

Assessment and Measurement of Atmospheric Pollution (Particulate Matter) Around Zawiya City-Libya

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Abstract

Total air suspended particulates (TSP) samples were collected over glass fiber filter and determined gravimetrically. The contents on the glass filter was digested in HF-HCl-HNO₃ mixture and the trace elemental analysis of Al, Fe, Mn, and Pb were performed using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) technique, which offers many advantages such as low detection limits, wide linear calibration range and no matrix interference in addition to simultaneous multi-element determination. The filter with TSP was weighted, dissolved in HF-HCl-HNO₃ acid mixture and the trace element such as Al, Fe, Mn and Pb were determined using (ICP-OES) technique.

This work was carried out at four sites around Zawia city. Three sampling location were selected on sites of heavy traffics and industrial activities. These sites were (A₁) at the center of Zawia city; (A₂) near the power station and the refinery; (A₃) nearby the main coastal road and (A₄) control) at zone where there are no industrial activities or any obvious source of pollution. These samples were collected during Summer, Autumn, Spring, and Winter. The daily variation of TSP during this period showed the lowest value 70 µg/m³ in January (Winter), and the highest value 587.121 µg/m³. This value is relatively high compared with EU limit values (300 µg/m³), USEPA (150 µg/m³), and WHO (150-230 µg/m³). The mean monthly variation of TSP showed the lowest measured result of 78.28 ± 0.08 µg/m³ in January and the highest value 306 µg/m³ in May. Seasonal variation of TSP showed high results during Spring season which is 239.44 µg/m³ and all other seasons showed lower values of 131.19 µg/m³, 198.28 µg/m³ and 159.85 µg/m³ for Winter, Autumn, and Summer, respectively compared with Spring season. The trace elements levels in TSP were Al>Fe>Pb>Mn. The concentration of Al, Fe, Mn and Pb are lower in site A₄ and A₁ and higher in sites A₃ and A₂ due to heavy traffic and industrial activities. The meteorological parameters over the study area showed some factors such as wind speed, humidity and temperature that may affect TSP concentrations.

Keywords: Atmospheric pollution; Heavy metals in air; TSP; SPM

Introduction

Due to the lack of TSP data in the ambient air around Zawia city, this experimental work provides a database of TSP and trace elements such as (Al, Fe, Mn, Cu, and Pb). Suspended particulate matter (SPM) is one of the most important atmospheric pollutants due to their adverse effect on human health, plants and aquatic life. The environmental materials of atmospheric particles are polluted due to the presence of heavy metals in their composition [1-4]. Recently, it has been that found particulate matter from air pollution is linked to autism [5].

Atmosphere suspended particulate matter (SPM) can be divided to airborne solid and low vapor pressure liquefied particles having aerodynamic particle sizes from below 0.01 up to 100 µm [6,7]. Particles can be also classified by their physical state; which is a measure of density and shape, to three sizes range (coarse, fine and ultrafine) (or PM10, PM2.5, and PM by the U. S. Environmental protection Agency, U. S. EPA).

The atmospheric lifetime of total suspended particulates (TSP) is related to the particle size. Larger particles (10 µm diameter) may be airborne for up to 20 h and may travel 20-30 km while smaller particles may travel several thousand kilometers [8]. Large particles tend to settle out of the air quicker than smaller particles which remain suspended in the atmosphere for extended periods [9].

Total suspended particulate (TSP) in the ambient atmosphere can arise from a wide variety sources, forest fires, sea spray, volcanic emission, dust storms, soil and rock erosion, [10-12]. Natural sources, like dust, generally contribute aerosols of sizes >10 µm in diameter, while anthropogenic sources contribute <10 µm (classified under PM10 sized aerosols) [13]. The TSP concentration from natural origin is

lower than 10 µg/m³. The natural sources that have the greatest impact on the TSP concentrations include suspended terrestrial dust, sea salt spray (mainly at coastal sites) and biomass burning (forest fires) [14], and the major sources of anthropogenic or man-made, particles include transportation, stationary combustion, space heating, biomass burning, and industrial and traffic-related fugitive emissions (street dust) [14].

