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COMPARISON OF INORGANIC CHEMICAL COMPOSITIONS OF TOTAL SUSPENDED AND RESPIRABLE PARTICULATES IN DIFFERENT REGIONS OF CAIRO

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ABSTRACT

The inorganic chemical composition of atmospheric Total Suspended Particulate (TSP) and Particulate Matter with an aerodynadic diameter less than 10 µm (PM_{10}) in different regions of Cairo, in spring and autumn of 2018 was illustrated in this work. The results showed that the highest concentration of TSP and PM_{10} were close to industrial and heavy traffic areas "Tabbin, Helwan, Shobra Elkhimah and Fifth Settlement area".

The results showed that dust mass concentrations in Shobra Elkhimah were higher than all the other locations in both TSP and PM_{10}. These results were pointed out in both spring and autumn.

The results showed that the concentration of heavy metals in Helwan area was higher than all other locations. These concentrations suggest that heavy metals pollution in Helwan was more serious.

Ration analysis of soluble ions showed that sodium and chloride were not from sea salt but sodium might be from the resuspension of soil dust, and chloride might be associated with the activities of burning. Potassium had diversity of sources other than burning of biomass. Sulfate and nitrate were mostly from fossil fuel origin.

The NO_3^-/SO_4^- ratios in Tabbin were higher than in Helwan and Shobra Elkhimah for two types of particles during spring and autumn, indicating that the contribution of stationary emission to total particles in Tabbin were higher than in Helwan and Shobra Elkhimah.

Key words: Particulate Matter; Tabbin; Helwan; Shobra Elkhimah

INTRODUCTION

Air pollution is a process that introduces diverse pollutants into the atmosphere that cause harm to humans, other living organisms, and the natural environment. The emission of Particulate Matter (PM), may cause visible effects in form of deposition on clothes, plants, buildings and observed health effects, was noticed as the first signs of air pollution. (Kim *et al.*, 2015, Wardencki *et al,* 2016).

PM can range in size from 0.001 µm to greater than 100µm in diameter. Generally, aerosols are classified according to their aerodynamic diameter. Coarse particles are in the fraction between 10 µm and 2.5 µm in diameter; fine particles are between 2.5 µm and 0.1 µm in diameter and ultra-fine particles are less than 0.1µm. PM with aerodynamic diameters less than 10µm are known as PM10 and PM with aerodynamic diameters less than 2.5µm are known as PM2.5. Total Suspended Particulate (TSP) includes all PM fractions (Pope, 2000).

Sources of PM are both natural and anthropological (Kumar, 2008). Several sources may contribute to the emission of suspended PM in the air.

The main contributors are sources of urban pollution, including vehicular and industrial exhaust emissions, biomass burning, natural disasters, and other localized sources from home and occupational activities. (Peixoto *et al.*, 2017)

Human activity affects the natural geological and biological redistribution of metals through pollution of the air, water, and soil. (Geiger and Copper, 2010).

Water-soluble ions are major components of atmospheric aerosols and can comprise up to 60–70% of particulate mass (Ali Mohamed., 1991). Water-soluble inorganic ions (WSIIs) are a major part of fine particles ($PM_{2.5}$, Particulate Matter with an aerodynamic diameter less than 2.5 µm). Of the various components, Secondary Inorganic Ions (SII), including sulfate ($SO4^{--}$), nitrate (NO_3^-), and ammonium (NH_4^+), are the predominant species and account for more than 90% of WSIIs (Zhang *et al.,* 2012). Moreover, they also play important roles in atmospheric acidification and climate change (Andreae *et al.,* 2008, Zheng *et al.,* 2015). Sulfate is primarily formed through homogeneous gas-phase oxidation of sulfur dioxide, while heterogeneous transformation processes, i.e., metal-catalyzed oxidation, H_2O_2/O_3 oxidation, and in-cloud process, are also reported (Seinfeld, 1986, Wang *et al.,* 2006). Both homogeneous reaction via NO_2 oxidation by OH radical and O_3, and the heterogeneous hydrolysis of N_2O_5 on preexisting aerosols, are important pathways of nitric acid formation (Khoder, 2002).

The objectives of this study are to quantify the various mass concentrations, inorganic chemical compositions and sources of TSP and PM_{10} in different regions of Cairo.

MATERIALS AND METHODS

The applied methodology in this study is based on US-EPA Compendium Method IO-2.1 (Sampling of TSP and PM10 Using High Volume (HV) Sampler). Concisely, the method is based on using a High-Volume Air Sampler for collection of dust particulates from ambient air onto the sampling module that consists of particle filter (i.e. glass fiber filter). This method is applicable for collecting and trapping dust particulate as well as inorganic materials present in dust and heavy metals.

This study was carried out from February to March 2018. The study areas are located in El Tabbin district with geographical coordinates of 29°46'55.60"N latitude and 31°18'10.32"E longitude, Helwan area with geographical coordinates of 29°51'10.69"N latitude and 31°20'16.35"E longitude, Shobra Elkhiema area with geographical coordinates of 30° 8'5.42"N latitude and 31°18'2.09"E longitude, Fifth settlement area with geographical coordinates of 30° 0'8.61"N latitude and 31°25'19.44"E longitude. The selected sampling area is surrounded by a mixture of urban, industrial, commercial and traffic activities. Furthermore, these areas represent a large urban industrialized area in El Tabbin district and Helwan city where metallurgical, chemical, coal, petrochemical, bricks, cementproducing plants are located, however in Shobra Elkhiema where Textile and Dying Plants, Lead and Cast-iron Foundries, Glass Plants, Fertilizer Plants, Soap and oil Plant, Aluminum Sulphate Plant, Petroleum Refining Plants and Gas Liquefaction Plants are located. Figure 1 shows the sampling site locations. With the aid of a global positioning system device (Garmin Global Positioning System; GPS), four sampling sites were chosen taking into consideration covering different activities.

RESULTS AND DISCUSSION

Differences in dust mass concentration: The atmospheric dust mass concentrations from different sampling sites and seasons under study are provided in Table 1. As illustrated in Table 1 and figures 2 to figure 5, the maximum value of mass concentration for TSP was 1424±8.6 µg/m^3 and 1294±7.8 µg/m^3 in Shobra Elkhimah and the minimum value was 394.7±79.6 µg/m3 and 439±88.4 µg/m^3 in Fifth settlement at spring and autumn respectively , meanwhile the maximum value of mass concentration for PM10 was 765±29.6 µg/m^3 and 695±26.9 µg/m^3 in Shobra Elkhimah and the minimum value was 296±45.2 µg/m^3 and 329±50.2 µg/m^3 in Fifth settlement at spring and autumn respectively.

Table(1): Statistic value for mass concentrations of TSP and PM10 at Autumn and Spring in Tabbin, Helwan, Sohbra Elkhimah and Fifth settlement.

		Particulate Matter		**Mass percentage (%)**
Area	**Mass concentration**	**TSP (µg/m^3)**	**PM_{10} (µg/m^3)**	**PM_{10}/TSP**
Tabbin				
Autumn	Min	512.0	300.0	58.6
	Max	579.0	374.0	67.3
	Median	556.0	367.0	63.4
	Mean	549.0	347.0	63.1
	SD	34.0	40.9	4.3
Spring	Min	403.0	330.0	58.6
	Max	639.0	411.0	102.0
	Median	563.0	403.0	63.1
	Mean	535.0	381.3	74.6
	SD	120.5	44.6	23.9
Helwan				
Autumn	Min	278.0	184.0	41.0
	Max	788.0	323.0	66.2
	Median	533.0	254.0	47.7
	Mean	533.0	253.7	51.6
	SD	255.0	69.5	13.1
Spring	Min	492.0	193.0	32.7
	Max	730.0	516.0	73.3
	Median	704.0	239.0	39.2
	Mean	642.0	316.0	48.4
	SD	130.6	174.7	21.8

Cont. **Table(1):** Statistic value for mass concentrations of TSP and PM10 at Autumn and Spring in Tabbin, Helwan, Sohbra Elkhimah and Fifth settlement.

