



Elemental Composition of PM_{2.5} Particles Sampled in Industrial and Residential Areas of Taif, Saudi Arabia

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ABSTRACT

This paper describes the first part of a project conducted to evaluate the trace element composition of atmospheric aerosol particles (PM_{2.5}) and to determine their influence on air quality in Taif city, Saudi Arabia. PM_{2.5} particles were collected from two different sites (industrial and residential) in Taif during the summer of 2011. The industrial site was situated in the largest industrial area of Taif, and the residential site was situated in the city's most crowded area. PM_{2.5} samples were collected on polycarbonate filters using a cyclonic collector. Each sample was collected over a 24 hour period and new samples were collected weekly. Average PM_{2.5} concentrations of 47 ± 15 and 46 ± 31 $\mu\text{g}/\text{m}^3$ were seen in the industrial and residential areas, respectively. An Energy Dispersive X-ray Fluorescence (EDXRF) spectrometer with a Mo secondary target was used to analyze the solid samples because of the relative simplicity of the technique for filter analysis. The use of a Mo secondary target is advantageous, because it decreases the impact of continuum radiation from the X-ray tube and increases the signal to background ratio. Quantitative X-ray Analysis Software (PyMca) was used to perform quantitative analysis of the atmospheric aerosols. The analysis resulted in detected concentrations for sixteen elements; Si, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Rb, Sr, Pb and Black Carbon (BC). Using Principal Component Analysis (PCA) it was possible to distinguish between natural and anthropogenic sources. The measured concentrations of the potentially hazardous trace elements Cu, Cr, Mn, Ni and Pb were below the limits defined by international guidelines and national standards for ambient air quality. However, further long-term research will be required to validate the quantification of trace elements in particulate matter in Taif.

Keywords: EDXRF; Aerosol particles; PM_{2.5}; Trace element determination; Metals.

INTRODUCTION

It is important to study the chemical composition of atmospheric particulate matter because of its effects on human health (Renwick *et al.*, 2001) and climate change (Karl *et al.*, 1997; Cahill, 1996). In addition, such studies provide information on the origins of the particulate material and can reveal whether it was emitted as primary or secondary particles. Smaller particles can penetrate more deeply into the lungs than larger ones and thus cause more severe harm (Schwartz and Neas, 2000). In addition, fine particulate matter affects the radiation balance of the earth (Horvath, 1998) because it scatters and absorbs much of the incident visible light from the sun. Furthermore, fine

particulate matter has a long atmospheric residence time, which facilitates its transnational and even transcontinental transport over thousands of kilometers, enabling particulate emissions from one country to affect air quality in others. For all these reasons, there is great interest in determining the concentration of fine particulate matter in ambient air. The bulk of these particles originate from anthropogenic emissions (Murray *et al.*, 2001; Ezzati *et al.*, 2002), both as direct products of human activity and as secondary particles formed in the atmosphere from gases such as SO₂, NO_x and volatile organic compounds (VOC). Local emissions of fine particles can cause issues of local and regional concern because they can become highly concentrated in the vicinity of their sources. Black carbon (BC) is one of the main anthropogenic components of particulate air pollution, being produced by incomplete combustion. When it is formed, it invariably mixed with other atmospheric constituents (Liousse *et al.*, 1993). Generally, there are two important reasons for determining the elemental content in airborne particulate matter. First, it can contain heavy elements

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such as Cd, Pb, As, and Sb, which are in themselves toxic to human health. It is of interest to follow the ecocycles of these metals as environmental hazards once they have been released into the atmosphere, biosphere and technosphere. The second aspect is that single elements or ratios of different elements can be used to fingerprint and monitor emissions from specific sources that may also be emitting more hazardous species that are less stable and more difficult to measure. Laws in both the USA and the European Union have established recommended limits on the concentrations of inhalable particles in ambient air (Mark, 1998).

The present work represents the first study on the composition of airborne particulate matter (PM_{2.5}) in Taif city, Saudi Arabia. Taif city is located in the Mecca province, in the western part of Saudi Arabia between longitude (E 40–42°) and latitude (N 20–22°). The cities of Taif and Mecca are closely dependent on one-another since Taif supplies the residents and pilgrims of Mecca with fresh produce from its fertile fields. Due to its location, Taif is also a gateway to Mecca for pilgrims coming from the east across the peninsula, as well as being the summer residence of Mecca's wealthy merchant families. This was mentioned in the Holy Qur'an, (Sura Al Zokhrof 43, 31) which refers to Mecca and Taif as "al-Qariyyatain" or the two cities. Taif is about 100 km and 190 km southeast of Mecca and Jeddah, respectively, and is one of the largest cities in Saudi Arabia. Its population has grown steadily and now stands at over one million based on the city's 2010 census (Central department of statistics and information, 2012). It is located at a relatively high altitude, 1879 meters above sea level on the eastern slopes of the Al-Sarawat Mountains. Its climate is relatively dry, with low humidity but is cooler than those of Jeddah or Mecca and the barren neighboring regions closer to the Red Sea due to its altitude. Even during the very hot summer months, the temperature in Taif ranges from 29°C to 35°C (Abulfaraj *et al.*, 1990). It is therefore a popular summer destination for Saudis, providing an escape from the uncomfortably high temperatures encountered in the country's other cities. In addition, thousands of vacationers from other Arab Gulf states spend the summer season in Taif to enjoy its green scenery and beautiful parks. Furthermore, it has become the official summer seat of the Saudi government. Due to its attractiveness, the city's infrastructure has been expanded and modernized over the decades in order to keep up with growth and to support the blooming tourist industry. The city's desert environment and its ongoing intensification of human activity (tourism, transport, industry, etc.) due to population growth are the main sources of its air pollution. During summer, the city's population density increases substantially, along with the severity of its air pollution problems.