Recent reports have showed the impact of atmospheric pollutants on health when they are present in relatively high concentrations of TSP [15-19]. In adults, SP exposure is also associated with increased incidence of respiratory symptoms, transient decrements in pulmonary function levels, and the onset of chronic pulmonary disease in adults [10]. Fine particles (<2.5 µm in diameter) are thought to be more dangerous because of the ability to penetrate deeper into lung tissue leading to blockage of the very small passages in the lungs and, therefore, are especially important in the absorption of heavy metals and other toxic contaminants [18-20].

Moreover, particulate materials also can effect vegetation and ecosystem (visibility) and can cause damage to paint and building materials. The effects on vegetation include reduced growth and productivity due to interference with plant photosynthesis and

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phytotoxic impacts. Visibility impairment is effected by the scattering and absorption of light by atmospheric aerosols, particularly those of <2.5 μm [13]. Buildings and materials are negatively affected through increased rates of corrosion, erosion, soiling and discoloration [18]. Chemical and physical compositions of total suspended particulates (TSP) depending on the location, time of year, and weather [21]. Trace elements such as Al, Pb, Mn and Fe are among the important natural and anthropogenic constituents of TSP [22].

Experimental

Reagents

MilliQ deionized water was used in all experiments: All chemicals used in this study were analytical grade; Nitric acid (70.5 w/w%, BDH), hydrochloric acid (36 w/w%, Breckland Scientific Suppliers), Hydrofluoric acid (47 w/w%, India), formaldehyde (37 w/w%, Riedel-Dehaen AG. Seezel) and Phosphoric acid, H₃PO₄ (85 w%, Merck). Mercuric chloride (HgCl₂) and Na₂EDTA (Breckland Scientific Supplies), potassium chloride (BDH), sulfamic acid and sodium bisulfite (>58.5% m Sigma) and pararasnilinic acetate (PRA) technical dyes HN. Metal standard stock solutions prepared from ultra-high purity grade chemicals (99% pure or greater).

Instrumentation

Total suspended particulate samples were collected in a sampling train consisting pump, drying tube, filter holder, and membrane filters (0.8 micrometer). The flow rate of the pump (Knf Neuberger Model D-79112 freibrg) was calibrated by flow rate measurement devices (Analis BELGIUM). The Mass of TSP samples were determined using a Mettler-Toledo sensitive of the balance (Model AG 204 and 0.1 mg sensitivity). TSP samples were analyzed for, Al, Fe, Mn, and Pb by using (ICP-OES) instrument, Model (EL04123360) VISTA-PRO CCD simultaneous ICP-OES (Libyan Petroleum Institute).

Methods

Sampling stations and location: Four Sampling sites (A₁, A₂, A₃, and A₄) around Zawia city were selected. Three sites were selected were heavy traffics and industrial activities. A₁ is at city center; A₂ is near the power station, and A₃ is on the main road. A₄ is located at a zone with no industrial activities or any obvious source of pollution.

Sample collection: TSP samples were filtered on 0.8 μm membrane filters, by drawing air valve at the rate of 1.0 L/min flow rate using a low-volume sampler with the filter head being at 3m above the ground air is drawn into a covered housing and through a filter by means of high-flow rate blower, that allows suspended particles having diameters 1-100 μm to be filtered on filters (during day light and an average of about 24 h sampling time). After sample collection completed, filters were put back into their containers and stored in a dark cold place until analysis were performed.

