

UC Irvine

UC Irvine Previously Published Works

Title

Chemical Characterization and Source Apportionment of PM2.5 in Rabigh, Saudi Arabia

Permalink

<https://escholarship.org/uc/item/80k8k5f5>

Journal

Aerosol and Air Quality Research, 16(12)

ISSN

1680-8584

Authors

Nayebare, Shedrack R
Aburizaiza, Omar S
Khwaja, Haider A
[et al.](#)

Publication Date

2016

DOI

10.4209/aaqr.2015.11.0658

Copyright Information

This work is made available under the terms of a Creative Commons Attribution License, available at <https://creativecommons.org/licenses/by/4.0/>

Peer reviewed



Chemical Characterization and Source Apportionment of PM_{2.5} in Rabigh, Saudi Arabia

Shedrack R. Nayebare^{1,2}, Omar S. Aburizaiza^{3**}, Haider A. Khwaja^{1,2*}, Azhar Siddique⁴,
Mirza M. Hussain^{1,2}, Jahan Zeb², Fida Khatib³, David O. Carpenter⁵, Donald R. Blake⁶

¹ Department of Environ. Health Sciences, School of Public Health, University at Albany, Albany, NY 12201, USA

² Wadsworth Center, New York State Department of Health, Albany, NY 12201, USA

³ Unit for Ain Zubaida Rehabilitation & Ground Water Research, King Abdulaziz University, Jeddah, Saudi Arabia

⁴ Qatar Environment and Energy Research Institute, Hamad Bin Khalifa University, Qatar Foundation, Doha, Qatar

⁵ Institute for the Health and the Environment, University at Albany, 5 University Place, Rensselaer, NY 12144, USA

⁶ Department of Chemistry, University of California, Irvine, CA 92617, USA

ABSTRACT

The present study describes the measurement, chemical characterization and delineation of sources of fine particulate matter (PM_{2.5}) in Rabigh, Saudi Arabia. The 24-h PM_{2.5} was collected from May 6th–June 17th, 2013. The sources of various air pollutants and their characterization was carried by computations of Enrichment Factor (EF), Positive Matrix Factorization (PMF) and Backward-in-time Trajectories. The 24-h PM_{2.5} showed significant temporal variability with average ($37 \pm 16.2 \mu\text{g m}^{-3}$) exceeding the WHO guideline ($20 \mu\text{g m}^{-3}$) by 2 fold. SO₄²⁻, NO₃⁻, NH₄⁺ and Cl⁻ ions dominated the ionic components. Two broad categories of aerosol Trace Elements (TEs) sources were defined as anthropogenic (Ni, V, Zn, Pb, S, Lu and Br) and soil/crustal derived (Si, Rb, Ti, Fe, Mn, Mg, K, Sr, Cr, Ca, Cu, Na and Al) elements from computations of EF. Anthropogenic elements originated primarily from fossil-fuel combustion, automobile and industrial emissions. A factor analysis model (PMF) indicated the major sources of PM_{2.5} as *Soil* (Si, Al, Ti, Fe, Mg, K and Ca); *Industrial Dust* (Ca, Fe, Al, and Si); *Fossil-Fuel combustion* (V, Ni, Pb, Lu, Cu, Zn, NH₄⁺, SO₄²⁻ and BC); *Vehicular Emissions* (NO₃⁻, C₂O₄²⁻, V and BC) and *Sea Sprays* (Cl⁻ and Na). Backward-in-time trajectories showed a significant contribution by long distance transport of fine aerosols to the overall daily PM_{2.5} levels. Results are consistent with previous studies and highlight the need for more comprehensive research into particulate air pollution in Rabigh and the neighboring areas. This is essential for the formulation of sustainable guidelines on air pollutant emissions in Saudi Arabia and the whole Middle East.

Keywords: Black carbon; Trace elements; Enrichment factor; PMF; PM_{2.5} mass reconstruction.

INTRODUCTION

Fine particulate air pollution is a key global health issue severely affecting human health and the environment mostly related to visibility (Cheung *et al.*, 2005; Kim *et al.*, 2006; Deng *et al.*, 2008; Hyslop, 2009). Chemical and physical characterization of these particles is crucial for understanding the possible sources as well as their toxicity on human health. Air pollution is one of the top causes of death globally,

accounting for over 7 million premature deaths annually (WHO, 2014). The International Agency for Research on Cancer classifies air pollution as a *Group 1* carcinogen to humans. Recent epidemiological studies indicate that exposure to PM_{2.5} is associated with increased cardiopulmonary morbidity and mortality (Laden *et al.*, 2000; Pope *et al.*, 2004; Chow *et al.*, 2006; Pope and Dockery, 2006; Peng *et al.*, 2008), exacerbation of the pre-existing medical conditions such as asthma, COPD (Sunyer *et al.*, 2000; Bernstein *et al.*, 2004; Peden, 2005; Karakatsani *et al.*, 2012) and other respiratory ailments especially among elderly and children (Cançado *et al.*, 2006). Some studies have indicated that levels of particulate matter are high in Saudi Arabia (Nasrallah and Seroji, 2008; Khodeir *et al.*, 2012; Munir *et al.*, 2013). This has mainly been attributed to rapid urbanization, vehicular traffic, industrialization (Al-Jeelani, 2009b; Khodeir *et al.*, 2012; Munir *et al.*, 2013) and an arid climate characterized by sand storms (Furman, 2003; Alharbi