		Particulate Matter		**Mass percentage (%)**
Area	**Mass concentration**	**TSP ($\mu g/m^3$)**	**PM_{10} ($\mu g/m^3$)**	**PM_{10}/TSP**
Shobra ElKhimah				
Autumn	Min	1286.0	668.0	51.9
	Max	1302.0	722.0	55.5
	Median	1294.0	695.0	53.7
	Mean	1294.0	695.0	53.7
	SD	8.0	27.0	1.8
Spring	Min	1415.0	34.0	2.4
	Max	1423.0	794.0	55.8
	Median	1423.0	764.0	53.7
	Mean	1420.3	530.7	37.3
	SD	4.6	430.4	30.2
Fifth Setlement				
Autumn	Min	350.0	279.0	71.9
	Max	527.0	379.0	79.7
	Median	439.0	329.0	74.9
	Mean	438.7	329.0	75.5
	SD	88.5	50.0	3.9
Spring	Min	314.0	250.0	71.9
	Max	474.0	341.0	79.6
	Median	395.0	296.0	74.9
	Mean	394.3	295.7	75.5
	SD	80.0	45.5	3.9
TSP: Total Suspended Particulate PM_{10}: Particulate Matter with an aerodynamic diameter less than 10 µm				

No significant seasonal variations of PM were observed in Tabbin, Helwan and Fifth settlement for two types of particles, but for Shobra Elkimah, TSP and PM10 were significantly different (ANOVA, $p < 0.05$), Meanwhile, from the linear regression analysis for TSP vs. PM10, all correlation coefficients (r^2) were higher than 0.28 ($p < 0.001$) for four areas and the two seasons (Table 2), indicating that they have common emission sources and could be used to estimate PM10 from TSP.

Table 3 shows the averages of the mass concentrations measured as well as the mass concentrations available from some other locations of Egypt.

Table(2): Linear regression analysis for TSP vs. PM10 for the four areas and two seasons.

Area	Season	Combination	Linear regression equation	r2
Tabbin	Autumn	TSP vs PM10	PM10 = 1.0906 TSP - 251.74	0.826a
	Spring		PM10 = 1.0906 TSP - 276.91	0.826
Helwan	Autumn	TSP vs PM10	PM10 = 0.2724 TSP + 108.32	1
	Spring		PM10 = 0.7028 TSP - 135.23	0.2773
Shobra Elkhimah	Autumn	TSP vs PM10	PM10 = 3.4289 TSP - 3742.5	0.9997
	Spring		PM10 = 3.4289 TSP - 4116.8	0.9997
Fifth Settlement	Autumn	TSP vs PM10	PM10 = 0.5675 TSP + 80.04	1
	Spring		PM10 = 0.5675 TSP + 72.036	1

r2: correlation coefficients.
a All significant level as $p < 0.001$
TSP: Total Suspended Particulate
PM10: Particulate Matter with an aerodynamic diameter less than 10 µm

Table(3): Comparison of PM concentration (µg/m3) in studied areas and some other locations of Egypt

Location	Sampling Time	TSP	PM10	Reference
Tabbin	2018	576	364	This study
	1999	762.2	---	Borai and Soliman. (2001)
Helwan	2018	588	285	This study
Shobra Elkhimah	2018	1359	730	This study
	1999	776	---	Borai and Soliman. (2001)
Fifth Settlement	2018	417	313	This study
Ramsis	1999	---	731.2	Borai and Soliman. (2001)
Nasr City	1999	---	132.8	Borai and Soliman. (2001)
10th of Ramadan	1999	---	83.2	Borai and Soliman. (2001)
6th of October	1999	---	97.5	Borai and Soliman. (2001)
TSP: Total Suspended Particulate PM_{10}: Particulate Matter with an aerodynamic diameter less than 10 µm				

- **Differences in Heavy metals elements concentration:** According to the results illustrated in table 4 and table 5 the measured concentrations for nine elements in TSP and PM_{10} in studies areas, element concentrations can be classified in to three categories
  - Elem
  - ents with high concentrations: Al, Mn, and Zn
  - Elements with low concentrations: Fe, and Mg
  - Trace elements: Co, Cu, Ni and Pb

Table(4): Statistical analysis of chemical species in TSP and PM10 at autumn from different areas of Cairo

	Tabbin		Helwan		Shobra Elkhimah		Fifth Settlement	
	TSP	**PM10**	**TSP**	**PM10**	**TSP**	**PM10**	**TSP**	**PM10**
Al	8.40±1.44	6.2580±2.3101	37.2563±26.8687	36.4535±28.7468	14.8810±2.7978	11.1512±0.0391	10.8883±4.7880	8.8548±3.4155
Co	0.008±0.001	0.0066±0.0016	0.0094±0.0066	0.0168±0.0128	0.0158±0.0057	0.0126±0.0033	0.0075±.0022	0.0095±0.004
Cr	UD	UD	UD	UD	UD	UD	UD	UD
Cu	0.023±0.006	0.0181±0.0058	0.0504±0.0274	0.0304±0.0158	0.0482±0.0187	0.0364±0.0035	0.0197±0.0074	0.0155±0.007
fe	3.2882±0.94	1.1790±1.5134	6.0272±3.8291	5.2654±3.7441	7.1009±1.0421	4.4600±0.1182	2.7246±0.2109	2.7551±0.696
Mg	1.6188±0.7249	1.5458±0.5974	3.6644±2.2731	1.7320±1.2316	6.5119±0.9882	2.6608±1.2284	5.2020±2.4825	2.8835±1.718
Mn	0.5314±0.1558	0.4476±0.2919	25.6848±16.23	17.9663±12.38	0.4673±0.1220	0.3025±0.0914	13.2279±1.204	10.3665±0.69
Ni	0.0221±0.0033	0.0263±0.0143	0.0276±0.0121	0.0304±0.0165	0.0373±0.0058	0.0231±0.0061	0.0132±0.0025	0.0075±0.003
Pb	0.2581±0.2512	0.0980±0.0870	0.0597±0.0496	0.0098±0.0009	0.0168±0.0049	0.0105±0.0005	0.0080±0.0020	0.0057±0.004
Zn	7.7579±2.8455	4.2841±2.3154	47.1068±35.068	43.7792±34.461	5.1039±1.4962	6.8652±1.4133	8.2039±4.1835	7.1112±3.273
SO_4^{2-}	16.5842±1.755	12.7377±1.038	54.7543±44.592	37.5612±30.348	21.7575±1.7675	16.9516±3.332	14.3465±4.184	12.9488±3.658
NO_3^-	19.1418±6.489	11.6432±5.749	22.8847±13.6369	35.1403±27.102	7.9971±2.0755	9.5924±0.4350	10.1218±6.0786	9.1986±5.3126
F^-	0.2253±0.1490	0.1279±0.0119	0.6328±0.4983	0.8181±0.7260	0.4974±0.2505	0.4675±0.1059	0.3528±0.2573	0.3025±0.1976
Cl^-	35.2605±8.779	27.5700±9.965	34.0770±27.685	33.6836±29.158	51.7647±36.012	13.8132±1.766	12.8465±1.855	13.4674±0.799
NH_4^+	2.0672±0.9220	2.6526±0.9130	UD	UD	UD	UD	UD	UD
Na^+	4.4645±3.2127	2.3807±1.0549	2.9499±0.9095	5.5406±4.2395	22.0250±17.4178	3.3585±0.5805	UD	UD
K^+	1.4713±0.4104	1.1149±0.3164	8.1166±6.8459	8.0539±6.8829	2.2835±0.2799	1.6430±0.1206	0.8379±0.3455	0.8897±0.2913
Ca^{2+}	22.3532±7.6761	13.9105±1.5283	31.8734±26.6703	19.2736±15.4603	19.5824±7.7858	10.9560±1.9442	6.5161±3.1196	4.9522±0.0287
Mg^{2+}	1.2115±0.1785	0.7820±0.1791	3.7953±3.2110	3.0715±2.4409	2.9695±1.5444	1.1228±0.0217	0.22450.1290	0.3803±0.2793

Table(5): Statistical analysis of chemical species in TSP and PM10 at spring from different areas of Cairo

