



Atmospheric conversion of sulfur dioxide to particulate sulfate and nitrogen dioxide to particulate nitrate and gaseous nitric acid in an urban area

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Abstract

Sulfur dioxide, nitrogen dioxide, particulate sulfate and nitrate, gaseous nitric acid, ozone and meteorological parameters (temperature and relative humidity) were measured during the winter season (1999–2000) and summer season (2000) in an urban area (Dokki, Giza, Egypt). The average particulate nitrate concentrations were 6.20 and 9.80 $\mu\text{g m}^{-3}$, while the average gaseous nitric acid concentrations were 1.14 and 6.70 $\mu\text{g m}^{-3}$ in the winter and summer seasons, respectively. The average sulfate concentrations were 15.32 $\mu\text{g m}^{-3}$ during the winter and 25.10 $\mu\text{g m}^{-3}$ during the summer season. The highest average concentration ratio of gaseous nitric acid to total nitrate was found during the summer season. Particulate sulfate and nitrate and gaseous nitric acid concentrations were relatively higher in the daytime than those in the nighttime. Sulfur conversion ratio (F_s) and nitrogen conversion ratio (F_n) defined in the text were calculated from the field measurement data. Sulfur conversion ratio (F_s) and nitrogen conversion ratio (F_n) in the summer were about 2.22 and 2.97 times higher than those in the winter season, respectively. Moreover, sulfur conversion ratio (F_s) and nitrogen conversion ratio (F_n) were higher in the daytime than those in the nighttime during the both seasons. The sulfur conversion ratio (F_s) increases with increasing ozone concentration and relative humidity. This indicates that the droplet phase reactions and gas phase reactions are important for the oxidation of SO_2 to sulfate. Moreover, the nitrogen conversion ratio (F_n) increases with increasing ozone concentration, and the gas phase reactions are important and predominant for the oxidation of NO_2 to nitrate.

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1. Introduction

Atmospheric chemical reactions transform primary pollutants into secondary air pollutants. The oxidation of sulfur dioxide and nitrogen dioxide and their conversion to particulate sulfate, and gaseous and particulate nitrates are important characteristic of urban air photochemistry. The conversion mechanisms and rates

for the formation of sulfate and nitrates in the atmosphere are of considerable interest. Because the conversion rates are important factors in controlling the concentrations of nitrate and sulfate. Moreover, the rate of the conversion of nitrogen oxides to nitrate affects ozone formation and ultimate fate of the nitrogen oxides in the atmosphere. The environmental effects of these secondary pollutants are associated with acidification of precipitation, visibility reduction and have deleterious effects on human health.

Sulfur dioxide is oxidized to sulfate and the oxidation rate determines its lifetime in the atmosphere. Sulfuric

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acid is produced from the oxidation of sulfur oxides, which in turn form sulfate particles (Matsumoto and Tanaka, 1996). Secondary sulfate aerosol occurs predominantly in the accumulation mode; diameter between 0.1 and 1.0 μm (Altshuller, 1982).

Atmospheric oxidation of SO_2 occurs by both heterogeneous and homogeneous paths and the oxidation rate is increased with increasing relative humidity through both paths involving OH production (Sander and Seinfeld, 1976). A large fraction of SO_2 is converted by heterogeneous reaction: $\text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_3$, and the sulfite is oxidized either directly by reaction with ozone and H_2O_2 or by reaction with catalytic metals (Monn and Schaeppi, 1993). They added that SO_2 can be converted directly to H_2SO_4 after reaction with the OH radical or H_2O_2 . Sulfur dioxide is oxidized to H_2SO_4 by homogeneous gas phase reactions followed by condensation of the H_2SO_4 both onto preexisting particles and into new particles with partial neutralization by NH_3 (Huntzicker et al., 1984). Sulfate is generated as H_2SO_4 mist by the homogeneous nucleation processes in the H_2SO_4 – H_2O system, followed by the transition to $(\text{NH}_4)_2\text{SO}_4$ and/or NH_4HSO_4 through reaction with gaseous NH_3 (Matsumoto et al., 1998). The droplet phase reactions are important for the oxidation of SO_2 to sulfate in the atmosphere (Kadowaki, 1986).