* Corresponding author.

Tel.: +1-518-474-0516

E-mail address: haider.khwaja@health.ny.gov

** Corresponding author.

Tel.: +966-2-6952821

E-mail address: aburizaiza@hotmail.com

et al., 2013; Munir et al., 2013).

Much as air pollution is globally known to be an environmental and public health issue, limited assessment of air quality and the associated health effects has so far been done in developing nations in Asia, Africa and the Middle East including Saudi Arabia. A few studies assessing chemical characterization and source apportionment of airborne particulate matter and the general state of air pollution in Saudi Arabia's cities of Jeddah (Khodeir et al., 2012) and Makkah (Al-Jeelani, 2009a, b; Munir et al., 2013) have been carried out during the past few years. Most of these studies reported poor air quality related to rapid urbanization, industrialization and vehicular traffic. Currently, Saudi Arabia lacks a functional regulation on particulate air pollution control. This study aimed to assess the state of air quality in Rabigh, one of the major industrialized cities of Saudi Arabia, and characterize the sources of fine particulate air pollutants. This is fundamental for the formulation and implementation of sustainable policy guidelines with regard to pollution control and ultimately, the preservation of human health and the environment.

MATERIALS AND METHODS

Sampling Site

Rabigh is an ancient town of Saudi Arabia (Makkah Province), located at the east coast of Red Sea, North of Equator between the 22nd and 23rd latitudes on the Tropic of Cancer. The town has an estimated population of 180,352 people (UNSD, 2014) and is characterized by extremely hot summer and warm winter seasons. Summer seasons are

typically characterized by elevated relative humidity with short and abrupt rain episodes. However, rainfall is scanty for most part of the year. Normally, the temperatures begin to rise in April exceeding 45°C around July–September. During the entire study period, the mean temperature was 32.4°C, wind speed was 11.04 km h⁻¹ and predominantly Northwesterly direction. Air pollution is an issue in Rabigh, as the city and the neighboring areas mostly in the North, South and East are heavily industrialized (Fig. 1).

PM_{2.5} Sample Collection and Analysis

The 24-h PM_{2.5} samples were collected on pre-weighed, sequentially numbered polypropylene ring supported Whatman 2 µm pore-size PTFE 46.2 mm filters, using a low volume air sampling pump. The PM_{2.5} sampler was installed for the period of 6th May–June 17th, 2013 at a fixed site in Rabigh and equipped with a housing unit, power supply, gooseneck, 5.27 cm inner diameter rubber stopper, 47 mm diameter filter holder, data logger, air volume totalizer, mass flow meter, a pump with a flow controller and elapsed time indicator, and an aluminum cyclone separator with a cut size of 2.5 µm, operated at a flow rate 16.67 L min⁻¹ optimum for sampling PM_{2.5}. The sampler inlets were fixed at 3–5 meters height above the ground so as to get a good representation of the ambient PM_{2.5} and to avoid ground dust. For each sampling day, the sampled filter was retrieved from the sampler placed in labeled clean polypropylene analysislide petri-dish and immediately refrigerated at 4°C. The petri-dishes containing PM_{2.5} filters were then shipped to the laboratory and analyzed for PM_{2.5} mass concentrations, black carbon (BC), trace