	Tabbin		Helwan		Shobra Elkhimah		Fifth Settlement	
	TSP	**PM10**	**TSP**	**PM10**	**TSP**	**PM10**	**TSP**	**PM10**
Al	10.1693±1.7468	7.2459±2.2374	33.5854±1.0819	11.4819±2.9853	18.0101±3.3884	13.4938±0.0447	8.8165±3.8761	7.1712±2.7698
Co	0.0093±0.0012	0.0077±0.0013	0.0087±0.0000	0.0055±0.0011	0.0191±0.0069	0.0152±0.0040	0.0060±0.0018	0.0077±0.0030
Cr	UD	UD	UD	UD	UD	UD	UD	UD
Cu	0.0284±0.0077	0.0210±0.0057	0.0570±0.0150	0.0132±0.0029	0.0583±0.0226	0.0441±0.0042	0.0160±0.0060	0.0126±0.0053
fe	3.9787±1.1425	2.1574±1.6676	6.1032±0.7747	1.8382±0.1609	8.5940±1.2623	5.3970±0.1440	2.2062±0.1705	2.2311±0.5648
Mg	1.9588±0.8771	1.7921±0.6110	3.7815±0.5716	0.6047±0.0529	7.8812±1.1970	3.2201±1.4871	4.2121±2.0097	2.8878±1.9446
Mn	0.6430±0.1885	0.5131±0.3051	26.1173±3.4552	6.4456±0.2883	0.5655±0.1478	0.3660±0.1105	10.7113±0.9733	8.3937±0.5656
Ni	0.0267±0.0040	0.0303±0.0147	0.0350±0.0135	0.0129±0.0025	0.0451±0.0070	0.0280±0.0074	0.0107±0.0020	0.0061±0.0023
Pb	0.3123±0.3039	0.1884±0.1929	0.0453±0.0137	0.0061±0.0038	0.0204±0.0060	0.0127±0.0006	0.0065±0.0017	0.0046±0.0035
Zn	9.3871±3.4431	4.9287±2.3602	41.0474±3.3781	13.8169±3.5438	6.1772±1.8116	8.3078±1.7118	6.6428±3.3868	5.7593±2.6532
SO_4^{2-}	32.2697±3.4156	23.9689±0.8949	42.7535±10.9551	11.5105±3.5578	26.3316±2.1357	20.5120±4.0274	11.6168±3.3865	10.4860±2.9678
NO_3^-	37.2464±12.6279	22.2253±11.6898	22.3539±3.3018	10.6824±2.2409	9.6788±2.5132	11.6075±0.5241	8.1956±4.9213	7.4505±4.3060
F^-	0.4384±0.2900	0.2409±0.0189	0.5161±0.0953	0.2221±0.1205	0.6020±0.3033	0.5658±0.1282	0.2857±0.2083	0.2450±0.1601
Cl^-	68.6103±17.0830	51.6311±17.6218	26.6955±6.6942	9.4668±4.4770	62.6423±43.5755	16.7147±2.1331	10.4028±1.5031	8.1432±2.1070
NH_4^+	4.0223±1.7941	5.0673±1.9397	UD	UD	UD	UD	UD	UD
Na^+	8.6871±6.2514	4.4910±2.0638	4.2355±2.1491	1.8023±0.3678	26.6529±21.0763	4.0639±0.7016	UD	UD
K^+	2.8629±0.7986	2.0828±0.4718	6.0325±2.0566	2.3027±1.0116	2.7635±0.3384	1.9881±0.1456	0.6785±0.2797	0.7205±0.2363
Ca^{2+}	43.4952±14.9362	26.1887±2.4692	23.9654±7.6846	5.9556±1.7515	23.6983±9.4197	13.2572±2.3500	5.2768±2.5267	4.0096±0.0208
Mg^{2+}	2.3573±0.3473	1.4668±0.2888	2.8080±0.9797	0.9592±0.2640	3.5935±1.8687	1.3587±0.0265	0.1818±0.1044	0.3080±0.226

- Heavy metals Enrichment Factors (EF): Enrichment Factors (EF) were assigned for different elements to distinguish between natural and anthropogenic sources. Therefore, its use helps to determine whether a certain element has additional or anthropogenic sources other than its major natural sources. The EF method normalizes the measured elemental content with respect to a sample reference element. Al, Si, Ti and Fe are commonly used as reference elements for the main source of the Earth's crust composition.

For this study, Al was used as a reference because it is a major constituent of clay minerals and has been successfully used by several researchers as tracer.

The EFs of the selected element detected in the four areas were calculated using the following equation: EFX = (Cx/Cref) PM / (Cx/Cref) crust

where EFx is the enrichment factor of species x that represents the chemical element of interest. Cx represents the concentration of the element of interest and Cref is the concentration of a reference element. (Cx/Cref) PM is the concentration ratio of element x to the reference element in the aerosol sample and (Cx/Cref) crust is the concentration ratio of x to the reference element in the upper continental crust. For analysis, elements with EF value close to 1, are considered as crustal or as natural, $EF < 10$ were considered as non-enriched, $10 < EF < 100$ as moderately enriched and $EF > 100$ as highly enriched (Silva et al., 2019).

From figure 6 to figure 13 represent the current elements concentrations and enrichment factors of elements in Particulate Matter from different areas in Cairo at autumn and spring seasons.

- **Heavy metals statistical analysis:** Table 6 represent bivariate Pearson correlations between heavy metals in Particulate Matter from different areas in Cairo at autumn and spring seasons.

Table(6): Bivariate Pearson correlations between heavy metals in TSP and PM10

Tabbin									
	Al	**Co**	**Cu**	**Fe**	**Mg**	**Mn**	**Ni**	**Pb**	**Zn**
TSP									
Al	1								
Co	-.008	1							
Cu	.829*	.246	1						
Fe	.471	-.405	-.102	1					
Mg	.878*	-.021	.963**	.044	1				
Mn	.057	-.205	-.491	.876*	-.414	1			
Ni	.707	-.178	.201	.941**	.295	.746	1		
Pb	.083	-.511	-.486	.916*	-.329	.946**	.734	1	
Zi	.959**	-.242	.816*	.420	.922**	-.054	.608	.062	1
PM10									
Al	1								
Co	.975**	1							
Cu	.939**	.880*	1						
Fe	.864*	.755	.969**	1					
Mg	.736	.819*	.466	.300	1				
Mn	.989**	.932**	.944**	.905*	.674	1			
Ni	.898*	.922**	.690	.571	.951**	.866*	1		
Pb	.978**	.916*	.911*	.878*	.699	.996**	.886*	1	
Zi	.977**	.963**	.845*	.760	.845*	.964**	.968**	.972**	1

Cont. Table(6): Bivariate Pearson correlations between heavy metals in TSP and PM10

Helwan									
	Al	**Co**	**Cu**	**Fe**	**Mg**	**Mn**	**Ni**	**Pb**	**Zn**
TSP									
Al	1								
Co	.999**	1							
Cu	.816*	.844*	1						
Fe	.963**	.975**	.942**	1					
Mg	.947**	.961**	.959**	.999**	1				
Mn	.959**	.972**	.946**	1.000**	.999**	1			
Ni	.560	.600	.936**	.764	.797	.771	1		
Pb	.968**	.954**	.644	.863*	.834*	.857*	.332	1	
Zi	.998**	.994**	.778	.944**	.924**	.940**	.507	.982**	1
PM10									
Al	1								
Co	1.000**	1							
Cu	.970**	.975**	1						
Fe	.998**	.999**	.982**	1					
Mg	.998**	.999**	.982**	1.000**	1				
Mn	.997**	.998**	.985**	1.000**	1.000**	1			
Ni	.977**	.980**	1.000**	.987**	.987**	.990**	1		
Pb	.457	.473	.658	.505	.505	.520	.638	1	
Zi	1.000**	1.000**	.971**	.999**	.999**	.997**	.977**	.458	1
Shobra Elkhimah									
	Al	**Co**	**Cu**	**Fe**	**Mg**	**Mn**	**Ni**	**Pb**	**Zn**
TSP									
Al	1								
Co	.971**	1							
Cu	.966**	1.000**	1						
Fe	.993**	.937**	.930**	1					
Mg	.995**	.943**	.935**	1.000**	1				
Mn	.991**	.994**	.992**	.969**	.973**	1			
Ni	.996**	.946**	.939**	1.000**	1.000**	.975**	1		
Pb	.985**	.998**	.996**	.958**	.963**	.999**	.965**	1	
Zi	.985**	.998**	.996**	.958**	.962**	.999**	.965**	1.000**	1
PM10									
Al	1								
Co	.373	1							
Cu	.753	.891*	1						
Fe	.968**	.595	.894*	1					
Mg	.215	.986**	.805	.454	1				
Mn	.385	-.712	-.317	.140	-.818*	1			
Ni	.427	-.680	-.274	.185	-.791	.999**	1		
Pb	.945**	.049	.496	.832*	-.116	.666	.699	1	
Zi	.465	.995**	.933**	.673	.965**	-.638	-.602	.150	1

