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Precipitation Quality and Related Atmospheric Chemistry over the Greater Damietta Area-Egypt

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Abstract: The present study investigates the chemical composition of wet atmospheric precipitation over Damietta City-Egypt. Precipitation samples were collected through rainy event (October to February) during 2001-2002 and from 2005-2006 in ten sampling locations. The concentrations of the chemical constituents of water-soluble ions Inorganic cations (NH_4^+) and anions (NO_3^- , NO_2^- , SO_4^{2-} , Cl^- and CO_3^{2-} were measured. Electric conductivity, pH and total dissolved solids of rainwater were also assessed. Results of the present study during 2005-2006 are almost similar to values observed during 2001-2002, excepting the concentration of NH_4^+ and SO_4^{2-} . The mean value of the precipitation pH indicates that rainfall is alkaline. Among the cations and anions, SO_4^{2-} deposition was maximum followed by CO_3^{2-} and then NO_3^- , Cl^- , NH_4^+ and NO_2^- . The results of the present study suggest that atmospheric precipitation is strongly modified due to various human activities, motor vehicles and furniture activities which are scattered all over the city.

Key words: Inorganic cations, atmospheric precipitation, Egypt, rain water

INTRODUCTION

Air gaseous pollutants have been recognized to have deleterious effect on water quality, soil properties, health of plants including forest trees and normal nutrient cycling patterns (Agrawal, 2002; Friedland and Miller, 1999). Rain is a cleaning agent for the atmosphere, since the removal of atmospheric particulates occurs by both dry and wet depositional processes. In the former, particulates are brought to the earth's surface in the absence of precipitation by a variety of processes including Brownian motion, gravitational settling and impaction. In wet deposition, particles are removed from the atmosphere by in cloud processes in which they participate in rain formation, rainout and by below cloud ice crystals, washout (Godish, 1997). Over the last few decades, simple rainfall has taken on a threatening complexity in some parts of the world. In these locals, the rain must pass through an atmosphere polluted with sulphur oxides (SO_x) and nitrogen oxides (NO_x). Consequently, the falling rain and snow react with these oxide pollutants to produce often a mixture of sulfuric acid, nitric acid and water. This is known as acid precipitation or acid rain (Dara, 1993). The normal resources at risk from acid rain sustain vital components of the economy and contribute to our quality of life (Chen *et al.*, 2003; Ocskay *et al.*, 2006; Zhang, 2006).

The behavior and impact of air pollutants have been widely studied in the past decades, most of these studies being conducted for industrial and urban areas (Dennis, 1996). The subject of acid precipitation and associated environmental problems has received a great special attention during recent decades and has been the subject of extensive researches (Hansen and Hidy, 1982; Zeng and Hopke, 1989).

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The potential health effects related to acid deposition has been focused on the effects of acute and chronic exposures to pollutants on respiratory function as well as on impact of acid deposition on drinking water quality (Franklin *et al.*, 1985). Both gases and particles have unique physiochemical properties, which are capable of challenging the respiratory defense mechanism. The primary target organ for predepositional effects is the lung. Epidemiologic studies of acute health effects have found to decrease lung function (Dockery *et al.*, 1993), increased respiratory symptoms and illness (Koutrakis *et al.*, 1989) and increased mortality (Altshuller, 1973; National Research Council, 1983), associated with current levels of particulate air pollution in many urban areas. Particle with strong acidity is found in the fine-size fractions of suspended particulates, raising the possibility that the observed chronic health effects associated with respirable particulate pollution may be attributable at least in part to the acidity of the particles (Raizenne *et al.*, 1996; Leudeser *et al.*, 1999).

Rain-water tends to be naturally acidic with a pH of 5.6 to 5.7 due to the reaction of atmospheric carbon dioxide (CO₂) with water to produce carbonic acid. This small amount of acidity is, however, sufficient to dissolve minerals in the earth's crust and makes them available to plant and animal life; yet not acidic enough to inflict any damage. Other atmospheric substances from volcanic eruptions, forest fires and other similar natural phenomena also contribute to the natural sources of acidity in rain. With the enormous amounts of acids created by nature annually, normal rainfall is able to assimilate them to the point where they cause little, if any, known damage. But, it is the contributions of SO₂, NO_x, etc from man-made activities that disturb this acid balance and convert natural and mildly acidic rain into precipitation with far-reaching environmental consequences (Dara, 1993).

The pH value of a given precipitation event is a consequence of the acid-base balance of all chemical species in the rain. Thus, pH alone provides rather incomplete information on the acidity of rain. In poorly buffered atmospheres, acid deposition leads to acidification and consequent damage to the ecosystem (Zhao *et al.*, 1988; Amaguchi *et al.*, 1991). The potentially harmful effect of acid deposition on the ecosystem has been the main reason behind this concern. However, in atmospheres highly loaded with alkaline species, such as CaCO₃ generated by wind erosion from soil dust and gaseous NH₃ released from either natural or/and agricultural and industrial activities, these species can neutralize anthropogenic acids and control the acidity of precipitation. Neutralization by CaCO₃ is a local process, occurring by incorporation of CaCO₃ contained in soil particles in rain primarily by below-cloud processes (Altwickler and Mahar, 1984).