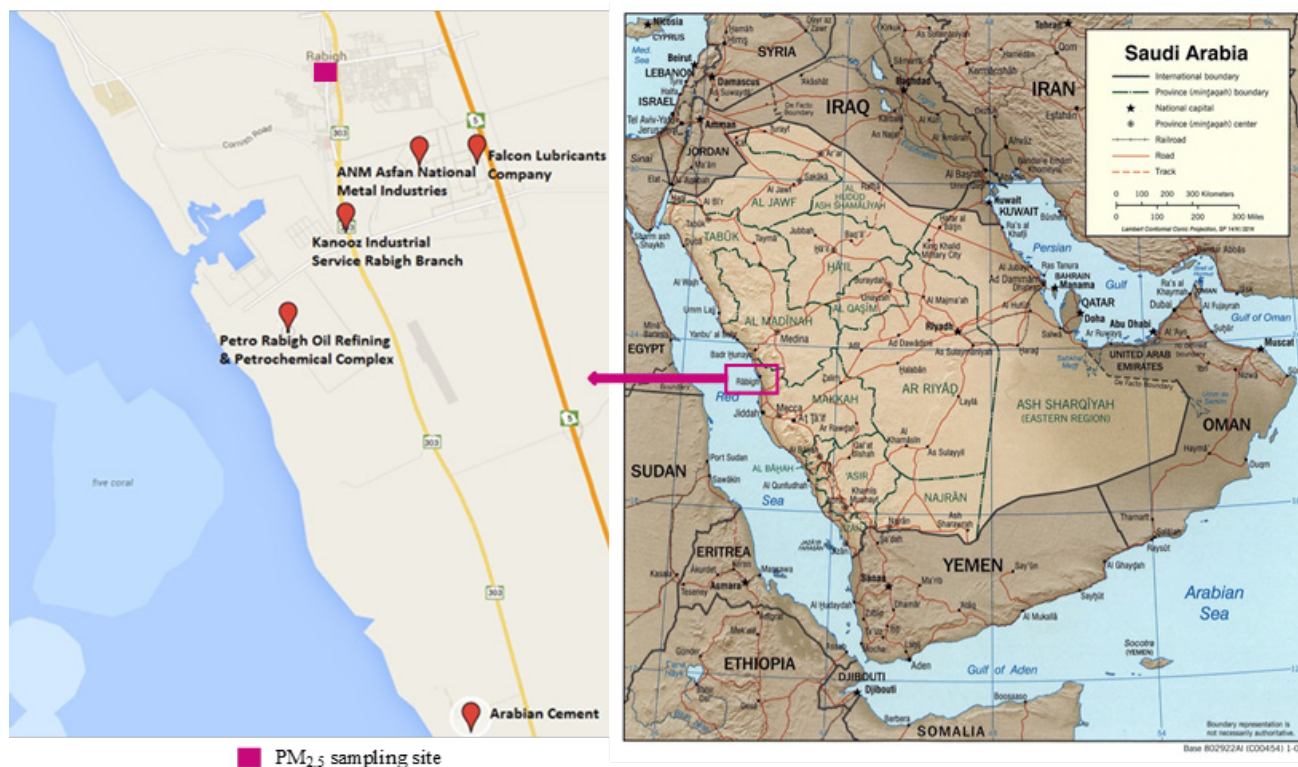


Fig. 1. Location of the PM_{2.5} sampling site and the industrial areas in Rabigh, Saudi Arabia.

elements, and the water soluble anions, and cations. Before shipment to the field site for sampling, the PM_{2.5} filters were first inspected for defects (pinholes, lose material, non-uniformity, and discoloration), conditioned for at least 24 hours in a clean room with controlled temperature (20–23°C) and relative humidity (20–30%), pre-weighed using a Micro-Analytical Balance (Model C-44, Mettler Toledo Inc. Hightstown NJ) to determine the weight, and shipped to the field. After sampling, the filters were shipped back to the laboratory, re-inspected, conditioned and post-weighed to determine the weight. As a QC measure, we incorporated field blank filters to monitor any possible contamination of samples during field sampling and transportation. The laboratory for conditioning and weighing was designed and maintained under strict operational criteria of controlled relative humidity, temperature and as close as possible to “clean room” conditions to minimize contamination and air flow interferences. Before weighing the filters were passed through a magnetic field of a BF2 Duo-stat Positioner/static-master (Model 2U500 NRD, LLC Grand Island, NY) for 10–20 times so as to remove any electrostatic force and allow for accurate measurement of filter weight. The total weight (mg) of PM_{2.5} on the filter was determined from the difference of the weights before and after sampling, and the concentration of PM_{2.5} in micrograms per cubic meter ($\mu\text{g m}^{-3}$) calculated incorporating the sampled air volume and sampling duration.

Analysis of Black Carbon (BC)

The PM_{2.5} sample filters were analyzed for BC loading using a nondestructive Dual-wavelength Optical Transmissometer Data Acquisition System [Model OT-21, 2007]. As a QC measure, we first analyzed a set blank filters to estimate the variations between blanks and to calibrate the instrument. The OT-21 collects absorbance data at both ultraviolet (370 nm) and infrared (880 nm) wavelengths (λ) and allows for measurement and recording of filter absorbance data relative to a blank reference filter. BC concentration ($\mu\text{g m}^{-3}$) was computed incorporating sampled air volume and the exposed area of a filter. To correct for the BC loading effects on the filters, attenuation coefficients for $\lambda = 880$ nm channel- $K_{\text{IR}} = 16.6 \text{ m}^2 \text{ g}^{-1}$ and