Cont. **Table(6):** Bivariate Pearson correlations between heavy metals in TSP and PM10

Fifth Settlement									
	Al	**Co**	**Cu**	**Fe**	**Mg**	**Mn**	**Ni**	**Pb**	**Zn**
TSP									
Al	1								
Co	.993**	1							
Cu	.999**	.997**	1						
Fe	.736	.812*	.767	1					
Mg	1.000**	.990**	.998**	.721	1				
Mn	.784	.853*	.812*	.997**	.771	1			
Ni	.953**	.982**	.966**	.907*	.946**	.935**	1		
Pb	-.731	-.644	-.698	-.076	-.746	-.150	-.490	1	
Zi	.999**	.988**	.996**	.710	1.000**	.760	.941**	-.756	1
PM10									
Al	1								
Co	1.000**	1							
Cu	1.000**	1.000**	1						
Fe	.993**	.993**	.990**	1					
Mg	.968**	.967**	.972**	.936**	1				
Mn	.804	.806	.791	.870*	.656	1			
Ni	-.840*	-.839*	-.852*	-.769	-.925**	-.353	1		
Pb	-.911*	-.910*	-.920**	-.855*	-.967**	-.488	.989**	1	
Zi	.999**	.999**	1.000**	.987**	.975**	.780	-.861*	-.927**	1
*. Correlation is significant at the 0.05 level (2-tailed).									
**. Correlation is significant at the 0.01 level (2-tailed).									

Differences in mass concentrations of water-soluble ions: Water soluble anions (sulfate, nitrate, fluoride and chloride) and cations (sodium, potassium, calcium, ammonium and magnesium) were determined with ion chromatography at TSP and PM10 in four regions (Tabbin, Helwan, Shobra Elkhimah and Fifth Settlement). In Autumn, the mass of total WSI contributed about 19%, 30% of the total TSP mass in Tabbin and Helwan, and 10% in Shobra Elkhimah and Fifth Settlement, meanwhile it contributed about 21%, 56%, 8% and 10% of the PM10 mass in Tabbin, Helwan, Shobra

Elkhimah and Fifth Settlement, respectively as shown in table 4. While in Spring, the mass of total WSI contributed about 33%, 20%, 11% and 9% of the total TSP mass in Tabbin, Helwan, Shobra Elkhimah and Fifth Settlement, respectively, meanwhile it contributed about 36%, 14%, 9% and 12% of the PM10 mass in Tabbin, Helwan, Shobra Elkhimah and Fifth Settlement, respectively as shown in table 5.

At Autumn and Spring, chloride, calcium, nitrate and sulfate are the main constituents in water soluble ionic species at TSP and PM10 in Tabbin, Helwan and Fifth Settlement while in Shobra Elkhimah, chloride, sodium, calcium and sulphate at TSP and chloride, calcium, nitrate and sulfate at PM10 are the main constituents.

- **Differences in specific ionic ratios**

○ Enrichment Factors (EF)

The suspended particles in air commonly hold marine and non-marine sources. The non-marine source hold both anthropogenic as well as crustal form. To detect the marine source, the soluble components compared with the sea water composition. To inspect the conceivable sources of the chemical components (marine, crustal or anthropogenic), the enrichment factor (EF) as defined below is used:

$$\mathbf{EF(X) = (X/Me)_{aer} / (X/Me)}$$

where (X/Me)aer is the ratio of any element X with respect to the reference element Me in the aerosol and (X/Me) is the conformable ratio in the seawater. For seawater, Me is constantly taken as Na+. Enrichment factor is an obvious indicator of the effect of Non Sea Salt (NSS) fraction of aerosols. Any particular component (X) derived from sea salt sources gets enriched only due to the effect of the same component derived from anthropogenic sources. (Das *et al*., 2011).

Using the relationship shown in table 7 and table 8, the nss (%) fraction for different ions were calculated as shown in table 9 and table 10. All ratios were higher than the sea water ratio. This indicates that the particulates matter at four areas consists of non-marine components.

NO_3^-/nns-SO_4^{2-} ratio

The mass ration of NO_3^-/nns-SO_4^{2-} has been as an index of the respective importance of mobile vs. stationary sources of sulfur and nitrogen in atmosphere (Wang *et al.*, 2017).

From table 9 in this study, all the ratios were lower than one except for TSP in Tabbin, the low mass ratios implicit stationary emissions were triumphant for Atmospheric Particulate Matter.

Table(7): Evaluation of sea salt ration, NSS and EF at Autumn season

Ratio	**Particulates type**	Cl^-/Na^+	SO_4^{2-}/Na^+	Ca^{2+}/Na^+	K^+/Na^+	Mg^{2+}/Na^+
Tabbin	TSP	3.71	7.90	0.33	5.01	0.27
	PM_{10}	5.35	11.58	0.47	5.84	0.33
Helwan	TSP	18.56	11.55	2.75	10.80	1.29
	PM_{10}	6.78	6.08	1.45	3.48	0.55
Shobra Elkhimah	TSP	0.99	2.35	0.10	0.89	0.13
	PM_{10}	5.05	4.11	0.49	3.26	0.33
Sea ratio (N. Das *et al.*, 2011)		1.167	0.125	0.044	0.227	0.022
Non sea salt (NSS) (%)						
	Particulates type	Cl^-	SO_4^{2-}	Ca^{2+}	K^+	Mg^{2+}
Tabbin	TSP	16.03	30.05	0.46	22.16	1.11
	PM_{10}	12.44	24.79	0.57	13.81	0.73
Helwan	TSP	54.39	30.63	7.45	31.74	3.73
	PM_{10}	36.87	27.22	6.80	19.03	2.95
Shobra Elkhimah	TSP	19.00	26.06	-2.72	18.61	2.48
	PM_{10}	16.53	9.89	0.88	10.81	1.05

Cont. Table(7): Evaluation of sea salt ration, NSS and EF at Autumn season

Enrichment Factor (EF) with respect to sea water						
	Particulates type	Cl^-	SO_4^{2-}	Ca^{2+}	K^+	Mg^{2+}
Tabbin	TSP	29.72	63.18	2.64	40.05	2.17
	PM_{10}	42.80	92.65	3.75	46.74	2.63
Helwan	TSP	148.49	92.42	22.01	86.44	10.29
	PM_{10}	54.23	48.64	11.63	27.83	4.43
Shobra Elkhimah	TSP	7.90	18.80	0.83	7.11	1.08
	PM_{10}	40.38	32.90	3.91	26.10	2.67