Digestion procedure: Prior to ICP-OES analysis it was necessary to dissolve the particulate matter collected on the filter and weighted. The

sample was digested in Poly tetrafluoroethylene (PTFE) container with 5 ml of hydrofluoric acid, 5 ml nitric acid, and 5 ml hydrochloric acid and heating for 1.0 h. The mixture was evaporated to dryness. The residue was dissolved by heating gently in 20 ml of 0.5 mol/l hydrochloric acid and filtered. The filtrate was diluted to 50 ml with 0.5 mol/l hydrochloric acid and stored in a dark and cold place (4°C) until analysis was performed [23].

Results and Discussion

TSP concentrations

In this study, total suspended particulate (TSP) samples were collected for determining their concentration in the atmosphere around Zawia city and an attempt to establish a local TSP database as a part of environmental data base for Libya. The ambient air quality standards for total suspended particulate matter are 75 μg/m³ annual geometric mean, and 150 μg/m³ maximum. National Ambient Air Quality Standards (NAAQS) was shown in Table 1 [24], while WHO advises that concentration of TSP in air should not exceed the annual average of 60-90 μg/m³. The ambient air quality standards for PM 2.5 particulate matter are 15 μg/m³, annual arithmetic mean concentration; and 65 μg/m³ [24].

The analytical results for TSP that summarized in Table 1 ranged from 70.0 to 587.121 μg/m³. The value 70.0 μg/m³ was in January (Winter), and the value 587.121 μg/m³ was in May (Spring) this value is relatively high compared with EU limit values 300 μg/m³, USEPA (150 μg/m³), and WHO (150-230 μg/m³).

Average monthly variation of TSP over study area (A₄) during Summer (June-August) is shown in Table 2. The monthly variation of this season shows a high value 204.8 μg/m³ in June compared with August and July. Also, the average wind speed showed a high value of 6.7 Knots in this month (June). The temperature and humidity were relatively the same in the three months of this season (Figure 1). Monthly variation of TSP over study area (A₃) during Autumn (September-November) is shown in Table 3. The monthly variation of this season shows a high value 248.9 μg/m³ in September compared with October and November. Also the average temperature and wind speed showed a high value 27°C and 5.6 Knots respectively in this month (September). The humidity relative during the three months of this season is similar (65%) (Figure 2).

Average monthly variation of TSP over study area (A₂, A₁) during Spring (March-May) is shown in Table 3. The monthly variation of this season showed a higher value (306.0 μg/m³) in the month of May, compared with March and April. Also the average temperature and the average wind speed showed higher value 24°C and 7.8 m/s respectively in this month (May), while humidity showed a higher value of 63% in May (Table 3).

Average monthly variation of TSP over study area (A₄) during Winter (December-February) is shown in Table 3. The monthly variation of this season shows a high value 177.39 μg/m³ in February compared with December and January. Also the average wind speed showed a higher value 5.8 m/s in this month (February).

standard or guideline	long-term (annual)		short-term (24 h)	
	PM ₁₀	TSP	PM ₁₀	TSP
EU limit values	-	150	-	300
USEPA primary and secondary standards	50	57	150	150
WHO guidelines	10	60-90	25	150
WHO guidelines for Europe	10	70	25	-

Sources: European Community 2006 (EU); United States, CFR (USEPA); WHO 2005 (WHO Guidelines).

Table 1: Reference standards and guidelines for average ambient particulate concentration (micrograms per cubic meter).

Months	TSP $\mu\text{g}/\text{m}^3$	W m/s	H%	T $^{\circ}\text{C}$
Jun-07	204.8	6.7	55	28.0
Jul-07	128.9	5.8	68	25.3
Aug-07	145.8	5.5	62	28.9
Sep-07	248.9	5.6	65	27.0
Oct-07	183.3	5.8	65	22.5
Nov-07	162.6	3.9	65	17.5
Mar-08	131.3	5.6	63	16.2
Apr-08	280.9	6	58	20.0
May-08	306.0	7.8	55	24.7
Dec-08	137.9	4.7	70	13.1

Table 2: The average air temperature, average humidity, average wind speed and monthly concentration of TSP samples.