Peters and Klemm (1989) stated that the acid fraction of precipitation water, i.e., the strong acid portion of all principal dissolved inorganic ions (cations and anions), can easily be computed from pH and electric conductivity. Since the acid fraction of soluble particulate matter is considerably lower than that of rain, the acid fraction of rainwater should drop when the concentration of scavenged aerosol increases and vice versa.

Sources of NH₃ are more variable. On a global scale, the ocean is the dominant source (Vong, 1990), but on a regional scale, the NH₃ present in precipitation is mostly due to livestock farming or the application of fertilizers containing NH₄⁺ (Bridgman, 1992). Atmospheric ammonia (NH₃) influences the acidity of solid and aqueous-phase aerosol species, cloud water and precipitation. Ammonia may be either wet- or dry-deposited as a gas or reacts with sulfuric (H₂SO₄), nitric (HNO₃) and hydrochloric (HCl) acids to form ammonium sulfate (NH₄)₂SO₄, bisulfate (NH₄HSO₄), nitrate (NH₄NO₃) and chloride (NH₄Cl) aerosols, thereby contributing to inorganic ambient particulate matter. In some cases, these inorganic species may contribute significantly to total PM_{2.5}, which is typically composed of sulphate (SO₄²⁻), nitrate (NO₃⁻), ammonium (NH₄⁺), organic carbon, elemental carbon, hydrogen ions and an assortment of transition metals (United States Environmental Protection Agency, 1997).

Egypt is a rapidly development country where air pollution levels are steadily rising especially in industrial and big cities related to population activities, industries and transportation. Consequently, the increasing concern about the air quality of our cities requires the monitoring of the pollutant agents

in the atmospheric particulate matter. Knowledge of the concentrations of potentially toxic substances in the airborne particulate is fundamental for assessing the pollution levels and provides important information for evaluating the long-term low levels exposure of the population (Rizzio *et al.*, 2000).

The objectives of this study were to characterize wet deposition in relation to different pollution loading and to estimate the influence of anthropogenic activities on the chemical composition of rainwater in the area, consequently, assess the risk to human health posed by atmospheric precipitation on human health.

MATERIALS AND METHODS

The Area of Study

Damietta City (31°N, 31°E) is the capital of Damietta Governorate and is located on the northern edge of the Nile's Delta, on the coastline of the Mediterranean Sea. Damietta's Mediterranean climate is characterized by a succession of one rainy season (October to February) and one long dry season (March to September). This generalization is modified by the influence of marine factors giving cooler summers and warmer winters near much of the coastlines. It is noted that January and February are the most cooler months while July and August are the hottest ones. Damietta City lies in the north of the Governorate and counts with a population of approximately 92 thousand inhabitants. The average temperature in Damietta is 22°C and the difference between the average temperature in summer and winter is 6°C (Damietta Governorate, the Administration of the Public Relations, 2003). It has a significant air pollution problem including industrial emissions from small factories as textile, sweet and milk manufactories, a lot of furniture and painting activities and a side from heavily traffic areas. Furniture activities include mechanical workshops and manual workshops. Figure 1 and 2 show Egypt map and the study area; ten sites were selected to represent the different activities.

Description of the Selected Sites

- The Gymnastic Stadium of Damietta and Al-mazloun Mosque (Abd Al-Rahem Nafea) are sites (1 and 3), respectively, residential areas with low population density located in the Southern part of Damietta City. They are characterized by many furniture and painting activities.
- Al-Sayalaa (Al-Mathan) is sites (6), it is a residential areas with moderate population density located in the Southern part of Damietta City. It is characterized by many furniture and painting activities.
- Yousiff Street, Fekri Zaher (Salah Al-Deen Street), Al-Nagda Land and Bab Al-Haraas are sites (2, 4, 5 and 7), respectively, residential areas with high population density located in the Eastern part of Damietta City. It is characterized by many furniture activities, commercial activities and low traffic density area.
- City Centre (Al-Kabass) is site (8), represents the centre of Damietta City. It is characterized as a heavy residential area with commercial activities. In this district there is a high density of motor vehicles.
- Ard Miriam is site (9), it is a residential area with high population density located in the Northern part of Damietta City. It is characterized by small furniture activities.
- Al-Herby Street is site (10), it is a residential area with high population density located in the Northern part of Damietta City. It is characterized by commercial activities, small furniture activities and small mechanical activities for repairing cars. In this district there is a high density of motor vehicles.