Table(8): Evaluation of sea salt ration, NSS and EF at Spring season

Ratio	**Particulates type**	Cl^-/Na^+	SO_4^{2-}/Na^+	Ca^{2+}/Na^+	K^+/Na^+	Mg^{2+}/Na^+
Tabbin	TSP	7.90	3.71	5.01	0.33	0.27
	PM10	11.50	5.34	5.83	0.46	0.33
Helwan	TSP	6.30	10.09	5.66	1.42	0.66
	PM10	2.35	0.99	0.89	0.10	0.13
Shobra Elkhimah	TSP	2.35	0.99	0.89	0.10	0.13
	PM10	4.11	5.05	3.26	0.49	0.33
Sea ratio (N. Das *et al.*, 2011)		1.167	0.125	0.044	0.227	0.022
Non sea salt (nss) (%)						
	Particulates type	Cl^-	SO_4^{2-}	Ca^{2+}	K^+	Mg^{2+}
Tabbin	TSP	58.47	31.18	43.11	0.89	2.17
	PM10	46.39	23.41	25.99	1.06	1.37
Helwan	TSP	21.75	42.22	23.78	5.07	2.71
	PM10	31.54	23.00	22.53	-3.29	3.01
Shobra Elkhimah	TSP	31.54	23.00	22.53	-3.29	3.01
	PM10	11.97	20.00	13.08	1.07	1.27
Enrichment Factor (EF) with respect to sea water						
	Particulates type	Cl^-	SO_4^{2-}	Ca^{2+}	K^+	Mg^{2+}
Tabbin	TSP	63.18	29.72	40.05	2.64	2.17
	PM10	91.97	42.70	46.65	3.71	2.61
Helwan	TSP	50.42	80.75	45.27	11.39	5.30
	PM10	18.80	7.90	7.11	0.83	1.08
Shobra Elkhimah	TSP	18.80	7.90	7.11	0.83	1.08
	PM10	32.90	40.38	26.10	3.91	2.67

In the current study, the NO_3^-/SO_4^{2-} ratios in Tabbin (0.94-1.19) were higher than in Helwan (0.42-0.95) and Shobra Elkhimah (0.42-0.58) for two types of particles in both spring and autumn, indication that the contribution of stationary emission to total particles in Tabbin were higher than in Helwan and Shobra Elkhimah.

Table(9): Mass ration of NO_3^-/NSS-SO_4^{2-}

area	**Particulates type**	**NO_3^-/SO_4^{2-}**	
		Autumn	**Spring**
Tabbin	TSP	1.19	1.19
	PM10	0.94	0.95
Helwan	TSP	0.42	0.53
	PM10	0.95	0.42
Shobra Elkhimah	TSP	0.42	0.42
	PM10	0.58	0.58

TSP: Total Suspended Particulate
PM_{10}: Particulate Matter with an aerodynamic diameter less than 10 µm
NSS: Non Sea Salt

- **Correlation Coefficient:** Table 10 represent bivariate Pearson correlations between soluble ions in particulate matter from different areas in Cairo at autumn and spring seasons.

Table(10): Bivariate Pearson correlations between heavy metals in TSP and PM10

Tabbin									
	SO_4^-	NO_3^-	F^-	Cl^-	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}
TSP									
SO_4^{2-}	1								
NO_3^-	.843*	1							
F^-	.690	.911*	1						
Cl^-	.665	.266	-.072	1					
NH_4^+	.820*	.735	.835*	.213	1				
Na^+	.325	.499	.152	.419	-.180	1			
K^+	.933**	.848*	.845*	.386	.968**	.062	1		
Ca^{2+}	.712	.232	.134	.769	.617	-.187	.640	1	
Mg^{2+}	.824*	.687	.341	.844*	.354	.742	.575	.509	1
PM_{10}									
SO_4^{2-}	1								
NO_3^-	.471	1							
F^-	.991**	.421	1						
Cl^-	.796	-.134	.842*	1					
NH_4^+	.633	.794	.666	.279	1				
Na^+	.541	.859*	.439	-.055	.467	1			
K^+	.855*	.283	.790	.665	.198	.615	1		
Ca^{2+}	.986**	.380	.999**	.865*	.645	.400	.785	1	
Mg^{2+}	.923**	.101	.943**	.965**	.410	.207	.805	.956**	1

Cont. Table(10): Bivariate Pearson correlations between heavy metals in TSP and PM10

Helwan								
	SO_4^{2-}	NO_3^-	F^-	Cl^-	NH_4^+	K^+	Ca^{2+}	Mg^{2+}
TSP								
SO_4^{2-}	1							
NO_3^-	.873*	1						
F^-	.998**	.899*	1					
Cl^-	1.000**	.875*	.999**	1				
NH_4^+	.045	.523	.102	.049	1			
K^+	.998**	.844*	.994**	.998**	-.011	1		
Ca^{2+}	.999**	.851*	.995**	.999**	.002	1.000**	1	
Mg^{2+}	.998**	.842*	.993**	.998**	-.015	1.000**	1.000**	1
PM$_{10}$								
SO_4^{2-}	1							
NO_3^-	.999**	1						
F^-	.999**	.997**	1					
Cl^-	.999**	.997**	1.000**	1				
NH_4^+	1.000**	1.000**	.997**	.998**	1			
K^+	1.000**	.998**	1.000**	1.000**	.998**	1		
Ca^{2+}	1.000**	.999**	.999**	.999**	1.000**	1.000**	1	
Mg^{2+}	1.000**	1.000**	.999**	.999**	1.000**	.999**	1.000**	1

Cont. Table(10): Bivariate Pearson correlations between heavy metals in TSP and PM10

Shobra Elkhimah								
	SO_4^{2-}	NO_3^-	F^-	Cl^-	NH_4^+	K^+	Ca^{2+}	Mg^{2+}
TSP								
SO_4^{2-}	1							
NO_3^-	-.189	1						
F^-	-.375	.981**	1					
Cl^-	.700	-.834*	-.924**	1				
NH_4^+	.686	-.844*	-.932**	1.000**	1			
K^+	.980**	-.383	-.553	.829*	.818*	1		
Ca^{2+}	.780	-.762	-.873*	.993**	.990**	.890*	1	
Mg^{2+}	.738	-.802	-.902*	.999**	.997**	.858*	.998**	1
PM_{10}								
SO_4^{2-}	1							
NO_3^-	.786	1						
F^-	-.535	.101	1					
Cl^-	.979**	.895*	-.353	1				
NH_4^+	.998**	.821*	-.485	.989**	1			
K^+	.890*	.982**	-.091	.964**	.915*	1		
Ca^{2+}	.999**	.814*	-.496	.988**	1.000**	.910*	1	
Mg^{2+}	.359	.859*	.597	.540	.412	.745	.401	1

Table(10): Bivariate Pearson correlations between heavy metals in TSP and PM10

Fifth settlement							
	SO_4^{2-}	NO_3^-	F^-	Cl^-	K^+	Ca^{2+}	Mg^{2+}
TSP							
SO_4^{2-}	1						
NO_3^-	.979**	1					
F^-	.971**	.999**	1				
Cl^-	-.418	-.593	-.622	1			
K^+	.994**	.996**	.992**	-.518	1		
Ca^{2+}	-.781	-.891*	-.907*	.894*	-.846*	1	
Mg^{2+}	.981**	1.000**	.999**	-.586	.997**	-.887*	1
PM_{10}							
SO_4^{2-}	1						
NO_3^-	.979**	1					
F^-	.973**	1.000**	1				
Cl^-	.758	.608	.588	1			
K^+	.999**	.988**	.984**	.723	1		
Ca^{2+}	.373	.174	.149	.887*	.323	1	
Mg^{2+}	.968**	.999**	1.000**	.571	.980**	.129	1

*. Correlation is significant at the 0.05 level (2-tailed).
**. Correlation is significant at the 0.01 level (2-tailed).

CONCLUSION

- In spring, the maximum concentration in the TSP of Co, Cu, Fe, Mg and Ni are recorded in Shobra Elkhimah, Al, Mn and Zn are found in Helwan, whereas in autumn, the maximum concentration in the TSP of Co, Cu, Fe and Ni is recorded in Shobra Elkhimah, Al, Cu, Mn and Zn are found in Helwan. At both seasons, Pb is found in Tabbin and Cr is not found in TSP for all filters sample. On the other hand, in spring, the maximum concentration of NO_3^-, Cl^-, and Ca^{2+} are found in Tabbin, F^-, Na^+, and Mg^{2+} are found in Shobra Elkhimah and SO_4^- and K^+ are recorded in Helwan, while in autumn, SO_4^-, NO_3^-, F^-, K^+, Ca^{2+} and Mg^{2+} are found in Helwan, Cl^- and Na^+ are recorded in Shobra Elkhimah. NH_4^+ is found only in Tabbin. Na^+ is not recorded in Fifth Settlement.