The main anthropogenic sources of air pollution in Taif are vehicle emissions and urban industrial operations. In conjunction with the ubiquitous desert dust and the area's low dispersion factor due to its lack of rain, these sources generate high localized pollutant concentrations. Fumes from vehicles together with suspended particulate matter and sand blown into urban areas from the surrounding desert create air pollution hazes in the city. In addition, the city's

system for collecting and managing solid waste is not optimal, and much of it is burned under un-controlled conditions, presenting a significant health hazard. Studies on atmospheric particulate matter and volatile organic compounds have been conducted in different cities in Saudi Arabia (Abulfaraj *et al.*, 1990; Sabbak, 1990; Ahmed and Al-Swaidan, 1993; Ahmed *et al.*, 1993; Al-Jeelani, 2009; Aburas *et al.*, 2011), but aside from a study on airborne bacteria (Mahdy and El-Sehrawi, 1997), there have been no investigations into particulate pollution in Taif.

The aim of the study was to evaluate trace elemental concentrations in fine particles (PM_{2.5}) and to investigate their influence on local air quality. Fifteen trace elements (Si, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Rb, Sr, and Pb) and black carbon (BC) were analyzed, and their concentrations were evaluated.

MATERIALS AND METHODS

Sampling Sites

In the present work, atmospheric PM_{2.5} aerosols from two different sites (industrial and residential) in Taif, Saudi Arabia, were sampled on polycarbonate filters. Samples were collected over 24 hours once per week from June to August 2011. A sampler consisting of a cyclone loaded with polycarbonate filters was installed at each sampling site. The industrial site was situated in a central location in an industrial area, 4.7 km south east of the Abdallah Ibn Abbas Mosque in the center of Taif city. The industrial area mainly consists of small scale industries; auto repair workshops, metallurgical workshops for auto spare part manufacturing and some food industries. Waste treatment is also done in the area, mainly sorting of material and waste burning. The residential site was located on Television street in a highly populated residential area 2 km the southeast of the Abdallah Ibn Abbas Mosque in the center of Taif city.

Sampling Equipment

Atmospheric aerosols, PM_{2.5}, were been collected on polycarbonate filters loaded inside a collection cartridge in a cyclone (CASELLA Company, UK). The cyclone creates a vortex by making the air-stream move in a cyclonic orbit in which larger particles are separated from the fine particles because their higher inertia prevents them from following the air flow. The cyclones were operated with a flow rate of 3 L/min, which was maintained by a critical orifice located between the pump and the cyclone. The polycarbonate filters had a diameter of 25 mm and a pore size of 0.4 µm; filters of this type have been used in previous studies and found to have high particle collection efficiency and to yield high purity samples (Wagner *et al.*, 2008). Each sample was collected over a 24 h period, with the filters being exchanged at 11 a.m. In order to avoid over-sampling traffic-derived pollutants, the equipment (i.e., the cyclone, flow meter, and pump) was mounted at a height of 20 m above ground level and more than 50 m from the nearest main road. Measurements were acquired simultaneously and in parallel using individual sets of apparatus at the two sites.

Micro Balance

The polycarbonate filters were weighed on a microbalance (Sartorius CC50) before and after sampling in order to determine the mass of the collected material. Prior to the initial and final weighing, the polycarbonate filters were conditioned in a desiccator to stabilize their weights. Filter conditioning and weighing were performed in a room that was maintained at a temperature of 17–23°C and a relative humidity of 45–55%.

EDXRF Setup

The particulate matter collected on the filters was quantitatively analyzed for trace elements by an Energy Dispersive X-ray Fluorescence (EDXRF) spectrometer. The EDXRF spectrometer used for the analysis of the particle samples has a three-axial arrangement built around a silver X-ray tube and uses a molybdenum secondary target that makes the beam nearly monochromatic before it reaches the sample (Boman, 1990; Chimidza, 2001). The quasi-monochromatic excitation of a Mo secondary target provides better sensitivity and selectivity than can be achieved with a direct excitation setup. This improves the method's limits of detection, compared to the more conventional direct excitation setup.

The spectra from the EDXRF were further processed using the PyMca software package (Solé *et al.*, 2007) and the results were converted into airborne concentrations (ng/m^3). The EDXRF method of analyzing samples is multi-elemental, easy to use and inexpensive. It gives elemental concentrations with a typical error margin of 10%, which includes statistical counting errors of the detected elements in the sample. The detection limits for the EDXRF analyses were calculated in accordance with the procedure and guidelines given by the International Union of Pure and Applied Chemistry (IUPAC, 1976) and are specified in terms of both absolute amounts and minimum airborne concentrations in Table 1. The certified reference material (CRM) sample SRM2783, which consists of airborne particulate matter trapped on a filter was used (National Institute of Standard and Technology (NIST), USA) to determine the analytical method's limits of detection. For elements that are not present in the CRM, limits of detection were determined by interpolation based on data for the available elements.