Sulfur dioxide can be converted to sulfur trioxide (SO_3) in the atmosphere by the gas phase oxidation of SO_2 by OH and peroxy radicals (Calvert and Stockwell, 1984). The reaction rate of $\text{SO}_3 + \text{H}_2\text{O}$ in the gas phase was generally considered to be very fast in the study of sulfuric acid formation process in the atmosphere (Castleman et al., 1975; Viggiano and Arnold, 1983; Toon et al., 1987). On the other hand, Wang et al. (1988) found that the reaction of $\text{SO}_3 + \text{H}_2\text{O}$ is quite slow in the gas phase. The reaction rate constant of $\text{SO}_3 + \text{NH}_3$ is more than 4 orders of magnitude larger than that of $\text{SO}_3 + \text{H}_2\text{O}$ in the gas phase (Shen et al., 1990).

The lifetime of nitrogen oxides in the troposphere ranges from less than one day in the summer at mid-latitudes to several days in the absence of active photochemistry (Logan, 1983; Liu et al., 1987). The actual NO_x removal rate is dependent on the degree of photochemical activity and it will vary from day to day (Chang et al., 1979). Nitrogen oxides are oxidized to nitric acid in the atmosphere, which in turn form the nitrate particles (Matsumoto and Tanaka, 1996).

Nitric acid is formed through either the homogeneous reaction of NO_2 with the OH radical, reaction of NO_3 with aldehydes or hydrocarbons or hydrolysis of N_2O_5 in the atmosphere (Richards, 1983; Russell et al., 1986). During daytime, the reaction of NO_2 with OH radical is important, whilst, N_2O_5 hydrolysis is believed to become an important source of HNO_3 during night (Russell et al., 1986). The fate of nitric acid is controlled by reaction with NH_3 and dry deposition (Harrison

et al., 1989; Harrison and Kitto, 1990). The prime influence upon nitric acid concentrations is expected to be ambient temperature, relative humidity and ammonia concentrations at sites where NH_4NO_3 is formed (Allen et al., 1989).

Most of the nitrate reveal a bimodal size distribution in urban atmosphere (Kadowaki, 1976; Hara et al., 1983). Ambient nitrates are considered to consist of NH_4NO_3 and NaNO_3 , and have sharp monomodal peaks in fine and coarse particles ranges, respectively (Yoshizumi and Hoshi, 1985). The majority of the NO_3^- mass was found in the accumulation mode (Appel et al., 1978; Countess et al., 1980). On the other hand, Mehlmann and Warneck (1995) reported that particulate nitrate existed mainly in the coarse size range. Inorganic aerosol nitrate formation is limited by the availability of NH_3 (Blanchard et al., 2000). Ammonium nitrate is unstable under normal atmospheric conditions, existing in the reversible phase equilibria with gaseous precursors (Matsumoto and Tanaka, 1996). The dissociation constant of the equilibria depends on the temperature, relative humidity and chemical composition of the aerosols and gases (Stelson and Seinfeld, 1982a,b; Matsumoto and Tanaka, 1996).

The main objectives of the present study are (i) to provide quantitative information on the concentrations of particulate sulfate and nitrate, and gaseous nitric acid during the winter and summer seasons, (ii) to calculate the sulfur and nitrogen conversion ratios during the period of study, and (iii) to understand the role of ozone and relative humidity on the oxidation of SO_2 and NO_2 , and their conversion ratios in urban air.

2. Materials and methods

2.1. Sampling site and periods

A narrow strip of Giza Governorate, runs along the western side of the Nile, opposite to the city of Cairo. Greater Cairo (Cairo, Giza and Shoubra El-Khiema) houses over 11.3 millions inhabitants and most of the polluting activities in the country. Consequently, Greater Cairo is one of the most polluted megacities in the world due to the emission of about 52% of the industries in Egypt, about 40% of electricity generated from thermal power station and more than 1.3 millions vehicles running in Cairo street (Nasralla, 2001). This high rate of emission coupled with low wind speeds and the frequent inversions in the area resulted in high local pollution load. All samples were collected from a point approximately 30 m above the ground level at the National Research Centre in the urban area of Giza (Dokki).

Daily samples were collected during the winter season, 1999–2000, (December, January and February) and

the summer season 2000 (June, July and August). Samples were collected for 24 h. On the other hand, only during six days (two days every month) the samples were collected daytime and nighttime separately during both seasons.