Sampling point	Mean TSP ($\mu\text{g}/\text{m}^3$)
A ₁	117.18 \pm 7.73
A ₂	199.49 \pm 2.33
A ₃	131.55 \pm 12.44
A ₄	119.66 \pm 6.09

Table 3: The mean variation of TSP concentration over the study area.

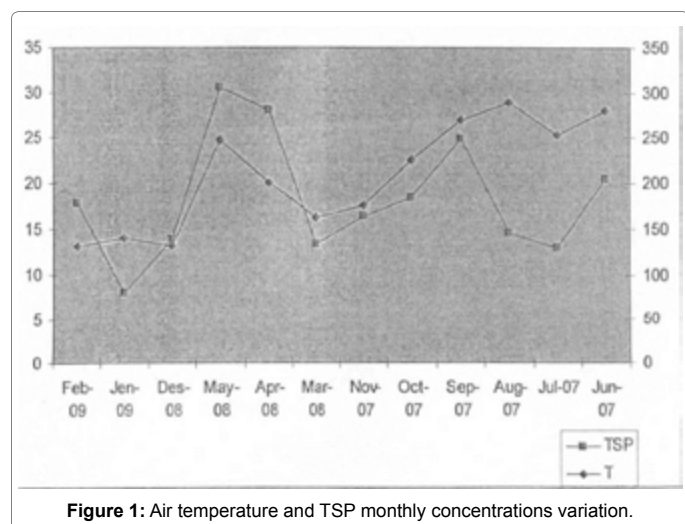


Figure 1: Air temperature and TSP monthly concentrations variation.

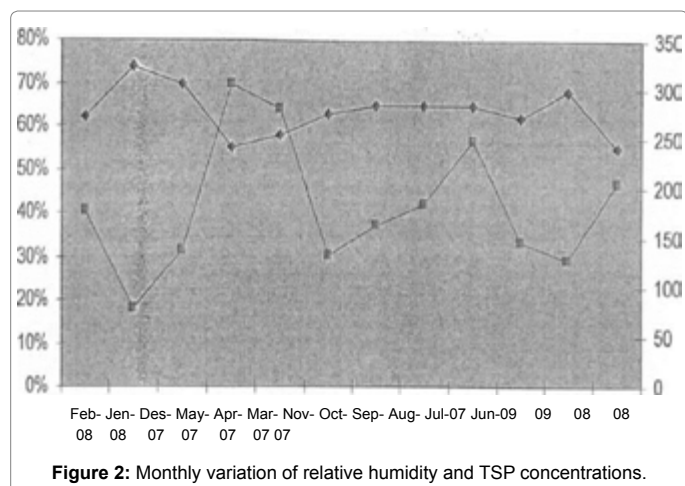


Figure 2: Monthly variation of relative humidity and TSP concentrations.

Table 4 showed the monthly average values of TSP during 2007, 2008 and 2009 over the study area (A1, A2, A3 and A4). The monthly average concentrations of TSP showed a strong peak between July and March. The average air temperature, average humidity, average wind

Size	Seasons	Mean	Max	Min	No.s
TSP	Summer 2007	159.85	315.65	63.13	26
	Autumn 2007	198.28	385.10	25.25	27
	Spring 2008	239.44	587.12	44.19	35
	Winter 2008-2009	131.19	505.05	37.87	32

Table 4: Average seasonal mass concentration of TSP ($\mu\text{g}/\text{m}^3$).

Site	A ₁ (n=6)	A ₃ (n=7)	A ₂ (n=6)	A ₄ (n=8)
Al $\mu\text{g}/\text{m}^3$	4617.15	19772.08	12789.83	714.53
Fe $\mu\text{g}/\text{m}^3$	2220.97	4432.21	4425.32	2527.98
Mn $\mu\text{g}/\text{m}^3$	23.29	135.91	82.85	62
Pb $\mu\text{g}/\text{m}^3$	634.75	1615.1	2504.94	1811.23

Table 5: The levels of Al, Fe, Mn, Cu, and Pb ($\mu\text{g}/\text{m}^3$) in TSP samples.

speed and monthly concentration of TSP samples are summarized in Table 2. The mean variation of TSP concentration in study areas (A1, A2, A3, and A4) has been shown in Table 3. The results showed relatively higher values in zone A2 which is (199.49 $\mu\text{g}/\text{m}^3$).