Samples and Analysis of Wet Deposition

During the study period 2001-2002 and 2005-2006, wet deposition (Ten samples for each site) were estimated across the sites through rainy event (October to February). Ten locations were chosen



Fig. 1: Egypt map

to provide a broad over view of a wide range of activities. Estimation of wet deposition was obtained from measurements of concentrations for inorganic ions, anions as nitrate (NO_3^-), nitrite (NO_2^-), chloride (Cl^-), sulphate (SO_4^{2-}) and carbonate (CO_3^{2-}) and cations as ammonium (NH_4^+) and their concentrations. Total dissolved solids, electric conductivity and pH were also measured. The wet-only samples were collected by means of a polyethylene tray, with a collecting area of 72.4 cm^2 , fixed on a support at 6 m from the ground. The tray was exposed to wet-deposition only during rainy event (October to February) and samples were frequently transferred to polyethylene flasks after filtering and stored in a freezer (-18°C) immediately afterwards (Fornaro and Gutz, 2003). The freezing procedure was chosen in order to prevent microbiologic action without sample contamination by added biocides. Blanks, consisting of flasks filled with double distilled water, were frozen together with samples and handled and stored (frozen) like real samples (Fornaro and Gutz, 2003).

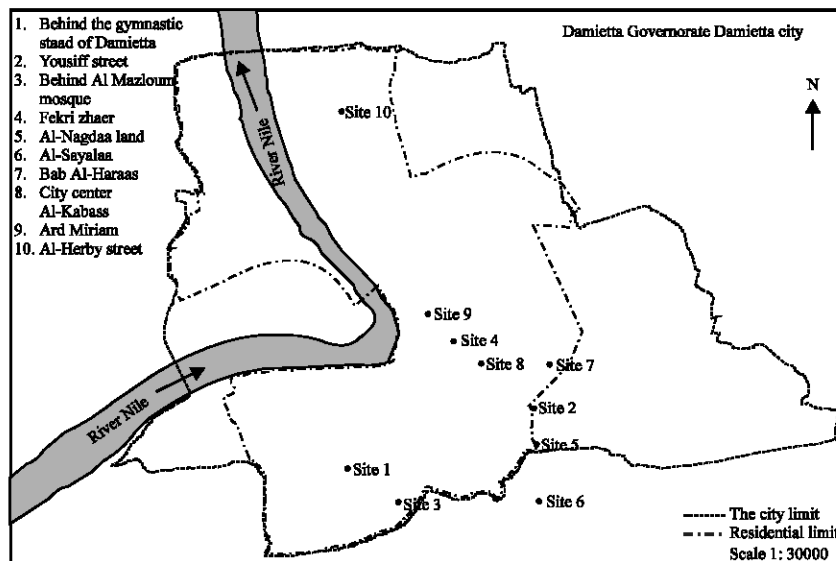


Fig. 2: Sites of measurements and Damietta city

Chemical Composition of Wet Deposition:

Total dissolved solids, electric conductivity and pH of the samples were measured with accurate equipments, respectively models TDS1 (Aqualytic, Germany with measuring range 0-10.000 mg L⁻¹, 8 ranges) and measuring cell (nickel rods in protective PVC tube, the meter is temperature resistance up to 60°C and temperature compensation 0-60°C manually) and pH (Redox Digimeter pH 21, Germany, provided with two buffer solutions (pH 4 and 7) and thermometer, after proper calibration). Rainwater samples were chemically analyzed for water-soluble and water insoluble portions. Cations ammonium (NH₄⁺) and anions (nitrate (NO₃⁻), nitrite (NO₂⁻), sulphate (SO₄²⁻), chloride (Cl⁻) and carbonate (CO₃²⁻) were determined in the water-soluble fraction.

Measurement of Sulfate (Turbidmetric Method)

Sulphate was determined turbidmetrically as barium sulphate and the turbidity of the suspension was measured by spectrophotometer at 500 nm (Harrison and Perry, 1986).

Measurement of Ammonium (Colorimetric Method)

Ammonium salts were determined colourimetrically by catalyzed indophenol-blue method and the blue dye was measured spectrophotometrically at 630 nm (Harrison and Perry, 1986).

Measurement of Nitrate (Colorimetric Method)

Nitrate ion was determined colourimetrically by converting to nitrite by copper-catalyzed reduction with hydrazine sulphate in alkaline solution. The nitrite was then measured spectrophotometrically at 540 nm (Harrison and Perry, 1986).

Measurement of Nitrite (Colorimetric Method)

The nitrite was determined by a modification of the method of Saltzman. It may be determined separately by the above procedure, omitting the hydrazine sulphate reduction and an appropriate correction was made (Harrison and Perry, 1986).

Measurement of Chloride (Mohr's Method)

Chloride ion was determined by Mohr's method employing silver nitrate as the titrant and potassium chromate as the indicator (American Public Health Association, 1992).

Measurement of Carbonate (Potentiometric and Colorimetric Method)

Carbonate ion was determined by Potentiometric and Colorimetric method employing sulphuric acid as the titrant and phenolphthalein as alkalinity indicator and methyl orange as acidity indicator (Adams, 1990).

Statistical Analysis

Statistical Analysis was conducted using the Statistical Program for the Social Sciences for windows version 10.0 (SPSS Inc., 1989-1999). Results were expressed as Mean \pm SD (Hollander and Wolfe, 1999).