Accuracy of the EDXRF Analysis

The effectiveness and validity of the EDXRF method for quantitative analysis of air particulates collected on a filter were tested by applying the method to a certified reference material (CRM; air particulate on filter media, SRM2783, National Institute of Standards and Technology (NIST), USA). The certified reference material was analyzed directly without being subjected to any preparatory steps, using the procedure described in the preceding section. Table 2 compares the results obtained for the reference material to the certified values. The certified levels of S and V in the CRM are below the limits of detection of the secondary target EDXRF method and thus could not be detected. Overall, the agreement between the measured and expected

Table 1. Limits of detection for the elements considered using EDXRF. The limits are given in ng (absolute mass) per filter, as well as in ng/m^3 for the lowest detectable atmospheric mass given a flow of 3 L/min and a collection time of 24 h.

Element	Detection Limits	
	ng	ng/m^3
Si	11000	2700
S	1000	230
Cl	500	120
K	110	25
Ca	77	18
Ti	31	7.1
V	20	4.6
Cr	10	2.3
Mn	9.2	2.2
Fe	8.5	2.0
Ni	6.0	1.4
Cu	4.5	1.0
Zn	4.8	1.1
Br	4.8	1.1
Rb	4.7	1.1
Sr	4.8	1.1
Pb	5.6	1.3

Table 2. Quantitative analysis of certified reference material (SRM2783, NIST) using the Mo secondary target EDXRF spectrometer.

Element	Measured Values, (ng/cm^2)	Certified Values (ng/cm^2)
S	Not detected	105.42 ± 26.10
K	530 ± 100	530.12 ± 52.21
Ca	1400 ± 60	1325.30 ± 171
Ti	160 ± 10	149.60 ± 24.10
V	Not detected	4.87 ± 0.60
Cr	17 ± 1.4	13.55 ± 2.51
Mn	58 ± 2.1	32.13 ± 1.21
Fe	3000 ± 39	2660.65 ± 161
Ni	8.5 ± 2.1	6.83 ± 1.21
Cu	59 ± 4.2	40.56 ± 4.22
Zn	210 ± 14	179.72 ± 13.1
Rb	6.0 ± 5	2.41 ± 0.55
Pb	31 ± 2.1	31.83 ± 5.42

elemental concentrations is good for most elements, with some exceptions. The quantitative results for the CRM were compared to the certified values using the student's 't' test to identify significant differences between the measured and certified values with a confidence threshold of $p = 0.05$. All of the observed differences between the measured and certified values were found to be non-significant, confirming the validity of the method used to determine the elemental composition of the CRM.

Black Carbon (BC) Determination

BC concentrations were determined using a black smoke detector (model FH621-N, ESM Emberline, Erlangen,

Germany). The instrument used is a reflectometer with light emitting diodes (LEDs) and photo sensors enclosed in a completely black casing. The LEDs illuminate the sample with optimized light that is tuned to a wavelength of 0.6 μm . The intensity of the reflected light is measured by photo sensors that transduce the light intensity into an electrical current. The potential generated in this way is related to the blackness of the sample and thus to its BC content. While BC is known to exhibit variable specific absorption (Heintzenberg and Bussemer, 2000; Reid *et al.*, 2005), which introduces errors that are not encountered using thermal analytical techniques, this method has the compensating advantages of being simple, cheap and nondestructive. The concentration of black carbon, C_R , was determined in $\mu\text{g}/\text{m}^3$ using the following equation;

$$C_R = -\frac{RM_1}{V} \ln \left(1 - \frac{RZ - RZ_0}{k \times RZ_{\max}} \right) \quad (1)$$

$$; RZ = RZ_{\max} \times \frac{U_{RZ_0} - U_{RZ}}{U_{RZ_0} - U_{RZ_{\max}}} \quad (2)$$

where,

RM_1 is the mass of smoke in a single dust layer on the filter.

V is the sample volume.

RZ_0 is the black smoke number of empty filter.

k is a constant that depends on the absorption coefficient of black smoke.

RM_{\max} is the upper range of calibration scale.

U_{RZ_0} is the voltage generated for empty filters.

$U_{RZ_{\max}}$ is the voltage generated for black filters.

U_{RZ} is the voltage generated for the sample filter.

Principal Component Analysis

Principal component analysis (PCA) was used in an attempt to identify possible sources for the detected elements. PCA reduces the number of elements into components by assembling a set of new variables based on the interrelations present in the original data set. Only PCA components with eigenvalues of more than 1 were considered in this work. To minimize the cross-loadings between the components, varimax rotation was applied. Elements that were present at levels below the limit of detection in more than half of the samples were excluded from the PCA. In cases where an element was included in the analysis but was below the limit of detection in a particular sample, its concentration was assumed to be half the limit of detection. This was done to avoid having to further reduce the size of the data set.