- The maximum concentration in the PM_{10} of Al, Co, Cu, Fe and Mg are found in Shobra Elkhimah, Ni and Pb are found in Tabbin, Mn is found only in Fifth Settlement and Zn is found only in Helwan. While in autumn, the maximum concentration in the PM_{10} of Al, Co, Fe, Mn, Ni and Zn is recorded in Helwan, Pb is found only in Tabbin, Cu is found in Shobra Elkhimah and Mg is found in Fifth Settlement. At both seasons, and Cr is not found in PM_{10} for all filters sample. On the other hand, in spring, the maximum concentration of SO_4^-, NO_3^-, Cl^-, Na^+, Ca^{2+} and Mg^{2+} are found in Tabbin, F^- is found in Shobra Elkhimah and K^+ is recorded in Helwan. NH_4^+ is found only in Tabbin also. Na^+ is not recorded in Fifth

Settlement also, while in autumn, SO_4^-, NO_3^-, F^-, Cl^-, Na^+, K^+, Ca^{2+} and Mg^{2+} are found in Helwan,. NH_4^+ is found only in Tabbin also. Na^+ is not recorded in Fifth Settlement also.

- Generally, it may be concluded that all heavy metals increase in Tabbin, Helwan, Shobra Elkhimah and Fifth Settlement in spring, otherwise decrease in autumn. On the contrary, all water-soluble ions increase in autumn in study areas and decrease in spring.
- The calculated EF revealed that all analyzed elements and Soluble ions are of anthropogenic origin
- From the point of occupational health, all areas are ranging from moderate to danger for both spring and autumn.

RECOMMENDATION

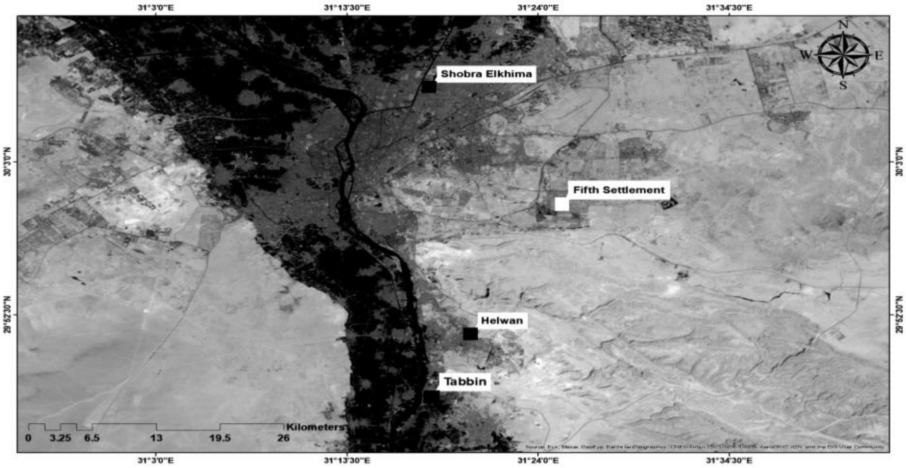
- From point of mitigation, other roads should be structured to motivate the air motion
- The landscape should be taken into consideration as an additional lung to the present citizens because of low pollution.
- Madinaty or El-Rehab areas should be taken as a reference areas instead of the Fifth Settlement.
- The results obtained from this project can be the base foundation of a new project funded by the Egyptian government to conduct the same

measurements for heavy metals and water-soluble ions in several area all over Egypt a data base for the concentration of Such pollutants in several areas in Egypt can be studied.

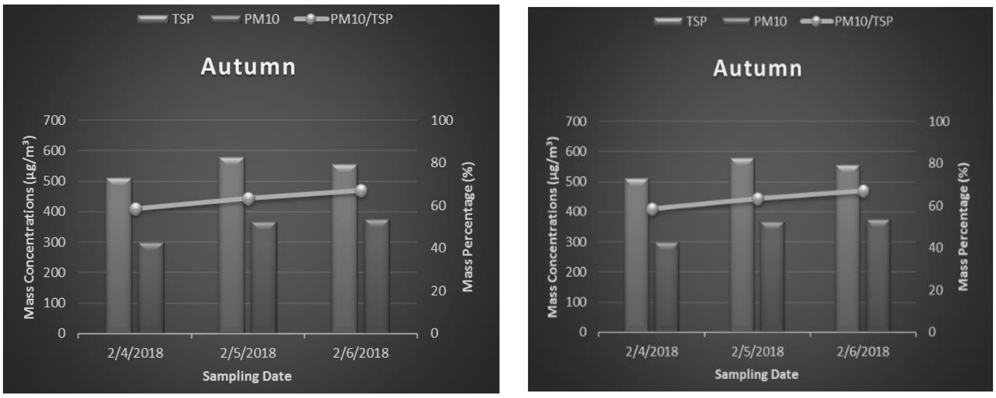
- The ministry of environment, ministry of health and ministry commerce can cooperate in a joint study to estimate the impact of such pollutants on the human health, local environment and Egyptian economy
- Perform continuous monitoring programs for the ambient air in areas under study.
- Applying stringent legislations through connecting the stack source emissions for different industrial processes to national network for air quality monitoring using CEMS (continuous emission monitoring systems).
- Applying treatment or filter systems for different industrial complexes such as electro-precipitators, bag filters and others.
- Finding other routes in order to decrease vehicles emission load resulted from heavy traffic roads.
- Applying precancerous monitoring programs in residential area, as we all know that early detection of problems is very best way to treat before developing.
- Further researches are required to draw a clearer picture for the current situation in terms of air quality and health impact of hazardous air pollutants.

- Air quality dispersion models have the ability to predict the future air quality conditions using a mathematical tool through using he collected data as an input data for the model which can predict the future conditions for the study area
- The study areas are highly populated area and also with high density, this study recommends to either reduce the number of industrial facilities in the area or to prevent any new industrial facilities installation.

Encourage the industrializing and using the electric traffics for people with tax free benefits or obligation for school buses for example

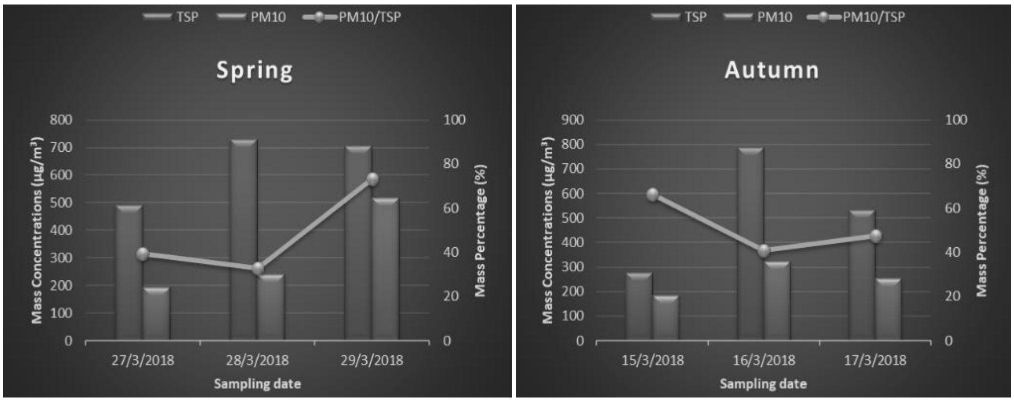


Figure(1): Map of the study area where the black spots indicate industrial sites and the white spot indicate reference area.