RESULTS AND DISCUSSION

Acidity and Ionic Composition of Wet Deposition pH in Wet Deposition

Figure (3a, b) shows an overview of the collected wet deposition samples during 2001-2002 and 2005-2006 at selected sites of the city, respectively. There were no noticeable differences between the pH values over the different locations during both the sampling period. The pH values ranged from a minimum of 6.29 and 6.20 at sites (5) and (1), during periods 2001-2002 and 2005-2006, respectively to the maximum pH of 7.37 and 7.95 at site (2) during 2001-2002 and 2005-2006, respectively. The mean pH of wet deposition samples were 6.94 \pm 0.31 and 7.162 \pm 0.51 during 2001-2002 and 2005-2006, respectively (Table, 1a, b).

The wet precipitation throughout Damietta City is classified as neutral due to the absence of additional acidic and basic species. Moreover, pH does not represent the total acidity of wet deposition; it characterizes only the concentration of acids in dissociated form. This part of acid is called free acidity (Radojevic and Harrison, 1992). Consequently, the high PH observed is not due to the lack of acidic contribution to rainwater, but indicates more or less complete neutralization of acidity by basic substances incorporated to the rainwater either in cloud droplets or in falling hydrometers.

The pH values of wet deposition vary throughout Egypt, Daifullah and Shakour (2003) found that 0.73% of 137 rainwater samples were in the pH range 5-5.5, 37.23% in 6-6.9, 37.96% in 7-7.5, 7.3% in 7.6-7.9 and 2% in 8-8.23. None was below 5 or over 8.23. The average pH of rainwater was 7.09 \pm 0.39. The minimum pH value measured in rainwater was in Alexandria. The range of pH was 5.35-7.4 with a mean value of 6.79. One sample only has a pH less than 5.6, indicating the occurrence of acid rain. They added that in central Cairo, although high levels of sulphates and nitrates were found in rainwater, the pH levels remain relatively high due to the highly basic soils resulting from the adjacent hills and the surrounding desert. This is confirmed by the data found by Mamane and Gottlieb (1995) who found that moderate basic and alkaline rain cases are associated with transport over the Mediterranean and North Africa desert. These results are in agreement with Kulshrestha *et al.* (1996) who found that the average pH of wet deposition in Delhi, India, was found to be 5.7, more alkaline than rainwater due to the contribution of soil derived particles in the atmosphere. Suspended soil derived particles are scavenged into rainwater during below cloud scavenging process and are found to buffer its acidity.

Singh and Agrawal (2001) found also that during the rainy season, the mean pH of clean wet deposition varied from 6.56 to 7.04 and through fall varied from 6.81 to 7.22. Moreover, the mean pH of depositions indicates that rainfall of a highly industrialized region in Sonbhadra district of India was ranged from 5.98 to 7.43. However, rainfall pH of 5.0 and 4.8 was reported at 2 sites close to thermal power stations in Singrauli region of Sonbhadra district, India.