$\lambda = 370$ nm channel- $K_{\text{UV}} = 39.5 \text{ m}^2 \text{ g}^{-1}$ (Ahmed *et al.*, 2009) were applied on BC measurements at respective channels. As shown in Eq. (1), the difference between the BC measurement at $\lambda = 370$ nm and $\lambda = 880$ nm gives the estimate for Delta-C which is a strong marker for organic matter combustion as a source of PM_{2.5} (Wang *et al.*, 2011; Wang *et al.*, 2012; Rattigan *et al.*, 2013).

$$\text{Delta-C} = \text{BC}_{370\text{nm}} - \text{BC}_{880\text{nm}} \quad (1)$$

Trace Elemental Analysis

The trace elements in PM_{2.5} samples were analyzed by a Thermo Scientific ARL QUANT’X energy dispersive X-ray fluorescence spectrometer (ED-XRF) (model AN41903-E 06/07C, Ecublens Switzerland) using six secondary fluorescers (Si, Ti, Fe, Cd, Se and Pb). Detailed operational procedure for ED-XRF is described elsewhere (Shaltout *et al.*, 2013). The instrument was energy (eV) calibrated for every batch sequence of samples. As a quality control, a QC sample was analyzed before and after every sequence. Additionally, the sample holders were cleaned with deionized (DI) water and a Micro[®] liquid soap for every analytical sequence so as to avoid cross contamination. ED-XRF has been used in a number of studies for trace elemental analysis in air particulate samples (Ozturk *et al.*, 2011; Yatkin *et al.*, 2012; Shaltout *et al.*, 2013) because it is fast and does not require chemical digestion of samples prior to analysis (Korzhova *et al.*, 2011) which minimizes sample contamination. The technique can perform multi-element analysis providing simultaneous measurements for concentration and uncertainty with a high precision and reliability (Thermo-Scientific, 2007). The validity of each measurement obtained was verified by computing the ratio of each concentration measurement to its uncertainty. Only those elemental concentrations above the detection limit and at least 3 times more than the uncertainty have been reported in this study. Typical detection limits of various elements measured by EDXRF Spectrometer have been summarized in Table 1. Conversion of elemental concentrations from ng cm^{-2} to ng m^{-3} was done incorporating the exposed area of the filter (16.764 cm^2) and the average 24-h volume of air sampled (24.0 m^3).

Table 1. Typical Detection Limits of Trace Elements Measured.

	ng m^{-3}		ng m^{-3}		ng m^{-3}		ng m^{-3}
Na	9.88	Mn	0.59	Zr	1.09	Eu	1.98
Mg	2.96	Fe	0.50	Nb	1.19	Tb	1.98
Al	2.57	Co	0.69	Mo	1.98	Hf	2.96
Si	2.47	Ni	0.50	Ag	5.93	Ta	1.98
P	2.37	Cu	0.59	Cd	5.93	W	1.58
S	1.98	Zn	0.59	In	7.90	Ir	1.29
Cl	1.68	Ga	0.59	Sn	9.88	Au	1.19
K	1.58	As	0.59	Sb	10.9	Hg	1.09
Ca	1.58	Se	0.50	Cs	2.96	Pb	1.09
Sc	1.19	Br	0.50	Ba	3.16		
Ti	0.98	Rb	0.59	La	2.47		
V	0.98	Sr	0.79	Ce	1.98		
Cr	0.69	Y	0.98	Sm	1.98		