2.2. Sampling and analysis procedures

For atmospheric particulate sulfate and nitrate, and gaseous nitric acid, a calibrated vacuum pump was used to draw 4 l min⁻¹. Air was drawn through the filter holder containing PTFE membrane filter (0.2 µm pore size and 37 mm diameter) to collect particulate sulfate and nitrate, followed by the impregnated filter (Whatman no. 41 cellulose filter impregnated in 5% aqueous analar NaCl solution) to collect gaseous nitric acid according to the procedure of Harrison and Perry (1986) and Kaneyasu et al. (1995). This method when applied for long sampling times, the appearance of artifacts on the separation of gaseous and particulate nitrate is inevitable (Forrest et al., 1980; Appel et al., 1981). The most probable effect could be the dissipation of NH₄-NO₃ from the filter due to volatilization. This influences the gas sampling results of the NaCl impregnated filter pack. However, Kadowaki (1986) found that the error in the gaseous nitrate concentrations from the volatilization of NH₄NO₃ from the filter to form HNO₃ during air sampling is very small. The amount of total nitrate (NO₃⁻ retained on the PTFE prefilter plus HNO₃ trapped on the NaCl impregnated filter) is preserved, regardless of the volatilization of nitrate on the PTFE filter.

After sampling time, the components on the exposed and impregnated filters were extracted in distilled water. Nitrate collected on PTFE filter and NaCl impregnated filter was determined by the method of Harrison and Perry (1986). Nitrate was reduced to nitrite by copper-catalyzed reduction with hydrazine sulfate in alkaline solution. The reduced nitrate (NO₂⁻) was determined by diazotization with sulfanilamide and coupling with *N*-(1-naphthyl)-ethylenediamine dihydrochloride to form highly colored azo dye. The absorbance of the sample was determined spectrophotometrically at 540 nm against the reagent blank. The nitrate content was determined from the calibration standard curve and then the air concentration of nitrate (µg m⁻³) was calculated. Nitrite was determined separately without reduction, and the value was subtracted from the total nitrate and nitrite as analyzed after reduction. The detection limit for nitrate was about 0.02 µg m⁻³ for 24 h sampling. The relative standard deviation (RSD) for replicate analyses of the calibration standard was 3%. Sulfate was determined by turbidimetric method (Harrison and Perry, 1986). One ml of 10 N HCl followed by 4 ml of glycerol–alcohol solution were added to the sample and blank, and mixed. A constant measure (0.5 spoon spatula) of

barium chloride crystals was added and allowed to stand for exactly 40 min. The absorbance of the BaSO₄ suspension was measured at 500 nm by a spectrophotometer against the reagent blank. The SO₄²⁻ concentration was determined directly from the calibration standard curve and the air concentration of SO₄²⁻ (µg m⁻³) was calculated. The detection limit for sulfate was about 1.74 µg m⁻³ for 24 h sampling. The RSD for replicate analyses of the calibration standard was 5%.

In the present study, SO₂, NO₂, ozone, relative humidity and temperature were measured only in the periods of particulate sulfate and nitrate, and gaseous nitrate sampling. The NO₂ and SO₂ gases were collected using a calibrated vacuum pump to draw 0.5 l min⁻¹. Nitrogen dioxide was collected by bubbling air through a sodium hydroxide–sodium arsenite solution to form a stable solution of sodium nitrite (Harrison and Perry, 1986). The nitrite ion produced during sampling is reacted with phosphoric acid, sulfanilamide and *N*-(1-naphthyl)-ethylenediamine dihydrochloride to form an azo dye and then the absorbance of the sample against the reagent blank was measured at 540 nm by a spectrophotometer. The air concentration of NO₂ (µg m⁻³) was calculated from the calibration standard curve and volume of air. The detection limit for NO₂ was about 4 µg m⁻³ for 24 h sampling. The RSD for replicate analyses of the calibration standard was 3%. West and Gaeke (colorimetric) method is used for determination of SO₂ (Harrison and Perry, 1986). This method is essentially specific for SO₂ and exposed samples are relatively stable after collection. It has been used widely as a reference method and is covered by an international standard (UNEP/WHO, 1994). Sulfur dioxide was absorbed in a solution of potassium tetrachloromercurate and the stable non-volatile dichlorosulfitomercurate ion was formed in this procedure. Addition of solutions of purified, acid-bleached pararosaniline and formaldehyde leads to the formation of intensely coloured pararosaniline methyl sulphonic acid and then the absorbance of the sample was measured at 560 nm by a spectrophotometer against the reagent blank. The SO₂ concentration was determined directly from the calibration standard curve and then the air concentration of SO₂ (µg m⁻³) was calculated. The detection limit for SO₂ was about 6 µg m⁻³ for 24 h sampling. The RSD for replicate analyses of the calibration standard was 4%.