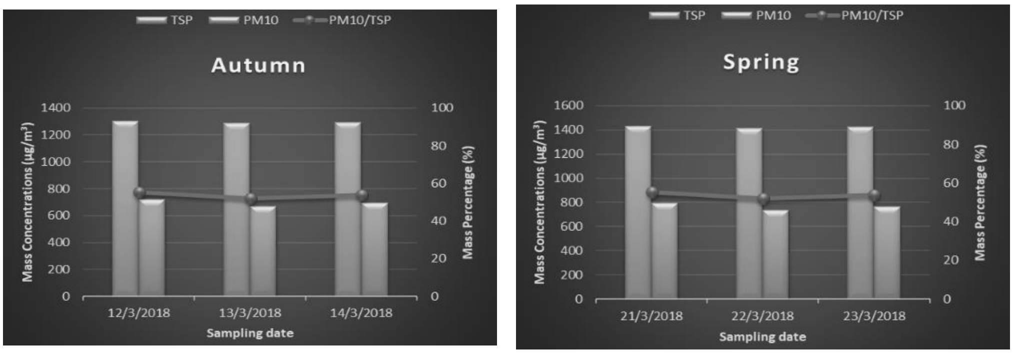
TSP: Total suspended Particulate **PM$_{10}$**: particulate matter with an aerodynamic diameter less than 10 µm

Figure(2): Time series of TSP and PM10 mass concentration and the mass percentages for PM10/TSP in different seasons for Tabbin



TSP: Total suspended Particulate **PM$_{10}$:** particulate matter with an aerodynamic diameter less than 10 µm

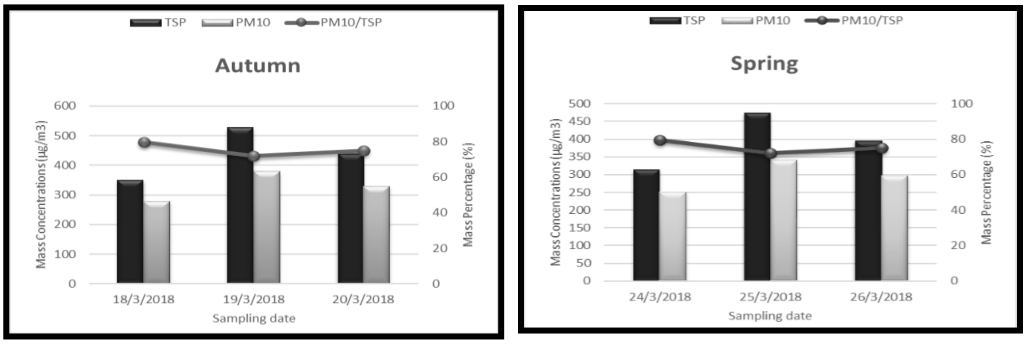
Figure(3): Time series of TSP and PM10 mass concentration and the mass percentages for PM10/TSP in different seasons for Helwan



TSP: Total suspended Particulate

PM10: particulate matter with an aerodynamic diameter less than 10 µm

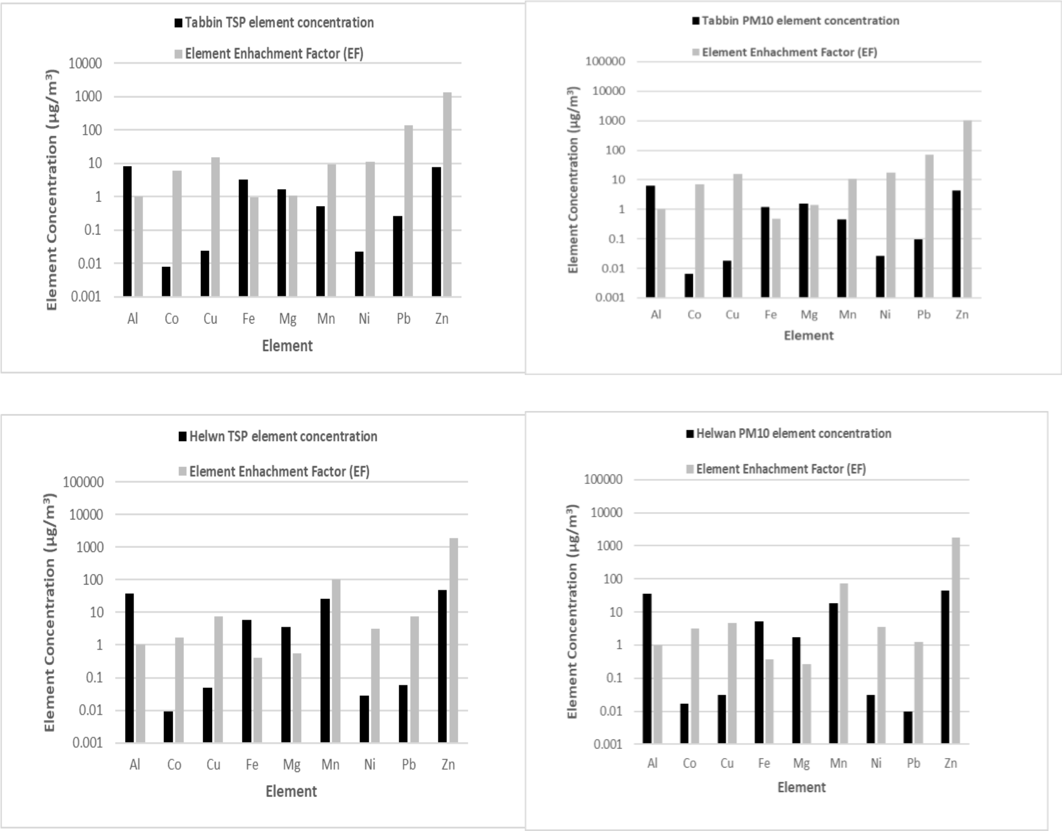
Figure(4): Time series of TSP and PM10 mass concentration and the mass percentages for PM10/TSP in different seasons for Shobra Elkhimah