Anionic and Cationic Analysis

Anions and cations were analyzed by ion exchange chromatography–IC (Dionex Corp. Sunnyvale CA, USA). One-quarter (¼) of each PM_{2.5} filter was cut and extracted in a plastic vial with 5.0 mL of Barnstead Deionized (DI) water (18.2 MΩ-cm resistivity). The extraction of water-soluble ionic species was accomplished by shaking using an advanced digital VWR shaker (Model 5000 ADV 120V) for at least 24 hours followed by 2 hours of ultrasonic sonication. Five cations (Na⁺, NH₄⁺, K⁺, Mg²⁺, and Ca²⁺) and five anions (SO₄²⁻, NO₃⁻, C₂O₄²⁻, Cl⁻, and F⁻) were analyzed in aqueous extracts of PM_{2.5} filters. The aqueous sample extracts were stored at 4°C until analysis. Cationic analysis was done using an ICS–2500 instrument with a Dionex IonPac[®] CS14 4mm analytical column and CG14 guard column utilizing 10.0 mM methanesulfonic acid (MSA) as an eluent. Separation of water soluble anions was done using an ICS–3000 instrument utilizing a Dionex IonPac[™] AS14 4 × 250 mm analytical column and AG14 guard column, and a mixed solution of 1.0 mM NaHCO₃ and 3.5 mM Na₂CO₃ as an eluent. Instrumental controls, data acquisition, and chromatographic integration were performed using Dionex Chromeleon software (version 6.60). For quality control (QC) purposes, instrument calibration was performed for each analytical sequence using certified analytical reference materials obtained from the Environmental Research Agency (ERA) and NSI laboratories. The instrument calibration curves were determined using 7 standard concentrations of 0.1, 0.25, 0.5, 1.0, 2.5, 5.0 and 10.0 mg L⁻¹ prepared from ERA stock solutions and a QC standard (5.0 mg L⁻¹) prepared from NSI stock solutions. Two reagent blanks were analyzed, one at the start and the other at the end of the calibration sequence. A continuous calibration verification (CCV) standard (5.0 mg L⁻¹) was analyzed for every 10 sample runs in the analytical sequence. Duplicate and Spike samples were also analyzed at the end of the analytical sequence as a QA/QC measure. The minimum reportable level (MRL) for each analyte was determined by performing 7 analytical runs using the lowest standard concentration of 0.1 mg L⁻¹. The observed results from all the 7 analytical runs were within ±15% change of the target concentration (0.1 mg L⁻¹) for each analyte. The MRL was set at 0.1 mg L⁻¹ for all the analytes.

PM_{2.5} Data Analysis for Source Apportionment

Source apportionment for PM_{2.5} was done using three tools: Enrichment Factor (EF), Positive Matrix Factorization (PMF), and plots of Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) Backward-in-time Trajectories.

Enrichment Factor (EF)

An enrichment factor (EF) was computed for each elemental component of PM_{2.5} aerosol, so as to broadly categorize the sources into anthropogenic and naturally/crustal derived as defined by EF values of each element. The extent of anthropogenic contribution was estimated by the degree of enrichment of these elements compared to their crustal composition. EF has been used in a number of studies to study the sources of pollutants (Aprile and Bouvy,

2008, Fabretti *et al.*, 2009). Aluminum (Al) was used as a reference element for computation of EF since it rarely enters the atmosphere from anthropogenic sources (Kłos *et al.*, 2011). Enrichment Factor was defined as shown in Eq. (2),

$$EF = [(C_X/C_{Al})_{\text{Aerosol}}] / [(C_X/C_{Al})_{\text{Crustal}}] \quad (2)$$

where C_X and C_{Al} are concentrations of element ‘X’ and ‘Al’ in PM_{2.5} aerosol and earth crust respectively. The relative abundances of trace elements in the earth crust were obtained from R. Taylor (1964) (Taylor, 1964). An EF value of 10 was used as a cut off, so as to account for any background contributions. The EF values less than 10 indicate significant contributions from the earth-crust/or soil, while EF values greater than 10 are indicative of significant anthropogenic contributions (Kłos *et al.*, 2011).

Positive Matrix Factorization (PMF)

The latest version (5.0.14) of the U.S. EPA mathematical receptor model, Positive Matrix Factorization (PMF) was used to delineate the individual source contributions of the different sources of PM_{2.5} in Rabigh. Though the filters were analyzed for all the elements from Na to U, only those elements whose concentrations from ED-XRF analysis were at least 3 times more than their respective estimates on uncertainty were included in the model. Ambient concentrations of BC, Na, Mg, Al, Si, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, Rb, Sr, Er, Lu, Pb, Cl⁻, C₂O₄²⁻, NH₄⁺, NO₃⁻ and SO₄²⁻ were used as independent variables for modelling the sources of PM_{2.5}. The identification of the sources was based on the existing knowledge of different trace elements serving as tracers/or markers for specific sources of PM_{2.5}. The PMF model basically utilizes the estimates for concentrations and the respective uncertainties of different aerosol species, to compute source profiles, source contributions, and source profile uncertainties. More details of PMF have been given elsewhere (Kim *et al.*, 2003).

Backward-in-Time Trajectories

Backward-in-time Hybrid Single Particle Lagrangian Integrated Trajectories (HYSPLIT) were used to determine the air mass flow with respect to our sampling site for each day of sampling. Trajectories covering a time period of up to 72 hours prior to sampling date were computed to determine the direction of air mass flow into the sampling site. The plots for backward-in-time trajectories were done using Manifold 5.5 software utilizing data downloaded from NOAA HYSPLIT website (Draxler and Rolph, 2013; Rolph, 2013). These trajectories were set at standard altitude of 500 meters above sea level.