RESULTS AND DISCUSSION

$PM_{2.5}$ Concentrations

Fig. 1 shows the mass concentrations of $PM_{2.5}$ collected from the two sites in Taif on each sampling week during the summer of 2011 (June–August). A group of samples was collected for each site. The average $PM_{2.5}$ mass concentrations measured over the entire experimental period were $46 \pm 31 \mu\text{g}/\text{m}^3$ and $47 \pm 15 \mu\text{g}/\text{m}^3$ for the residential and industrial sites, respectively. The $PM_{2.5}$ concentrations in the residential site ranged from 36–62 $\mu\text{g}/\text{m}^3$ whereas those for the industrial area ranged from 29–68 $\mu\text{g}/\text{m}^3$. The highest measured $PM_{2.5}$ mass concentrations at both sites are thus approximately twice as high as the upper limit specified in the ambient air quality standards published by the European commission (European Commission, 2012), which require a yearly mean of no more than 25 $\mu\text{g}/\text{m}^3$. Compared to the advisory air quality guidelines by WHO (WHO, 2006) the concentrations in this study are all above

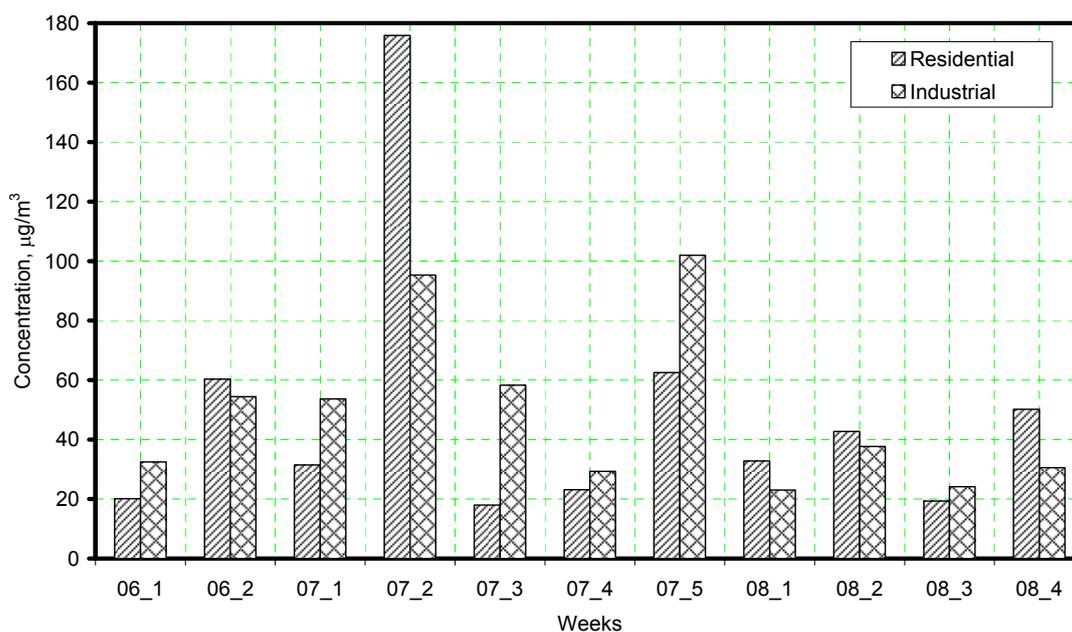


Fig. 1. Variation in the mass concentration of $PM_{2.5}$ during the period from June 2011 to August 2011.

the WHO annual mean of $10 \mu\text{g}/\text{m}^3$. Since the measurements in this study were carried out during the dry summer period a lower yearly average $\text{PM}_{2.5}$ concentrations could be expected. If a yearly mean $\text{PM}_{2.5}$ concentration of $30\text{--}40 \mu\text{g}/\text{m}^3$ is assumed, this corresponds to an increased risk of long-term mortality of 8 to 12% for the inhabitants in Taif according to the WHO review (WHO, 2006). As shown in Fig. 1, the lowest $\text{PM}_{2.5}$ mass concentrations for both the industrial and residential areas were observed in August 2011, while the highest levels were observed in July 2011 for both areas. This is presumably due partly to the large dust storm that occurred in the area during July 2011, and partly to seasonal variation. In general, the measured concentrations of $\text{PM}_{2.5}$ in the industrial and residential areas were similar over the entire measurement period with the exception of the second week of July, as shown in Fig. 1. This may be because the two sites are located in relatively close proximity to one-another. The $\text{PM}_{2.5}$ concentrations measured in this work are comparable to those reported elsewhere in the literature (Abu-Allaban *et al.*, 2002; Götschi *et al.*, 2002; Wang *et al.*, 2005; Abu-Allaban *et al.*, 2007; Gatari *et al.*, 2009; Saliba *et al.*, 2010; Boman *et al.*, 2012) for cities such as Beirut (Lebanon), Nairobi (Kenya), Athens (Greece), and Cairo (Egypt) in 2010, as shown in Table 3. However, the measured values are three times lower than those reported for industrial and residential areas in Cairo (Egypt) in 2001 and Beijing (China). Particulate matter pollution is a major problem in urban areas of Africa and Asia but is also a matter of global concern. A press release from the European Commission (European Commission, 2012a) noted that 30% of Europe's urban population is exposed to concentrations of $\text{PM}_{2.5}$ that exceed the annual limit stipulated by the EU.