Dasibi ozone monitor (Dasibi, Model 1003-AH, Environmental Corp. Glendale, Calif. 91205) was used to monitor ozone concentration.

2.3. Meteorological parameters

The temperature and relative humidity during every sampling were measured using a Sigma-II thermohygrograph (no. 7210), SK Sato Keiryoki MFG-Co., Ltd., Japan.

2.4. Statistical analysis

The correlation coefficient (r) and the correlation significant t -test were determined using the alternative method of calculation (Gregory, 1963).

3. Results

The range and the mean values of ozone and meteorological parameters (temperature and relative humidity) during the field measurements of sulfate and nitrate are listed in Table 1. The highest mean ozone concentration was recorded during the summer season. The mean values of ozone were 33 and 64 ppb during the winter and summer seasons, respectively. The average daily values of relative humidity were 66.4% during the winter and 60.8% during the summer season. Moreover, the averages daily temperature were 14.4 and 29.5 °C during the winter and summer seasons, respectively (Table 1).

Nitrogen dioxide, particulate nitrate, gaseous nitric acid and total nitrate (particulate nitrate + gaseous nitric acid) concentrations are summarized in Table 2. The highest concentration of NO₂ was recorded during the winter, whereas, the highest concentrations of particulate nitrate, gaseous nitric acid as well as the total nitrate were found during the summer season. The mean values

of NO₂ were 185 and 132 μg m⁻³ during the winter and summer seasons, respectively. Moreover, the mean concentrations of particulate nitrate were 6.20 μg m⁻³ during the winter and 9.80 μg m⁻³ during the summer season. The highest mean concentration of gaseous nitric acid was found during the summer (6.70 μg m⁻³), whereas, the lowest mean concentration was recorded during the winter (1.14 μg m⁻³). The mean concentrations of total nitrate were 7.34 μg m⁻³ during the winter and 16.50 μg m⁻³ during the summer season. The average concentration ratios of gaseous nitric acid to total nitrate were 15.53% and 40.60% in the winter and summer seasons, respectively (Table 2). On the other hand, the average concentration ratio of particulate nitrate to total nitrate was 84.47% during the winter and it was 59.40% during the summer season.

The highest concentration of SO₂ was found in the winter season, whereas, the highest sulfate concentration was detected in the summer season (Table 3). The mean values of SO₂ were 125 and 83 μg m⁻³ during the winter and summer seasons, respectively. Moreover, the mean sulfate concentrations were 15.32 μg m⁻³ during the winter and 25.10 μg m⁻³ during the summer season.

The nitric acid concentration possibly includes small overestimate error, due to the formation of gaseous nitric acid from the volatilization of NH₄NO₃ from the filter during air sampling (Kadowaki, 1986). In the present study, a relatively small difference was observed

Table 1

Daily ozone concentration, temperature and relative humidity during nitrate and sulfate measurements in the winter and summer seasons (1999–2000)

Parameter	Winter				Summer			
	<i>N</i>	Range	Mean	SD	<i>N</i>	Range	Mean	SD
Ozone (ppb)	24	25–41	33	4.70	28	48–78	64	7.89
Temperature (°C)	24	11.1–17.5	14.4	1.59	28	24.7–34.6	29.50	1.95
Relative humidity	24	49.9–74.5	66.4	6.18	28	30.5–73	60.80	9.21

N: number of daily samples.

SD: standard deviation.

Table 2

Daily nitrogen dioxide, particulate nitrate, gaseous nitric acid concentrations, particulate nitrate to total nitrate ratio, gaseous nitric acid to total nitrate ratio and nitrogen conversion ratio (F_n) during the winter and summer seasons (1999–2000)

Pollutant	Winter				Summer			
	<i>N</i>	Range	Mean	SD	<i>N</i>	Range	Mean	SD
NO ₂ (μg m ⁻³)	24	140–225	185	27.60	28	90–170	132	22.30
PNO ₃ ⁻ (μg m ⁻³)	24	2.40–8.80	6.20	1.67	28	4.60–16.50	9.80	2.66
GNO ₃ ⁻ (μg m ⁻³)	24	0.74–2.10	1.14	0.28	28	3.60–9.10	6.70	1.28
PNO ₃ ⁻ + GNO ₃ ⁻ (μg m ⁻³)	24	3.24–10.60	7.34	1.85	28	8.20–23.20	16.50	3.15
PNO ₃ ⁻ /PNO ₃ ⁻ + GNO ₃ ⁻ (%)	24	74.10–89.10	84.47	3.69	28	42.80–74.0	59.40	7.70
GNO ₃ ⁻ /PNO ₃ ⁻ + GNO ₃ ⁻ (%)	24	10.94–25.93	15.53	3.69	28	26.01–57.20	40.60	7.70
F_n (%)	24	1.08–5.30	2.86	1.12	28	4.62–16.10	8.48	2.96