RESULTS AND DISCUSSION

PM_{2.5} Mass and Chemical Composition — Implications on Air Quality

A total of 40 daily PM_{2.5} samples were collected over a period of May 6th through June 17th 2013. The average concentration measurements for different chemical constituents of PM_{2.5} including black carbon (BC), trace

elements (TEs), water soluble anions and cations are shown in Table 2. The daily PM_{2.5} measurements ranged from 12.2–75.9 $\mu\text{g m}^{-3}$ with a very significant temporal variability. The overall average of PM_{2.5} measured at Rabigh ($37 \pm 16.2 \mu\text{g m}^{-3}$) exceeded the 24-h WHO air quality guideline (20 $\mu\text{g m}^{-3}$) by almost 2-fold with 90% of the daily samples having a PM_{2.5} measurement that exceeded this guideline (Fig. 2).

Daily PM_{2.5} had a significant moderate correlation with relative humidity ($r = -0.22$, p -value = 0.0002) and mean daily temperature ($r = 0.33$, p -value < .0001) and not significantly correlated with wind speed ($r = -0.07$, p -value = 0.2416). This implies that the daily levels of PM_{2.5} were

significantly influenced by variations in mean ambient temperature and relative humidity throughout the study period. However, this was a short-term sampling and these meteorological effects on PM_{2.5} may not be extrapolated over a longer period. Though PM_{2.5} had a stronger positive correlation with NO₃⁻ ($r = 0.3$, p -value < .0001) than with SO₄²⁻ ($r = 0.1$, p -value = 0.06), the mean daily SO₄²⁻ levels ($7.01 \pm 4.8 \mu\text{g m}^{-3}$) were consistently higher than NO₃⁻ levels (mean = $2.36 \pm 1.37 \mu\text{g m}^{-3}$) for the entire study period. This is indicative of a more contribution from industrial than vehicular emissions towards the overall observed PM_{2.5} levels since SO₄²⁻ is predominantly of industrial origin while NO₃⁻ is closely linked to vehicular emissions. SO₄²⁻ and NO₃⁻

Table 2. Average daily PM_{2.5}, BC, Trace Elements (TEs), Anions, Cations and Meteorology (Temperature, Relative Humidity and Wind Speed) during the Sampling Period.

Component	Mean \pm SD	Min.	Max.
PM _{2.5} ($\mu\text{g m}^{-3}$)	37 \pm 16.2	12.2	76
BC _{IR} ($\mu\text{g m}^{-3}$)	1.11 \pm 0.38	0.6	2.06
BC _{UV} ($\mu\text{g m}^{-3}$)	0.95 \pm 0.31	0.49	1.69
Delta-C	-0.16 \pm 0.17	-0.58	0.11
Humidity (%)	50.4 \pm 11.7	22	71
Temperature ($^{\circ}\text{C}$)	32.4 \pm -15.3	28.9	40
Wind Speed (km h^{-1})	10.9 \pm 3.4	4.8	17.7
Trace Elements (ng m^{-3})			
Silicon (Si)	4616 \pm 3428	459	13294
Sulfur (S)	3181 \pm 2181	1151	10759
Calcium (Ca)	2425 \pm 1942	474	8491
Aluminum (Al)	1742 \pm 1375	65.4	5041
Iron (Fe)	1667 \pm 1294	199.2	5807
Sodium (Na)	1092 \pm 667	353	3172
Chlorine (Cl)	979 \pm 1332	< 1.68	5706
Magnesium (Mg)	662 \pm 421	200	1966
Potassium (K)	639 \pm 404	149	1639
Titanium (Ti)	168 \pm 130	20.2	505
Bromine (Br)	55.4 \pm 18	18.4	98.7
Manganese (Mn)	33.7 \pm 25.6	4.7	131.9
Zinc (Zn)	21 \pm 7.7	10.7	48.1
Strontium (Sr)	15.6 \pm 9.8	4.3	41.9
Vanadium (V)	14.5 \pm 14.6	< 0.98	54
Lutetium (Lu)	9.6 \pm 3.7	3.2	17.7
Nickel (Ni)	9.4 \pm 4.1	3.2	21.3
Erbium (Er)	8.4 \pm 4.9	1.0	21.6
Lead (Pb)	7.0 \pm 6.0	< 1.09	22.7
Copper (Cu)	5.1 \pm 3.3	1.3	17.0
Chromium (Cr)	4.8 \pm 4.2	< 0.69	15.7
Rubidium (Rb)	1.6 \pm 1.6	< 0.59	6.0
Anions ($\mu\text{g m}^{-3}$)			
Sulfate – SO ₄ ²⁻	7.01 \pm 4.79	2.80	24.9
Nitrate – NO ₃ ⁻	2.28 \pm 1.36	0.03	5.96
Chloride – Cl ⁻	0.64 \pm 0.85	< 0.02	3.95
Oxalate – C ₂ O ₄ ²⁻	0.23 \pm 0.07	< 0.02	0.39
Cations ($\mu\text{g m}^{-3}$)			
Ammonium – NH ₄ ⁺	1.89 \pm 1.51	< 0.02	6.69
Na ⁺	1.31 \pm 0.92	0.19	3.72
K ⁺	0.38 \pm 0.18	0.07	0.98
Mg ²⁺	0.20 \pm 0.07	0.09	0.48
Ca ²⁺	1.36 \pm 1.07	0.28	5.41