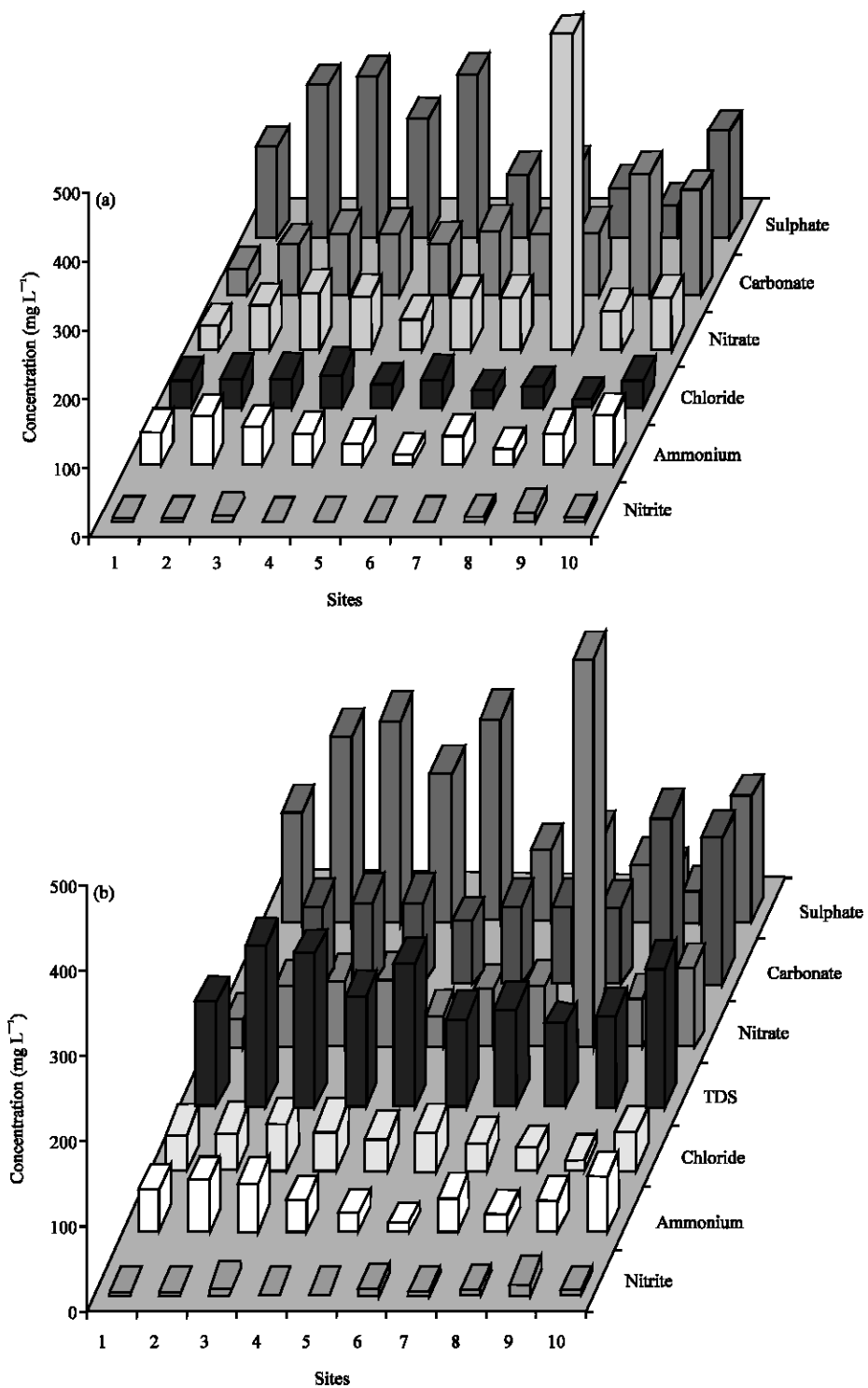


Fig. 3: Composition of wet deposition in Damietta city atmosphere during (a) 2001-2002 and (b) 2005-2006

Table 1a: Sampling parameters of the wet deposition samples over different sectors at Damietta city during 2001-2002

Parameters	pH	TDS at 18.2°C							
		(mg L ⁻¹)	EC (μS cm ⁻¹)	NH ₄ ⁺ (mg L ⁻¹)	SO ₄ ²⁻ (mg L ⁻¹)	NO ₃ ⁻ (mg L ⁻¹)	NO ₂ ⁻ (mg L ⁻¹)	Cl ⁻ (mg L ⁻¹)	CO ₃ ²⁻ (mg L ⁻¹)
Mean	6.94	139	289	37.45	143.06	102.30	3.73	38.88	104.11
SD	0.31	35	95	20.17	73.76	125.65	3.96	14.33	46.80

SD = Standard Deviation

Table 1b: Sampling parameters of the wet deposition samples over different sectors at Damietta city during 2005-2006

Parameters	pH	TDS at 18.2°C						
		NH ₄ ⁺ (mg L ⁻¹)	SO ₄ ²⁻ (mg L ⁻¹)	NO ₃ ⁻ (mg L ⁻¹)	NO ₂ ⁻ (mg L ⁻¹)	Cl ⁻ (mg L ⁻¹)	CO ₃ ²⁻ (mg L ⁻¹)	
Mean	7.162	43.28	144.02	104.84	4.60	35.38	94.70	
SD	0.510	18.60	69.64	125.01	3.50	13.25	38.55	

SD = Standard Deviation

Total Dissolved Solids (TDS) and Electric Conductivity (EC) in Wet Deposition during 2001-2002

Total dissolved solids values of wet deposition at the different districts during periods 2001-2002 ranged from a minimum of 94 mg L⁻¹ at site (8) to a maximum of 194 mg L⁻¹ at site (2) with an average of 139 mg L⁻¹. The Egyptian Standard Limits for TDS = 1200 mg L⁻¹. This indicates that the atmosphere in this site is moderately loaded with suspended particulate matter, which dissolves in wet deposition (Table, 1a). It seems that the commercial and traffic areas are significant contributors to air pollution, in addition to soil resuspension and sea spray. Ravichandran and Padmanabhamurthy (1994) documented that concentrations of ions decrease with increased rainfall and that shower in the initial stage had higher total dissolved solids and decrease later. Residence times of particles in the atmosphere are also decreased during extended periods of cold, wet weather (Beckett *et al.*, 1998).

The electric conductivity values of wet deposition during periods 2001-2002 ranged from a minimum of 187 μS cm⁻¹ at site (8) to a maximum of 501 μS cm⁻¹ at site (2) with an average of 289 μS cm⁻¹ (Table 1a). The Standard Limits for EC = 250-750 μS cm⁻¹. This indicates that EC for wet deposition is in the range of the permissible limit.

Chemical Composition of Precipitation

The average measured concentrations of major cation and anions in rain at same investigated sites during 2001-2002 and 2005-2006 are given in Table 1a, b and Fig. 2a, b.