Elemental Composition Determined by Secondary Target EDXRF

Fig. 2 shows the characteristic fluorescent radiation spectra of an empty polycarbonate filter, air particulate filters collected from the residential site during July 2011, and an air particulate filter carrying the certified reference material. Empty filters were analyzed to determine the background signal, which was subtracted from the results obtained for the sample filters. Mo scattering radiation could be recognized at photon energy higher than 16 keV. The $K\alpha$ and $K\beta$ characteristic lines were predominant for all elements other than Pb, for which the $L\alpha$ and $L\beta$ lines were predominant. Consequently, analyses were conducted using the PyMca software package based on the $K\alpha$, $K\beta$ and $L\alpha$ characteristic

lines for each element.

It was possible to determine the levels of fifteen elements in most (but not all) of the sample filters: Si, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Rb, Sr, and Pb.

Other potentially toxic heavy elements such as Cd and Sb were present below the limit of detection and so could not be measured with the spectrometer used in this work due to their low ambient concentrations. A group of single element filters (Micromatter) with known concentrations of different elements were used to establish calibration curves in order to permit the quantitative determination of trace elements trapped on the air particulate filters. The calibration curves were established by comparing the sensitivities of the elements in the standard filter group to their atomic numbers. The final concentrations of the elements in the polycarbonate filter were converted into units of ng/m^3 based on the filter area and the sampled air volume. Tables 4 and 5 show the average concentrations of the measured elements in the aerosol particles collected from the industrial and residential sites during each month and over the entire sampling campaign. Black carbon (BC) levels were determined using a black smoke reflectometer. Its concentration is given in ng/m^3 and each reported value represents either the average of the concentrations found for each filter in a given month or for the entire sampling period. As shown in Tables 4 and 5, it was not always possible to determine concentrations for every trace element, since some were below the method's limit of detection in some samples. Importantly, the concentrations of the heavy elements, and especially those of Ni and Pb, were consistently below the maximum levels permitted by the European commission on air quality (European Commission, 2012a).

High concentrations of Si, S, K, Ca and Fe were generally found in both the industrial and the residential locations, and the concentrations of these species did not differ between the two (Table 5). These elements presumably originate from natural sources such as mineral dust, as well as human activities such as waste burning. In addition, Taif is located in an area that is partially enclosed by the Red Sea and is surrounded by the Saharan and Arabian deserts, which are the main sources of the airborne sandy mineral dust. The concentrations of Ca and Fe in industrial and residential areas were comparable, which may be due to the relatively short distance between the residential and the industrial areas. However, the concentrations of Cu and Zn in the industrial area were substantially higher than those in the residential area. These presumably come from more

Table 3. $\text{PM}_{2.5}$ concentrations measured in this work and published data for different urban areas.

References	Industrial, $\mu\text{g}/\text{m}^3$	Residential, $\mu\text{g}/\text{m}^3$	Year	Country
Present work	47 ± 15	46 ± 31	2011	Taif, Saudi Arabia
Abu-Allaban <i>et al.</i> (2002)	216.1 ± 11.0	61.9 ± 3.2	2001	Cairo, Egypt
Saliba <i>et al.</i> (2010)	40.95	38.86	2003	Beirut, Lebanon
Abu-Allaban <i>et al.</i> (2007)	150.3 ± 80.2	78 ± 48	1999, 2002	Cairo, Egypt
Götschi <i>et al.</i> (2002)		37.3 ± 27.4	2002	Athens, Greece
Gatari <i>et al.</i> (2009)	30 ± 9.4		2001	Nairobi, Kenya
Wang <i>et al.</i> (2005)		154.26 ± 145.65	2001–2003	Beijing, China
Boman <i>et al.</i> (2012)	70 ± 34	55 ± 20	2010	Cairo, Egypt

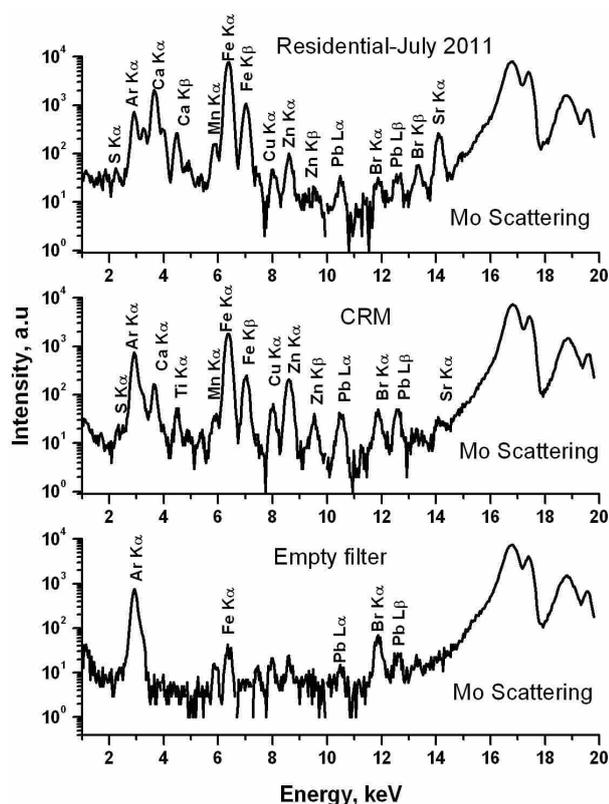


Fig. 2. EDXRF spectra of the polycarbonate filters used in this work with and without air particulates and for filters loaded with the certified reference material (CRM) SRM2873.

local, anthropogenic sources in the industrial area as these elements are typical for metallurgical activities. On the other hand, Ti was found in higher concentrations in the residential area than in the industrial area. Other elements were present at comparable levels in both the industrial and residential locations. Table 5 shows that the average

concentration of BC in the industrial area was three times higher than that in the residential area. This is probably due to the industrial activities such as blacksmithing and construction, waste burning and to increased use of internal combustion engines. Notably, the level of motorized traffic in the industrial area seemed to be heavier than that in the residential area. As such, it is not surprising to find higher levels of soot in the industrial area.