PNO₃⁻: particulate nitrate, GNO₃⁻: gaseous nitric acid, F_n (%): nitrogen conversion ratio, *N*: number of daily samples, SD: standard deviation.

Table 3

Daily sulfur dioxide and particulate sulfate concentrations, and sulfur conversion ratio (F_s , %) during the winter and summer seasons (1999–2000)

Pollutant	Winter				Summer			
	<i>N</i>	Range	Mean	SD	<i>N</i>	Range	Mean	SD
SO ₂ (μg m ⁻³)	24	90–160	125	21.60	28	55–122	83	17.60
PSO ₄ ²⁻ (μg m ⁻³)	24	9.50–23.60	15.32	3.88	28	14–46	25.10	8.76
F_s (%)	24	3.22–14.88	7.55	3.34	28	8.77–27.99	16.77	5.32

N: number of daily samples, SD: standard deviation.

PSO₄²⁻: particulate sulfate, F_s (%): sulfur conversion ratio.

between the ratios of gaseous nitric acid to total nitrate concentration for the daytime (42.21%) and nighttime (37.60%) during the summer season (Table 4). This indicates that, the error from the volatilization of NH₄NO₃ from the filter to form HNO₃ during air sampling seems to be small.

The daytime and nighttime concentrations of gaseous nitric acid, particulate nitrate and sulfate on some days are shown in Table 4. The average daytime concentration of particulate nitrate was relatively 1.50 times higher than that in the nighttime during the winter, as well as, it was relatively 1.60 times higher than that in the nighttime during summer season. The average daytime concentrations of gaseous nitric acid were about 3.7 and 1.9 times higher than those in the nighttime during the winter and summer seasons, respectively. With regard to sulfate, the average daytime concentrations were about 1.21 and 1.53 times higher than those in the nighttime during the winter and summer seasons, respectively (Table 4).

Grosjean and Friedlander (1975) and Kadowaki (1986) defined the conversion ratios for sulfur (F_s) and nitrogen (F_n) in the modified forms of the gas–particle distribution factors:

$$\text{Sulfur conversion ratio } (F_s) = \frac{\text{SO}_4^{2-}}{\text{SO}_2 + \text{SO}_4^{2-}}$$

where SO₄²⁻ is the particulate sulfate concentration, as SO₂, μg m⁻³; SO₂ is the gas phase SO₂ concentration, converted from ppm to μg m⁻³, averaged over the sampling period.

$$\text{Nitrogen conversion ratio } (F_n) = \frac{\text{PNO}_3^- + \text{GNO}_3^-}{\text{NO}_2 + \text{PNO}_3^- + \text{GNO}_3^-}$$

where PNO₃⁻ is the particulate nitrate concentration, as NO₂, μg m⁻³; GNO₃⁻ is the gaseous nitrate concentration, as NO₂, μg m⁻³; NO₂ is the gas phase NO₂ concentration, converted from ppm to μg m⁻³, averaged over the sampling period.

These equations are used to calculate the conversion ratios for nitrogen (F_n) and sulfur (F_s) in order to clarify the difference between the oxidation process of NO₂ to nitrate and SO₂ to sulfate.

Sulfur conversion ratio (F_s) and nitrogen conversion ratio (F_n) calculated from the above equations are summarized in Tables 2 and 3. The daily nitrogen conversion ratios (F_n) ranged from 1.08% to 5.30% (with a mean value of 2.86%) in the winter and from 4.62% to 16.10% (with a mean value of 8.48%) in the summer season (Table 2). Nitrogen conversion ratio (F_n) in the summer was about 2.97 times higher than that in the winter. However, the daily sulfur conversion ratios (F_s) covered the range 3.22–14.88% (with a mean value of 7.55%) during the winter; and 8.77–27.99% (with a mean value of 16.77%) in the summer season (Table 3). Sulfur conversion ratio (F_s) in the summer was about 2.22 times higher than that in the winter season. On some days, the nitrogen conversion ratio (F_n) and sulfur conversion ratio (F_s) in the daytime and nighttime calculated and are presented graphically in Fig. 1. The highest values of F_n and F_s were found in the daytime during the winter and summer seasons.