Variations of Cation Concentration Ammonium (NH₄⁺) and Anion Concentrations Nitrate (NO₃⁻), Nitrite (NO₂⁻) and Sulphate (SO₄²⁻) in Wet Deposition

Figure 3a, b shows that the ammonium NH₄⁺ concentrations in wet deposition vary across sites, these are ranged from (non-detectible limit to 70.40) mg L⁻¹ during 2001-2002 and from 12.90 to 62.56 mg L⁻¹ during 2005-2006 at sites (6) and (10), respectively. This could be attributed to a high-density traffic at site 10. Ammonium is one of the auto-exhaust emitted compounds in the form of PbBrCl. 2NH₄Cl (Habibi 1973; Biggins and Harrison, 1979). Ammonium flux can be attributed mainly to agricultural practices like the intensive use of fertilizers. Emissions from the human population itself and from limited/poor treatment of wastes generated in the residential and commercial areas of the city are also major sources of ammonium (Rocha *et al.*, 2003).

Figure 3a, b shows that the nitrate NO₃⁻ and nitrite NO₂⁻ concentrations in wet deposition. Nitrate NO₃⁻ concentrations ranged from a minimum of 28.55 and 35.55 mg L⁻¹ at site (1) during periods 2001-2002 and 2005-2006, respectively, to the maximum 455.69 and 457.90 mg L⁻¹ at site (8) (City Centre) during 2001-2002 and during 2005-2006, respectively. It is characterized with heavy traffic density. The mean NO₃⁻ values were 102.30±125.65 and 104.84±125.01 during periods 2001-2002 and 2005-2006, respectively (Table 1a, b), which are much higher than the values reported

by Daifullah and Shakour (2003) who found that the average concentration of nitrates in the rainwater in Egypt was 14.09 mg L^{-1} . They added that, Alexandria City has a significant high concentration of nitrate ions. These values are the consequence of human activities as this station is subjected to the influence of the airplane exhaust (Nozha airport). This indicates that nitrate may be introduced by the direct dissolution of nitrogen dioxide followed by oxidation and oxidation of nitrogen dioxide to nitrate particles, which dissolved in rainwater.

On the other hand, the highest nitrite NO_2^- concentration was 13.79 and 12.97 mg L^{-1} recorded at site (9) during 2001-2002 and 2005-2006, respectively. Particle nitrite was probably in disequilibrium with gas phase, suggesting a heterogeneous source for gaseous nitrous acid (HONO) (Li, 1993). Nitrate and nitrite are probably derived from continual anthropogenic emissions of NO_x from industries and fuel combustion processes; especially motor vehicles. The large electric power plants and motor vehicles are major sources of particle and nitrogen oxide emissions (Stockwell *et al.*, 2000). Furthermore, it seems that the burn of refuse is also a source of nitrates and nitrites, which are generated by the reaction of nitrogen oxides. Wet deposition is one of the important sources of nitrogen input into the ecosystem. It also contributes to rain acidity in some environments (Paramee *et al.*, 2005).

These results are confirmed also with Rimmelin *et al.* (1999) who found that nitrate and ammonium concentrations of wet deposition in the southwestern French Atlantic coast are high. This region seems to be in less industrialized coastal regions, which is under a medium influence of atmospheric pollution and influence of onshore winds. The present results are much higher than the others found in many countries and higher than found in other cities in Egypt. Zhang (2006) reported that the nitrogen content in the rainwater of Sanghal area was rather high, with an average concentration of NO_3^- and NH_4^+ being 2.59 and 2.16 mg L^{-1} , respectively and so the effects of atmospheric nitrogen wet deposition on the eutrophication of the wetland water environment should be paid more attention. Moreover, Paramee *et al.* (2005) found that the average NO_3^- and NH_4^+ concentration in rainwater from the rural sites was around 0.2 - 0.3 , while that from the urban areas of Chiang Mai and Nan in Thailand were 0.4 - 0.5 mg L^{-1} .

Sulphates SO_4^{2-} concentrations in wet deposition change between 34.13 and 45.13 mg L^{-1} at site (9) and 242.38 and 235.52 mg L^{-1} at site (5) during 2001-2002 and during 2005-2006, respectively (Fig. 2a, b). The mean values SO_4^{2-} were similar during the two period of study (Table 1a, b). The major primary source of sulphate in urban atmosphere at Damietta City could be attributed to marine source as natural sources and human activities such as combustion of fuel, transportation and chemical reactions of sulfur dioxide.

Daifullah and Shakour (2003) reported that in Egypt, the highest values of SO_4^{2-} concentrations in rainwater are found at Alexandria City, 24 mg L^{-1} . These high concentrations of SO_4^{2-} may be due to local sources of human activities beside the influence of the marine emissions; much of the dissolved sulphate in seawater transported through the atmosphere after evaporation of the water the dry aerosol particles are subsequently redissolved in rain. Also Alexandria City is affected by the northern wind which may loaded with SO_2 and H_2SO_4 from south Europe. The H_2SO_4 remains stable in the air for several days and can travel hundreds of kilometers depending on the direction and movement of winds. Rain also can dissolve gases produced by combustion of fossil fuels. Experimental studies of sulphur dioxide and particulate pollutants have indicated adverse health effects in both animals (Dockery and Pope, 1994) and human subjects (Dockery *et al.*, 1992).