Seasonal variation of TSP during 2007, 2008 and 2009 over the study area has been shown in Table 2 and Table 5. The results showed relatively higher values during Spring season which equal to 239.44 \pm 2.76 $\mu\text{g}/\text{m}^3$, other seasons showed less values ranged from \sim 131.19 $\mu\text{g}/\text{m}^3$ to 159.85 $\mu\text{g}/\text{m}^3$.

Elemental concentration

The levels of trace elements are varying according to the sources of particles [25]. Trace elements are of particular importance due to their potential toxicity for the environment and human being. Metals are non-degradable, and can accumulate in the human body system, causing damage to internal organs and systems [26,27]. Chemical analysis for elements Al, Fe, Mn, and Pb present in the total suspended particulates were analyzed using ICP-OES. The results are shown in Table 4. The results showed that, the concentrations of Al, Fe, Mn and Pb are low in A1 and A4 and high at sites A2 and A3. A2 and A3 areas have heavy traffic and a lot of industrial activities.

The sources of Aluminum in atmospheric samples may include highly contaminated soil derived dusts (clay dust or Aluminum silicate) and nearby agriculture areas. These natural processes far outweigh direct anthropogenic contributions to the environment [27,28]. Long lasting uptakes of significant concentrations of aluminum can lead to serious health effects [29]. Iron is one of the most abundant elements in atmospheric samples. In this study, iron could be introduced into the atmosphere as soil dust and fly ash from Zawya power plants, exhaust of vehicle's combustion engines, and from industrial operations [29]. Iron may cause conjunctivitis, choroiditis, and retinitis if it contacts and remains in the tissues. Chronic inhalation of excessive concentrations of iron oxide dusts may result in development of a benign pneumoconiosis, called siderosis.

In this study, the major sources of atmospheric manganese could be suspension of road dust by vehicles, wind erosion and suspension of soil [30]. Exposure to manganese can affect lung, central nervous system, and some biological indices. The principal effects of long-term occupational exposure to inorganic manganese compounds are "manganese pneumonia" or pneumonitis and, more commonly, manganese. About 90% of lead in the atmosphere comes from the exhaust gases of motor vehicles, due to the application of lead in fuels. In vehicles engines lead is burned, so that lead salts (chlorides, bromides, and oxides) will originate. The reported lead salts concentrations

could have entered the study sites environment through the exhausts of vehicles, from petrol stations dispensing leaded fuel, exhaust from local power station, Zawya oil refinery, the huge area of vehicle scrabs nearby and small amounts in the earth's crust as lead sulfide, lead oxide or lead carbonate. Lead can have the most damaging effects on human health, such as: Disruption of the biosynthesis of hemoglobin, anemia, blood cells miscarriages and subtle abortions. The ambient air quality standard for lead is 1.5 µm elemental lead per cubic meter, maximum.

Conclusions

This study presented analytical data of TSP during the studied periods. From the literature review no data was found. Total suspended particulates content can be variable with location, time of year, and weather conditions with maximum monthly concentration of TSP found to be in May 2008, which is characterized by high wind speed (7.8 knots) compared to other months of the year. The seasonal variation exhibits maximum mean concentration of TSP in Spring (239.44 µg/m³) and minimum mean concentration in Winter (131.199 µg/m³) due to the characteristic enhanced rain falls which caused the decrease in the TSP concentration. The order of trace elements in TSP was Al>Fe>Pb>Mn. The fluctuations in the concentration levels could be a direct function of emission sources.

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