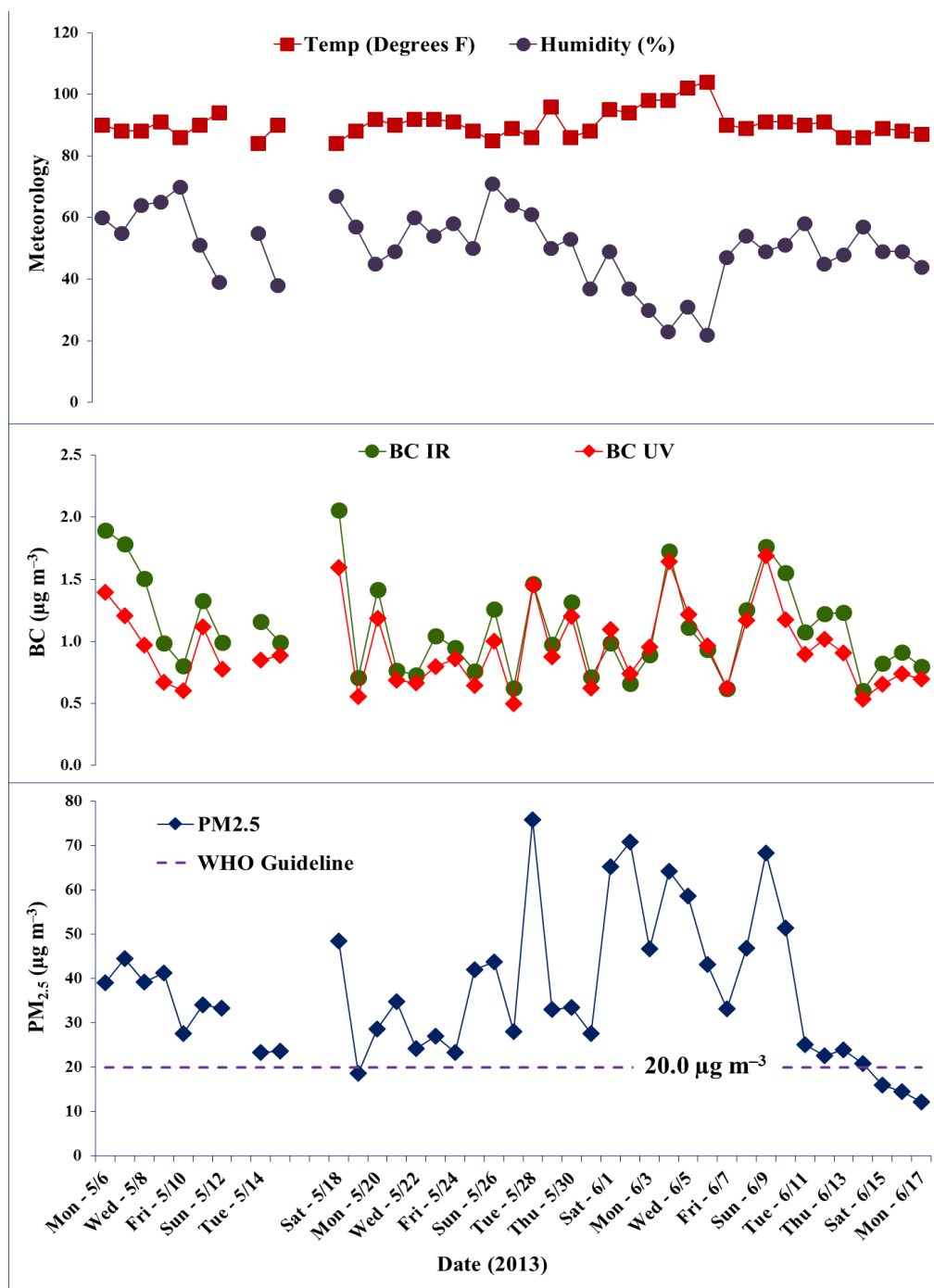


Fig. 2. Time-series plots for the daily levels of $\text{PM}_{2.5}$, BC and Meteorology (Temperature and Relative Humidity) during the study period.

are secondary aerosol species formed by gas phase oxidation of SO_2 and NO_x ($\text{NO}_2 + \text{NO}$) that are predominantly from industrial and vehicular emissions respectively.