Kulshrestha *et al.* (1996) found that NH_2^+ and SO_4^{2-} concentrations at New Delhi, India were high in wet deposition. Higher concentrations of NH_2^+ were expected due to agriculture activities. Higher ratios of SO_4^{2-} than NO_3^- ratios suggest that the free acidity of the rainwater was due to SO_4^{2-} rather than NO_3^- , this acidity is buffered by NH_2^+ . However, the SO_4^{2-} and NO_3^- concentrations are comparable to those measured in other regions such as Albany, NY and Ontario, Canada, where acid depositions are known to be a problem.

The ratio of $\text{SO}_4^{2-}/\text{NO}_3^-$ in the rain in the present study is 1.375, which indicates that the contribution of H_2SO_4 and HNO_3 to the acidity of precipitation are 33 and 24%, respectively. This is due to the more intense emissions of SO_2 compared to NO_2 . This is in agreement with Al-Momani *et al.* (1995) who stated that the ratio of $\text{SO}_4^{2-}/\text{NO}_3^-$ in the rain at Menemen is 2.9 and the acidity of precipitation are 70 and 30%, respectively. de Mello and de Almeida (2004) found that at the Tatiana massif, Southeastern Brazil, SO_4^{2-} , NO_3^- and NH_4^+ comprised together about 60% of total inorganic ions and appear to exert the major control on rainwater pH.

Chloride Concentration (Cl^-) in Wet Deposition

Figure (3a, b) shows summary for Chloride Cl^- concentrations in wet deposition over the studied locations. The minimum Cl^- (10 mg L^{-1}) was recorded at site (9) during 2001-2002 and during 2005-2006, while the maximum Cl^- values 54.70 and 52.98 mg L^{-1} were found at sites (3) and (4) during 2001-2002 and during 2005-2006, respectively, with a mean values of 38.88 ± 14.33 , 35.38 ± 13.25 measured during 2001-2002 and during 2005-2006, respectively (Table 1a, b), mainly from natural sources. Damietta is a coastal area and is the most influenced by the northerly winds from Mediterranean Sea and is affected by the winds that disperse chloride particles over the city. In other words, maximum concentrations of chlorides were associated with the wind blown from the direction of Mediterranean Sea. Moreover, beside sea spray, emissions of chlorides from motor vehicles and other urban activities located at Damietta City also play a role in maximizing the concentrations of chlorides over the city. In this study chloride ion may originate from human activities and also contribute to atmospheric chlorides. Fuzzis *et al.* (1984) reported that automobile exhaust is a source of chloride salts. It may be also a result from refuse incineration, such as PVC, which produces HCl in gas phase (Sigg *et al.*, 1987). Harrison and Perry (1986) documented that chloride ion is often assumed to be solely of marine origin, but it can originate from other sources such as coal combustion and industrial emissions. In addition, it is in agreement with Harrison and Yin (2000) who stated that the main sources of chloride are sea spray even at locations hundreds of miles far from the coast and during the winter months road de-icing salt. Singh and Agrawal (2005) reported that industrial activities and soil might be the possible sources of chloride.

It may be concluded that there are two major sources of chlorides over Damietta City. These are sea spray and motor vehicles emissions.

Carbonate (CO_3^{2-}) Concentration in Wet Deposition

The maximum CO_3^{2-} values of 198.68 and 172 mg L^{-1} were found at site (9) during 2001-2002 and during 2005-2006, respectively, while the minimum CO_3^{2-} values of 40 and 35 mg L^{-1} were recorded at site (1) during 2001-2002 and during 2005-2006, respectively (Fig. 3a, b). The mean CO_3^{2-} values were 104.11 ± 46.80 and 94.70 ± 38.55 , respectively (Table 1a, b). It is obviously noticed that the slightly high values of pH of precipitation over Damietta City were attributed to the neutralization by natural alkaline dust of CO_3^{2-} . From the previous results, it can be concluded that the major source for carbonate in precipitation are the oxidation of carbon dioxide that may be emitted at high concentrations from fuel combustion processes and leads to high concentrations of carbonates, beside the natural sources.

This is confirmed by Shakour (1982) who stated that the potential sources of carbonates in Cairo atmosphere are natural sources and man-made sources. Due to the wind effects as an erosion tool on the limestone, wind also is responsible for the transportation of these limestone fine particles across the city. She added that carbonates are also formed from the atmospheric reaction of carbon dioxide emitted at high concentrations from fuel combustion processes.

These results are also in agreement with Rocha *et al.* (2003) who reported that in regions that can be influenced by sea breeze, it is common to distinguish the marine and the excess fractions (from

Table 2: Correlation coefficients between Inorganic Ions in wet deposition over different districts at Damietta city during 2001-2002 (a) and 2005-2006 (b)

	2001-2002						2005-2006					
	NH ₄ ⁺	SO ₄ ²⁻	NO ₃ ⁻	NO ₂ ⁻	Cl ⁻	CO ₃ ²⁻	NH ₄ ⁺	SO ₄ ²⁻	NO ₃ ⁻	NO ₂ ⁻	Cl ⁻	CO ₃ ²⁻
NH ₄ ⁺		0.98	-0.27	-0.03	0.34	0.19		0.45	-0.42	0.20	0.25	0.16
SO ₄ ²⁻			-0.34	-0.42	0.70	-0.38			-0.39	-0.38	0.63	-0.57
NO ₃ ⁻				0.02	-0.39	-0.04				-0.02	-0.15	-0.16
NO ₂ ⁻					-0.62	0.65					-0.62	0.75
Cl ⁻						-0.48						0.02
CO ₃ ²⁻						1.00						1.00