Table 4

Daytime and nighttime concentrations of particulate sulfate and nitrate, and gaseous nitric acid, and the ratio of gaseous nitric acid to total nitrate concentration on some days during the winter and summer seasons (1999–2000)

Season	<i>N</i> daytime/ nighttime	Particulate sulfate (μg m ⁻³)		Particulate nitrate (μg m ⁻³)		Gaseous nitric acid (μg m ⁻³)		Gaseous nitric acid/ total nitrate ratio (%)	
		Daytime	Nighttime	Daytime	Nighttime	Daytime	Nighttime	Daytime	Nighttime
Winter	6/6	18.32	15.20	8.49	5.80	1.95	0.53	18.68	8.37
Summer	6/6	32.57	21.27	12.46	7.80	9.10	4.70	42.21	37.60

N: number of samples.

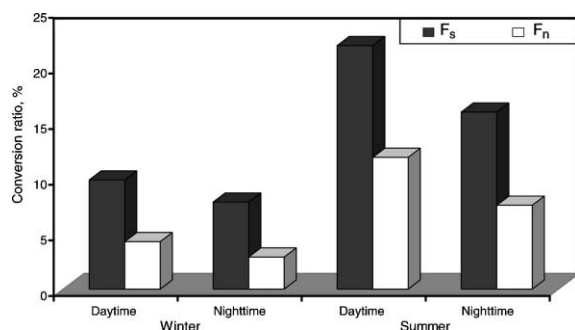


Fig. 1. Daytime and nighttime nitrogen conversion ratio (F_n) and sulfur conversion ratio (F_s) on some days during the winter and summer seasons.

Significant positive correlation coefficients were found between the sulfur conversion ratio (F_s) and relative humidity and ozone concentration during both seasons (Table 5). Moreover, significant positive correlation coefficients were found between the nitrogen conversion ratio (F_n) and ozone concentration during both seasons. On the other hand, insignificant positive correlation coefficients were found between nitrogen conversion ratio (F_n) and relative humidity during the winter and summer seasons (Table 5).

4. Discussion

The higher concentration of ozone during the summer season in the present study may be attributed to the higher solar radiation intensity and photochemical reactions. The highest ozone concentrations were recorded during the summer season, due to higher solar radiation intensity and photochemical reactions (Rizk, 1992; Khoder, 1997). The highest concentrations of particulate nitrate, gaseous nitric acid and total nitrate were found during the summer season (Table 2). This may be attributed to the higher photochemical reactions and ozone concentration, which lead to increase the oxidation of NO_2 and its rate of conversion to nitrate. The diurnal pattern of particulate nitrate was closely related

to ozone concentration (Grosjean and Friedlander, 1975). Both particulate and gaseous nitrate concentrations and their formations are increased in the summertime conditions, with high oxidant concentrations (Kadowaki, 1986). The higher concentration of particulate nitrate during the summer season in the city centre of Cairo was attributed to the higher ozone levels and photochemical activities (Khoder, 1997). The maximum concentrations of HNO_3 were found during the summer season (Eleftheriadis et al., 1998; Lee et al., 1999). The results in the present study can be compared with the results reported by other investigators. Braman and Shelley (1981) found that the gaseous HNO_3 concentrations ranged from 0 to $11.3 \mu\text{g m}^{-3}$ (with a mean value of $7.0 \mu\text{g m}^{-3}$, based on eight samples) during two days in August 1980. They added that the particulate nitrate concentrations ranged between 2.9 and $7.6 \mu\text{g m}^{-3}$ (with a mean value of $5.6 \mu\text{g m}^{-3}$) in the vicinity of Columbus. The average concentrations of particulate nitrate were 4.27, 1.88 and $2.01 \mu\text{g m}^{-3}$, whereas, the gaseous nitrate averages were 3.62, 2.64 and $0.33 \mu\text{g m}^{-3}$, in an urban area in Nagoya during June, August, 1983, and December 1983 to January 1984, respectively (Kadowaki, 1986). The average concentrations of particulate nitrate were 11.6 and $4.8 \mu\text{g m}^{-3}$ in the city centre of Cairo during the summer and winter seasons, respectively (Khoder, 1997). In addition, Spicer (1986) found that the average levels of the total inorganic nitrate in the central Ohio river valley varied between 3.0 and $4.5 \mu\text{g m}^{-3}$ over the four seasons, with the highest concentrations during the spring and summer seasons.