Table 6 shows the result of the principal component analysis (PCA) of the data set. From the table it can be seen that three components can explain 91.5% of the variation in the total data set. Component 1 is clearly dominant, having high loadings for most of the elements and the overall $PM_{2.5}$ mass. This component reflects the desert dust, whose sampling is unavoidable when collecting $PM_{2.5}$. Most of the naturally occurring dust consists of coarse particles that are larger than $2.5 \mu m$ in diameter, but some falls within the $PM_{2.5}$ range. The high influence of mineral dust on the PCA illustrates both the dominance of mineral dust at the measurement sites and the fact that the cut-off of the cyclone is not very sharp, and so some larger particles are unavoidably sampled. Component 2 explains 13% of the variance and has high loadings for elements that are related to anthropogenic activities and black carbon (BC). Component 3 of the PCA has high loadings for Cl and moderate loadings for Cu, Zn and BC. The source responsible for this combination is hard to identify, but the elements involved suggest another anthropogenic source that could be waste burning. Looking at Table 7, which only shows data for the industrial site, the general pattern described above holds and the dominant component is Component 1 with high loadings for mineral dust elements. Component 2 is similar to Component 2 in Table 6 but also has high loadings for Cl. This shows that both of the anthropogenic sources responsible for components 2 and 3 in Table 6 are largely due to industrial activities. The high loadings of Ca and Sr in Component 3 for the industrial site, Table 7, are

Table 4. Monthly average elemental concentrations of $PM_{2.5}$ (ng/m^3) collected from industrial and residential areas in Taif during summer 2011, using Mo Secondary target EDXRF. < DL denotes a measurement below the limit of detection.

	Industrial Area, ng/m^3			Residential Area, ng/m^3		
	June	July	August	June	July	August
Si	7000	12000	4000	6000	11000	4000
S	520	430	310	650	390	300
Cl	180	200	130	140	180	150
K	550	790	320	470	830	330
Ca	3100	3900	1400	2900	4100	1600
Ti	310	400	200	140	310	140
Cr	5.5	8.8	< DL	2.4	5.8	< DL
Mn	55	79	26	32	67	32
Fe	2200	3500	1200	1500	3200	1400
Ni	3.8	5.5	0.8	5.8	7.2	1.1
Cu	11	14	14	5.1	6.4	4.3
Zn	46	42	30	18	20	23
Rb	2.2	3.4	1.4	2.2	3.5	1.7
Sr	15	18	6.9	13	18	7.4
Pb	6.7	7.6	6.9	7.2	5.8	4.9
BC	780	1300	470	360	540	61

Table 5. Average concentrations of elements including black carbon (BC) in ng/m³ at the residential and industrial sites.

	Industrial, ng/m ³			Residential, ng/m ³			QL
	Concentration	Range	N	Concentration	Range	N	
Si	7500 ± 4000	3800–12000	11	7200 ± 3300	4400–11000	11	
S	420 ± 110	310–520	11	450 ± 180	300–650	11	
Cl	170 ± 36	130–200	11	150 ± 22	140–180	11	
K	550 ± 240	310–790	11	550 ± 260	330–830	11	
Ca	2800 ± 1200	1400–3800	11	2900 ± 1300	1600–4100	11	
Ti	300 ± 100	200–400	11	200 ± 100	140–310	11	
Cr	5.1 ± 3.9	1.1–8.8	9	3.4 ± 2.0	2.1–5.8	11	
Mn	53 ± 26	26–79	11	44 ± 20	32–67	11	
Fe	2300 ± 1100	1200–3500	11	2000 ± 1000	1400–3200	11	
Ni	3.4 ± 2.4	0.8–5.5	9	4.7 ± 3.2	1.1–7.2	11	20
Cu	13 ± 1.7	11–14	11	5.3 ± 1.1	4.3–6.4	11	
Zn	40 ± 8.6	30–46	11	20 ± 2.7	18–23	11	
Rb	2.3 ± 1.0	1.4–3.4	11	2.5 ± 0.9	1.7–3.5	11	
Sr	13 ± 5.8	6.9–18	11	13 ± 5.1	7.4–18	11	
Pb	7.1 ± 0.5	6.7–7.6	11	6.0 ± 1.1	4.9–7.2	11	500
BC	860 ± 440	470–1300	8	32 ± 240	61–540	7	

Table 6. The rotated component matrix for the principal component analysis of all samples from Taif. Elements that were present at levels below the limit of detection in more than half the samples were removed. % var is the percentage of the total variance explained by the component.