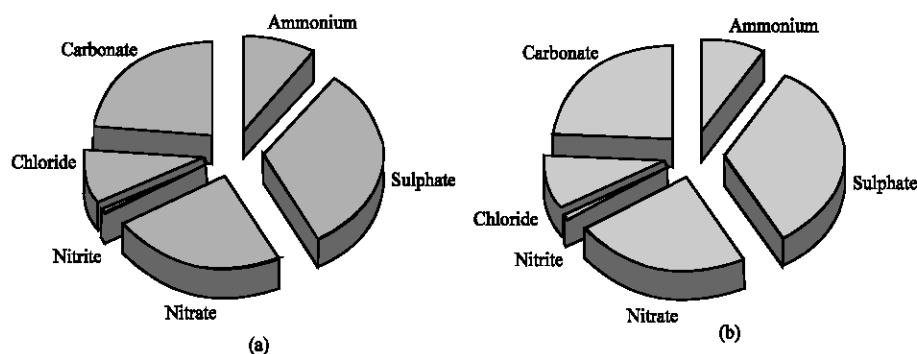


Fig. 4: Composition of wet deposition in Damietta city atmosphere during (a) 2001-2002 and (b) 2005-2006

continental and/or anthropogenic sources) of the major ions. In addition, they stated that the increased presence of calcium, possibly as carbonate, can be a relevant factor for the decrease of the free acidity.

Zunckel *et al.* (2003) reported that terrigenous sources (e.g., rock, soil and dust) and agricultural sources (e.g., livestock and crop fertilization) contribute to rainwater chemistry on a local and sub-regional scale. Influx of marine air from the Atlantic Ocean has a regional-scale influence while biomass burning contributes at both local and sub-regional scale (e.g., fuel wood and agroindustries) and through long-range transport (forest fires and land clearing).

In a correlation between ions, Table 2 indicates that the main compounds in rain-water sampled in different districts in Damietta City during the study period 2001-2002 and 2005-2006 follow the order: $(\text{NH}_4)_2\text{SO}_4 > \text{NH}_4\text{Cl} > (\text{NH}_4)_2\text{CO}_3$. Sulfate may be formed from the reaction between sulfur dioxide and alkaline gases especially NH_3 and water-soluble aerosols such as Ca^{2+} . On the other hand, chloride may be formed from the reaction between sea spray chloride and chloride from auto-exhaust and ammonium from auto-exhaust.

Moreover, it is obvious that the concentrations of the ions in wet deposition sampled in different districts during the study period follow the order: $\text{SO}_4^{2-} > \text{CO}_3^{2-} > \text{NO}_3^- > \text{Cl}^- > \text{NH}_4^+ > \text{NO}_2^-$, Fig. 4. On the other hand, during the same period from 2001 to 2002, El-Gammal *et al.* (2006) found that the ions concentrations in dry deposition for the same sites at Damietta City follow the order: $\text{NO}_3^- > \text{SO}_4^{2-} > \text{NH}_4^+ > \text{NO}_2^-$. This may be attributed to the fact that SO_4^{2-} ions are more dissolved in water than NO_3^- ions. On the other hand, Demirak *et al.* (2006) reported that the equivalent concentration of components followed the order: $\text{Ca}^{2+} > \text{SO}_4^{2-} > \text{NH}_4^+ > \text{NO}_3^-$.

CONCLUSION

As Damietta city is a commercial city with extensive vehicle emissions and street configurations, we can conclude that the environmental pollution by suspended particles and their chemical composition are at high concentrations. The present study has pointed out that rainwater at various

sites is greatly influenced by anthropogenic sources in city. Among the cation and anion measured during sampling periods 2001-2002 and 2005-2006, SO_4^{2-} deposition was maximum followed by CO_3^{2-} and then NO_3^- , Cl^- , NH_4^+ and NO_4^- . Even if the levels of SO_4^{2-} in precipitation are frequently greater than those measured in other places, the pH values are still high. The mean pH of the precipitation indicates that rainfall is alkaline and was attributed to the neutralization by natural alkaline dust, which contains large fractions of carbonate. Furthermore, the major sources for ions in precipitation over Damietta City are marine aerosol, occupational activities, chemical reactions and motor vehicles. However, Egypt is characterized by high levels of ammonium, calcium and basic substances, which can neutralize the acids, formed and increase pH of the rain. The major problem in Damietta City is nitrogen and sulfur oxide emissions related to human activity, transportation, industrial sources and from surrounding agricultural beside the sea spray. Atmospheric deposition processes have been recognized as important components of nutrient cycles in ecosystems. These observations illustrate that atmospheric pollutants have effects on the soil characteristics and affect the respiratory function in healthy individuals.

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