The highest concentration ratio of particulate nitrate to total nitrate was found during the winter season (Table 2). This indicates that the particulate nitrate concentration was predominant during the winter season. In contrast, the highest concentration ratio of gaseous nitric acid to total nitrate was found during the summer season in this study. This may be attributed to the higher photochemical reactions and dissociation of fine mode nitrate under the effect of higher temperature during the summer season, which may lead to an increase in the formation of gaseous nitric acid. The average concentration ratio of gaseous nitrate to total

Table 5

Correlation coefficients between ozone concentration, relative humidity and sulfur conversion ratio (F_s), nitrogen conversion ratio (F_n) during the winter and summer seasons (1999–2000)

Conversion ratio (%)	Winter ($N = 24$)		Summer ($N = 28$)	
	Ozone	Relative humidity	Ozone	Relative humidity
Nitrogen conversion ratio	0.77 ^a	0.20	0.91 ^a	0.15
Sulfur conversion ratio	0.55 ^b	0.81 ^a	0.89 ^a	0.78 ^a

N : number of samples in statistical analysis.

^a Significant ($p < 0.001$).

^b Significant ($p < 0.01$).

nitrate was high in the summer and particulate nitrate was predominant in the winter season (Kadowaki, 1986). Under high temperature condition, the nitrate in the fine mode tends to be volatile, and transform to gaseous nitric acid (Matsumoto and Tanaka, 1996). Moreover, the concentration ratios of gaseous nitric acid to total nitrate in the present study can be compared with ratios reported by other investigators. Braman and Shelley (1981) reported that the ratio was 0.56 outside of Columbus for two days in August 1980. Spicer et al. (1982) found that approximately one-half of total inorganic nitrate was present as HNO_3 , during hot weather in Claremont, CA. The average of HNO_3 to total inorganic nitrate ratios were 0.28 and 0.59 in the winter and summer seasons, respectively (Spicer, 1986). The ratios of gaseous nitrate to total nitrate in an urban area in Nagoya were 46%, 58 % and 14% during June, August 1983, and December 1983 to January 1984, respectively (Kadowaki, 1986).

The highest sulfate concentrations were found during the summer season (Table 3). This may be due to the higher photochemical activities and ozone concentration, which increase the oxidation of SO_2 and its conversion rate to sulfate. The sulfate concentrations were highest in the summer season (Spicer, 1986). The highest concentrations of sulfate were found during the summer season at Cairo city centre, due to the higher ozone concentration and photochemical reactions (Khoder, 1997). In addition, ammonia is important for its ability to neutralize H_2SO_4 , which is produced from the oxidation of SO_2 , forming ammonium salts (Brauer et al., 1989). Acidic aerosols can react with gaseous ammonia (NH_3) to form completely or partially neutralized ammonium salts (Koutrakis et al., 1988). The extent of aerosol neutralization is dependent principally on the rate of SO_2 oxidation to sulfate (SO_4^{2-}) and on the ambient concentration of NH_3 (Huntzicker et al., 1981). In the study area, the maximum concentration of NH_3 was recorded during the summer season (Hassan, 2000). It is suggested that the reaction of NH_3 with H_2SO_4 may lead to an increase in the formation of sulfate during the summer season.

In the present study, the relatively higher concentrations of particulate nitrate and gaseous nitric acid in the daytime than those in the nighttime may be attributed to the higher oxidation of NO_2 and its conversion rate to nitrate during daytime, with high ozone concentration and photochemical reactions. Hydroxyl radical formed by photochemical reactions is probably high leading to nitric acid production by reaction of NO_2 with the OH radical, which in turn form particulate nitrate. Daytime concentrations of HNO_3 were higher than nighttime concentrations (Cobb and Braman, 1995; Mehlmann and Warneck, 1995; Aneja et al., 1996). High correlation was found between HNO_3 and ozone (Skov et al., 1997). Gaseous nitric acid concentration was high

during the daytime, which may be due to the formation of HNO_3 via reaction of NO_2 with OH radical or more substantially to dissociation of ammonium nitrate aerosol (Kitto and Harrison, 1992). The average daytime concentrations of gaseous nitric acid were about 3.7 and 1.9 times higher than those in the nighttime during the winter and summer seasons, respectively (Table 4). The relatively higher ratio during the winter than that found during the summer may be due to the relatively lower nighttime concentration of the nitric acid in the winter. The lower nighttime ozone concentrations during the winter lead to decreasing the formation of nitric acid. The nitrate radical (NO_3) is generated through the reaction of ozone with nitrogen dioxide during nighttime (Russell et al., 1986). They added that nitrate radical reacts with NO_2 to form N_2O_5 and nitric acid is formed from the reaction of N_2O_5 with water vapor.