	Component		
	Component 1	Component 2	Component 3
Si	.959	.200	.144
S	.367	.753	-.139
Cl	.085	.147	.864
K	.922	.366	-.004
Ca	.830	.484	-.122
Ti	.879	.179	.351
Cr	.898	.252	.248
Mn	.915	.248	.304
Fe	.950	.192	.208
Ni	.818	.510	-.087
Cu	.215	.780	.530
Zn	.295	.762	.491
Rb	.962	.251	.032
Sr	.872	.473	-.018
Pb	.438	.749	.105
Black carbon	.200	.780	.526
PM _{2.5} mass	.929	.345	.073
% var	72	13	6.5

characteristic of construction-related sources. The moderate loadings of K, Ni and Zn reflect the mixed composition of the particles, but are also consistent with industrial sources. A third PCA was performed using only data for the residential area (results not shown). In this case, only two important components were identified. The first explained 85% of the observed variation and contains all of the variables considered other than Cl. Chlorine is the only element with a high loading in the second component. It is not clear why this should be so, since no source that produces Cl alone has yet been identified.

Table 7. The rotated component matrix for the principal component analysis of the samples from the industrial site in Taif. Elements that were present at levels below the limit of detection in more than half the samples were removed. % var is the percentage of the total variance explained by the component.

	Component		
	Component 1	Component 2	Component 3
Si	.974	.097	.186
S	.133	.873	.000
Cl	.442	.743	.454
K	.744	.221	.625
Ca	.358	.244	.888
Ti	.960	.212	.049
Cr	.818	.128	.394
Mn	.904	.290	.307
Fe	.971	.166	.166
Ni	.482	.417	.749
Cu	.012	.946	.186
Zn	.103	.790	.558
Rb	.923	.051	.372
Sr	.629	.354	.678
Pb	.350	.766	.388
Black C	.182	.964	.114
Total M	.887	.222	.353
%	69	19	6.4

CONCLUSIONS

The present work represents the first part of an initiative to evaluate the trace element composition of atmospheric aerosols, PM_{2.5}, in two different areas (industrial and residential) of Taif city, Saudi Arabia. It can be concluded that the chosen sites are well suited for this kind of study since it was possible to identify effects due to different sources at each one. It can also be concluded that despite its location in a desert area, Taif does not suffer from more

severe particulate pollution than many other urban areas in the world. Its PM_{2.5} mass concentration exceeds the European Union's yearly mean upper limit by a factor of two, suggesting that it will be necessary to perform measurements over a longer period of time in order to obtain a more detailed picture of air pollution in the area. Fortunately, the measured concentrations of potentially hazardous trace elements were below the limits specified in international guidelines and national standards for ambient air quality. The measured elemental compositions of the samples indicate that the use of a cyclonic sampler with an EDXRF spectrometer is appropriate for studies of this type and should be suitable for related studies conducted under similar conditions. It was also demonstrated that this method can be used to identify and discriminate between natural and anthropogenic sources of airborne particulate matter in Taif.