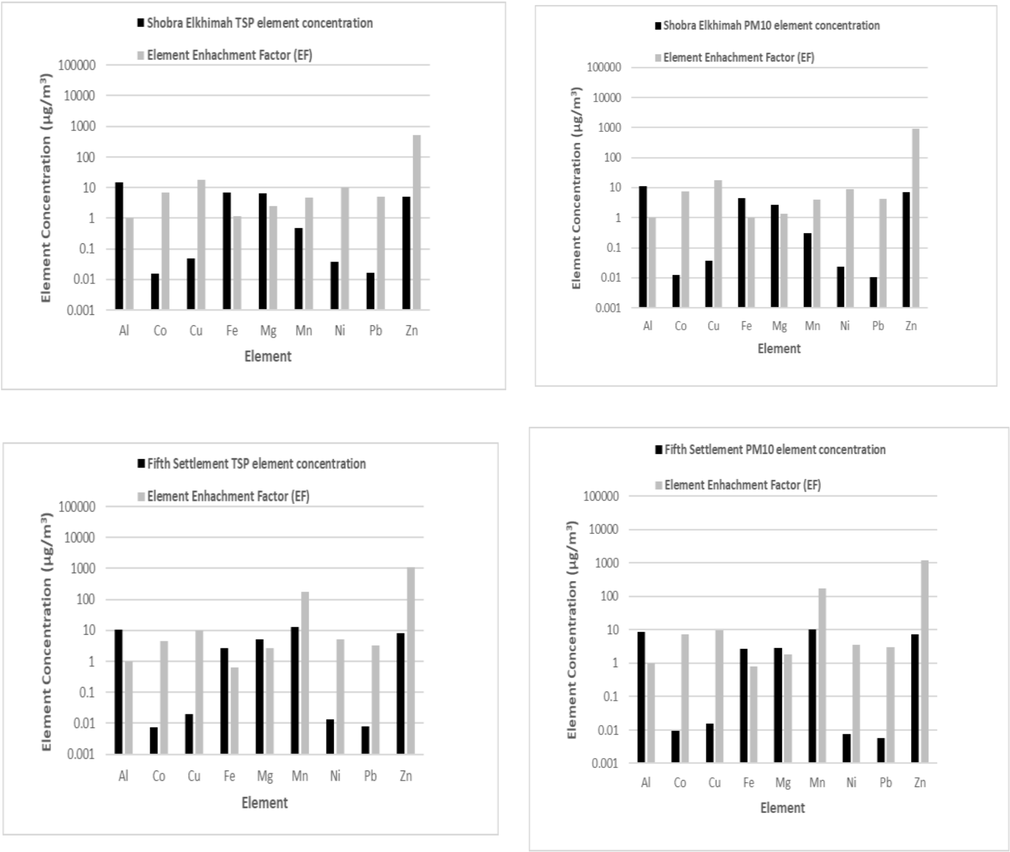
TSP: Total suspended Particulate

PM10: particulate matter with an aerodynamic diameter less than 10 µm

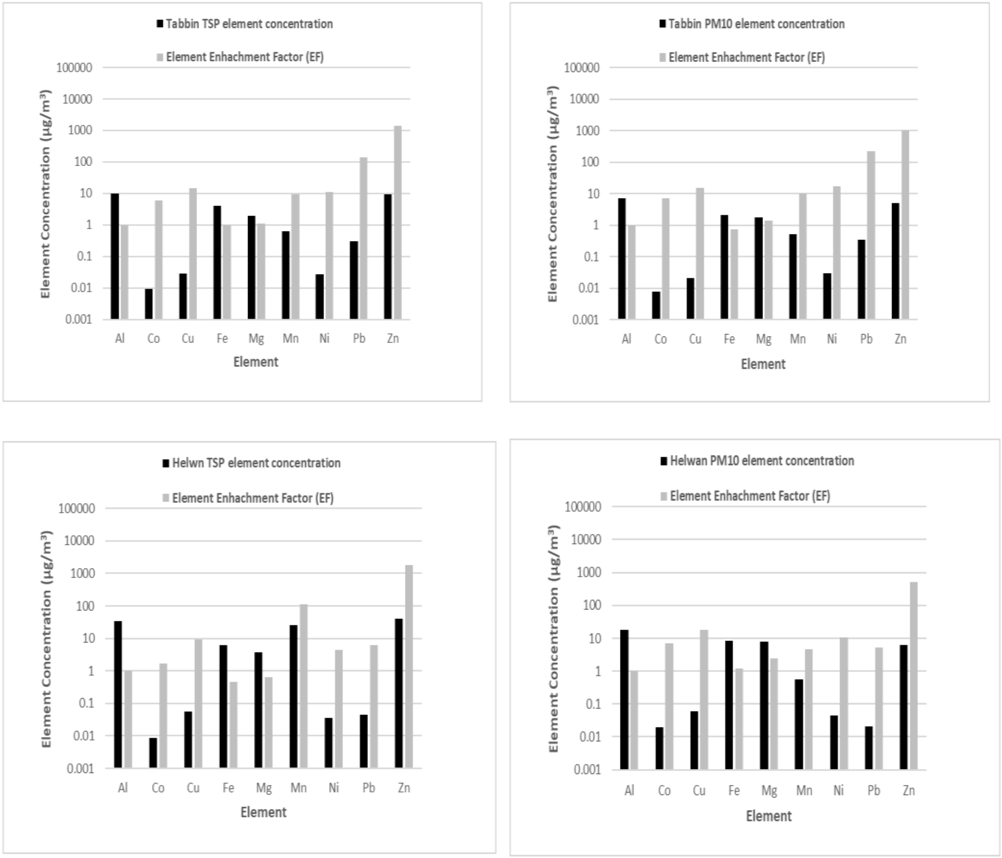
Figure (5): Time series of TSP and PM10 mass concentration and the mass percentages for PM10/TSP in different seasons for Fifth settlement



Figure(6): Heavy metals concentrations and their enrichment factors for all areas at Autumn season



Figure(6): (Cont.) Heavy metals concentrations and their enrichment factors for all areas at Autumn season



Figure(7): Heavy metals concentrations and their enrichment factors for all areas at Spring season

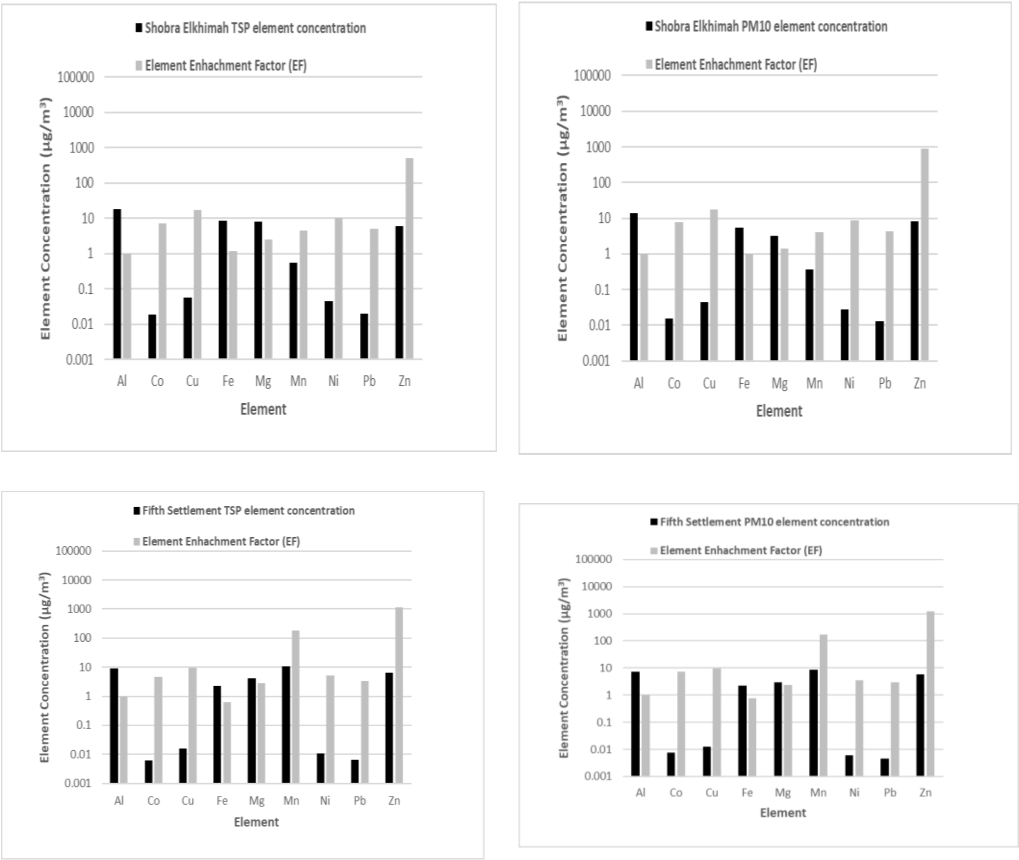


Figure (7): (Cont.) Heavy metals concentrations and their enrichment factors for all areas at Spring season

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مقارنة التركيب الكيميائى غير العضوى للجسيمات العالقة الكلية والمستنشقة فى مناطق مختلفة من القاهرة

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المستخلص

تم إيضاح التركيب الكيميائى غير العضوى للجسيمات العالقة والمستنشقة فى مناطق مختلفة من القاهرة فى هذه الدراسة. توضح النتائج أن أعلى تركيز للجسيمات العالقة الكلية (TSP) والجسيمات ذات قطر ديناميكى اقل من ١٠ ميكرون (PM10) يكون مجاور للمناطق الصناعية والمناطق ذات الكثافات المرورية العالية.

أوضحت النتائج أن تركيز الأتربة بمنطقة شبرا الخيمة أعلى من نظيراتها فى المناطق الأخرى فى كلا من الجسيمات العالقة الكلية والجسيمات المستنشقة. وتم ملاحظة هذه النتائج فى فصلى الربيع والخريف.

كما أظهرت النتائج أن تركيز العناصر الثقيلة فى حلوان أعلى من مثيلاتها فى المناطقة الأخرى. تشير هذه التركيزات إلى أن تلوث المعادن الثقيلة في حلوان كان أكثر خطورة.

أظهر تحليل النسب أن أيون الصوديوم والكلوريد لا ينتمان فى الأصل إلى أملاح البحر ولكن ربما يكون مصدر الصوديوم من إعادة تعليق غبار التربة، ومصدر الكلوريد بإرتباطه بأنشطة الاحتراق

كما أن وجود البوتاسيوم يرجع إلى مصادر متنوعة بخلاف حرق الوقود الحيوى. معظم الكبريتات والنترات ذات أصل الوقود الأحفوري.

أظهرت نسبة أيونات السلفات مع ايوانت النترات فى التبين أكبر من حلوان وشبرا الخيمة فى نوعين الأتربة فى فصلى الربيع والخريف، وهذا يشير إلى أن مساهمة المصادر الثابتة في إجمالي الجزيئات في التبين أعلى منها في حلوان وشبرا الخيمة.

الكلمات الافتتاحية: الجسيمات الدقيقة؛ التركيب الكيميائي غير العضوي؛ التبين؛ حلوان؛ شبرا الخيمة؛ التجمع الخامس