The relatively higher daytime concentrations of sulfate than that nighttime (Table 4) indicate that the formation of sulfate was relatively increased in the daytime than that in the nighttime. This may be attributed to the relatively higher oxidation of SO_2 to sulfate in the daytime under the effect of solar radiation, higher photochemical reactions, ozone concentration and OH radical. This is in agreement with Roberts and Friedlander (1976) who found that a sharp increase in the SO_2 oxidation rate occurred when the ozone concentrations exceeded 0.05 ppm. The afternoon peak concentration of sulfate occurs during the period of maximum sunshine and photochemical activity and corresponds approximately to the time of maximum ozone (Wolff et al., 1979). In polluted atmospheres reaction with OH radicals is the dominant gas phase removal process for SO_2 (Harrison and Perry, 1986). In the present study, fog has been observed during nights of high relative humidity due to the sufficient moisture in the air near to the ground surface. During these nights, SO_2 is oxidized to sulfate through droplet reactions. The SO_2 can be absorbed by dry or moist particles or droplets and then be oxidized to sulfate once in the particulate phase (Seinfeld, 1986). On the foggy nights, absorption of SO_2 into the fog droplet can occur leading to the oxidation of SO_2 in the droplets containing ozone (Erickson et al., 1977). Moreover, Brimblecombe and Spedding (1974) and Barrie and Georgii (1976) found that Fe and Mn have been shown to enhance the conversion of SO_2 to SO_4^{2-} in fog droplets.

In the present study, the highest nitrogen conversion ratio (F_n) and sulfur conversion ratio (F_s) were found in the daytime during both seasons. Moreover, the sulfur conversion ratio (F_s) and nitrogen conversion ratio (F_n) in the summer were about 2.22 and 2.97 times higher than those in the winter season, respectively. These results indicate that the oxidation of SO_2 to sulfate and NO_2 to nitrate and their conversion depend on the photochemical oxidation. This is in agreement with Kadowaki (1986) who found that the sulfur conversion

ratio (F_s) and nitrogen conversion ratio (F_n) in the summer were about 2 and 4 times higher than those in the winter at Nagoya urban area, respectively. He added that the photochemical oxidation plays an important role in the oxidation of SO_2 and NO_2 . Pinto et al. (1998) found that the average values of the conversion ratios of SO_2 to sulfate were 24% and 6% during two different episodes in Teplice, Czech.

With respect to the relation between ozone concentration, relative humidity and sulfur conversion ratio (F_s), nitrogen conversion ratio (F_n) (Table 5), it is concluded that, the ozone and relative humidity are important factors for the conversion of SO_2 to sulfate. The enhancement of the conversion requires high relative humidity and ozone concentration. Moreover, both droplet phase reactions and gas phase reactions are important for the oxidation processes of SO_2 to sulfate. In addition, ozone concentration is important factor for the conversion of NO_2 to nitrate, and the gas phase reactions are important and predominant for the oxidation processes of NO_2 to nitrate.

5. Conclusions

The highest concentrations of particulate sulfate and nitrate and gaseous nitric acid were found in the summer season. The highest ratio of gaseous nitric acid to total nitrate concentration was recorded in the summer season. The highest concentrations of particulate sulfate and nitrate, and gaseous nitric acid were found in the daytime during the winter and summer seasons. These results indicate that the oxidation processes and conversion of SO_2 to sulfate and NO_2 to nitrate depend on the photochemical oxidation. The highest nitrogen conversion ratio (F_n) and sulfur conversion ratio (F_s) was found in the summer season. Also, the highest F_n and F_s were found in the daytime during both seasons. The sulfur conversion ratio (F_s) increases with increasing ozone concentration and relative humidity, and both droplet phase reactions and gas phase reactions are important for the oxidation of SO_2 to sulfate. The nitrogen conversion ratio (F_n) increases with increasing ozone concentration and gas phase reactions are important and predominant for the oxidation of NO_2 to nitrate.

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