{2-}$ in the TSP were 0.41 on weekdays and 0.34 on weekends. The chemical form of sulfate and ammonium in aerosol particles varies with TSP and Ca^{2+} levels. At high TSP and Ca^{2+} levels, and $\text{NH}_4^+/\text{SO}_4^{2-}$ molar ratios less than one, SO_4^{2-} in aerosol particles may be present as CaSO_4 and $(\text{NH}_4)_2\text{SO}_4 \cdot \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, whereas it is expected to be present as $(\text{NH}_4)_2\text{SO}_4$, $(\text{NH}_4)_2\text{SO}_4 \cdot \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and CaSO_4 at low levels of the TSP and Ca^{2+} , and $\text{NH}_4^+/\text{SO}_4^{2-}$ molar ratios between 1 and 2. The mean pH values of the TSP were 7.65 on weekdays and 6.97 on weekends, indicating that aerosol particles might alleviate the tendency of acidification. The relationships between the concentrations of acidic components and basic components on weekdays and weekends indicate that the acidity of aerosol particles is neutralized. The major neutralization of acidic components of aerosols in the atmosphere of the city center of Cairo during weekdays and weekends had occurred by Ca^{2+} and NH_4^+ .

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