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REFERENCES

- Abu-Allaban, M., Gertler, A.W. and Lowenthal, D.H. (2002). A Preliminary Apportionment of the Sources of Ambient PM₁₀, PM_{2.5}, VOCs in Cairo. *Atmos. Environ.* 36: 5549–5557.
- Abu-Allaban, M., Lowenthal, D.H., Gertler, A.W. and Labib, M. (2007). Sources of PM₁₀ and PM_{2.5} in Cairo's Ambient Air. *Environ. Monit. Assess.* 133: 417–425.
- Abulfaraj, W.H., Ahmed, M., Mousli, K.M. and Erturk, F. (1990). Measurement of Ambient Air Lead Concentrations in the City of Jeddah, Saudi Arabia. *Environ. Int.* 16: 85–88.
- Aburas, H.M., Zytoon, M.A. and Abdulsalam, M.I. (2011). Atmospheric Lead in PM_{2.5} after Leaded Gasoline Phase-out in Jeddah City, Saudi Arabia. *CLEAN–Soil Air Water* 39: 711–719.
- Ahmed, K.O. and Al-Swaidan, H.M. (1993). Lead and Cadmium in Urban Dust of Riyadh, Saudi Arabia. *Sci. Total Environ.* 136: 205–210.
- Ahmed, K.O., Al-Swaidan, H.M. and Davies, B.E. (1993). Simultaneous Elemental Analysis in Dust of the City of Riyadh, Saudi Arabia by Inductively Coupled Plasma-Mass spectrometry (ICP/MS). *Sci. Total Environ.* 138: 207–212.
- Al-Jeelani, H.A. (2009). Air Quality Assessment at Al-Taneem Area in the Holy Makkah City, Saudi Arabia. *Environ. Monit. Assess.* 156: 211–222.
- Boman, J. (1990). Detector Performance Measurement Techniques and Computer Software in an EDXRF-spectrometer Applied to Environmental and Medical Studies, PhD Thesis, Göteborg University, Göteborg, Sweden.
- Boman, J., Shaltout, A.A., Abozied, A.M. and Hassan, S.K. (2012). Spectroscopic Determination of the Elemental Composition of PM_{2.5} Particles Sampled in Industrial and Urban Areas of Greater Cairo, Egypt. *X-Ray Spectrom.* 42: 276–283
- Cahill, T.A. (1996). Climate Forcing by Anthropogenic Aerosols: The Role for PIXE. *Nucl. Instrum. Methods Phys. Res., Sect. B* 109–110: 402–406.
- Central Department of Statistics & Information (2012). Population Census 2010, Kingdom of Saudi Arabia (<http://www.cdsi.gov.sa/2010-07-31-07-00-05>), Accessed in 30 September 2012.
- Chimidza, S. (2001). Characterization and Source Apportionment of Airborne Particles in Eastern Botswana, PhD Thesis, Göteborg University, Göteborg, Sweden.
- European Commission (2012a). <http://ec.europa.eu/environment/air/quality/standards.htm>, Visited 30 September 2012.
- European Commission (2012b). Press Release IP/12/1002 Issued 24 September 2012, Environment: Many Europeans Continue to Face Hazardous Air Pollutants.
- Ezzati, M., Lopez, A.D., Rodgers, A., Hoorn, S.V. and Murray, C.J.L. (2002). Selected Major Risk Factors and Global and Regional Burden of Disease. *Lancet* 360: 1347–1360.
- Gatari, M.J., Boman, J. and Wagner, A. (2009). Characterization of Aerosol Particles at an Industrial Background Site in Nairobi, Kenya. *X-Ray Spectrom.* 38: 37–44.
- Götschi, T., Oglesby, L., Mathys, P., Monn, C., Manalis, N., Hanninen, O., Polanska, L. and Künzli, N. (2002). Comparison of Black Smoke and PM_{2.5} Levels in Indoor and Outdoor Environments of Four European Cities. *Environ. Sci. Technol.* 36: 1191–1197.
- Heintzenberg, J. and Bussemer, M. (2000). Development and Application of a Spectral Light Absorption Photometer for Aerosol and Hydrosol Samples. *J. Aerosol Sci.* 31: 801–812.
- Horvath, H. (1998). In *Atmospheric Particles*, Harrison, R.M. and Van Grieken, R.E. (Eds.), Wiley, Chichester, p. 543–596.
- IUPAC (1976). Nomenclature, Symbols, Units, and their Usage in Spectrochemical Analysis. Part II: Data Interpretation. *Pure Appl. Chem.* 45: 99–103.
- Karl, T.R., Nicholls, N. and Gregory, J. (1997). The Coming Climate. *Sci. Am.* 276: 54–59.
- Lioussé, C., Cachier, H. and Jennings, S.G. (1993). Optical and Thermal Measurements of Black Carbon Aerosol Content in Different Environments-variation of the Specific Attenuation Cross-section, Sigma (σ). *Atmos. Environ. Part A* 27: 1203–1211
- Mahdy, H.M. and El-Sehrawi, M.H. (1997). Airborne Bacteria in the Atmosphere of El-Taif Region, Saudi Arabia. *Water Air Soil Pollut.* 98: 317–324.
- Mark, D. (1998). In *Atmospheric Particles*, Harrison, R.M. and Van Grieken, R.E. (Eds.), Wiley, Chichester, p. 29–94.
- Murray, F., McGranahan, G. and Kuylenstierna, J. (2001). Assessing Health Effects of Air Pollution in Developing Countries. *Water Air Soil Pollut.* 130: 1799–1804.

- Reid, J.S., Koppmann, R., Eck T.F. and Eleuterio, D.P. (2005). A Review of Biomass Burning Emissions Part II: Intensive Physical Properties of Biomass Burning Particles. *Atmos. Chem. Phys.* 5: 799–825.
- Renwick, L.C., Donaldson, K. and Clouter, A. (2001). Impairment of Alveolar Macrophage Phagocytosis by Ultrafine Particles. *Toxicol. Appl. Pharmacol.* 172: 119–127.
- Sabbak, A.O. (1990). Distribution of Total Hydrocarbons in Jiddah Atmosphere. *Environ. Int.* 16: 273–282.
- Saliba, N.A., El Jam, F., El Tayar, G., Obeid, W. and Roumie, M. (2010). Origin and Variability of Particulate matter (PM₁₀ and PM_{2.5}) Mass Concentrations over an Eastern Mediterranean City. *Atmos. Res.* 97: 106–114.
- Schwartz, J. and Neas, L. (2000). Fine Particles are More Strongly Associated than Coarse Particles with Acute Respiratory Health Effects in Schoolchildren. *Epidemiology* 11: 6–10.
- Solé, V.A., Papillon, E., Cotte, M., Walter, Ph. And Susini, J. (2007). A Multiplatform Code for the Analysis of Energy-dispersive X-ray Fluorescence Spectra. *Spectrochim. Acta, Part B* 62: 63–68
- Wagner, A., Boman, J. and Gatari, M.J. (2008). Elemental Analysis of Size-fractionated Particulate Matter Sampled in Göteborg, Sweden. *Spectrochim. Acta, Part B* 63: 1426–1431.
- Wang, Y., Zhuang, G., Tang, A., Yuan, H., Sum, Y., Chen, S. and Zheng, A. (2005). The Ion Chemistry and the Source of PM_{2.5} Aerosol in Beijing. *Atmos. Environ.* 39: 3771–3784.
- WHO (2006). Air Quality Guidelines, Global Update 2005, Particulate Matter, Ozone, Nitrogen Dioxide and Sulfur Dioxide, World Health Organisation Regional Office for Europe, Copenhagen, http://www.euro.who.int/__data/assets/pdf_file/0005/78638/E90038.pdf, ISBN 92 890 2192 6.

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