Ammonium (NH_4^+) had a weak negative correlation with $\text{PM}_{2.5}$ ($r = -0.13$, p -value = 0.03) but had a very high positive correlation with SO_4^{2-} ($r = 0.94$, p -value < .0001) which may imply a common source for both SO_4^{2-} and NH_4^+ . However, since SO_4^{2-} and NH_4^+ were not correlated with $\text{PM}_{2.5}$ in a similar manner, it is likely that the high correlation between these two aerosol species may entirely be due to the fact that

both of them are predominantly formed in the fine aerosol mode as opposed to having a common source. Secondary species including SO_4^{2-} , NO_3^- , NH_4^+ and $\text{C}_2\text{O}_4^{2-}$ contributed 31.8% of the overall $\text{PM}_{2.5}$.

Daily $\text{PM}_{2.5}$ measurements were highly correlated with the crustal elements including Mg, Al, Si, K, Ca, Ti and Fe ($r > 0.9$, p -value < .0001). Saudi Arabia having a semi-arid climate, soil resuspension by dust storms is more frequent which manifested in the proportion of the overall daily $\text{PM}_{2.5}$ (51.5%) that was explained by crustal elements alone.

Anthropogenic trace elements including S, Cr, Mn, Ni, Cu, and Sr were also highly correlated ($r > 0.6$, p -value $< .0001$) with $PM_{2.5}$. However, these contributed a small proportion (0.64%) of the overall $PM_{2.5}$ but they play a vital role in delineation of anthropogenic sources of $PM_{2.5}$. $PM_{2.5}$ was weakly correlated with Cl^- ($r = 0.23$, p -value $< .0001$) but not correlated with Na. Chloride (Cl^-) predominantly comes from sea sprays which helps to explain the significant proportion (4.5%) of $PM_{2.5}$ coming from marine contribution as sea spray. Rabigh is located at the eastern coast of the Red Sea, so the influence of sea sprays on the air quality is significant.

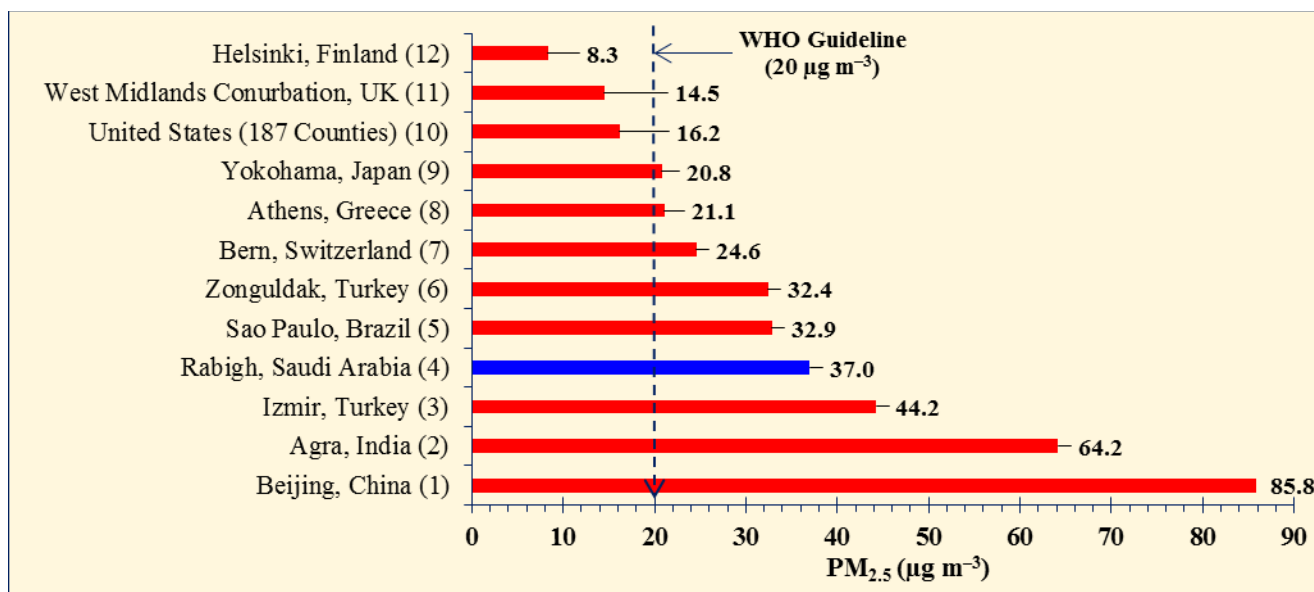
The 24-h Black Carbon (BC) levels showed a significant temporal variability (Fig. 2) with an average of $1.11 \pm 0.38 \mu g m^{-3}$ for BC_{IR} and $0.95 \pm 0.31 \mu g m^{-3}$ for BC_{UV} . BC_{IR} represents the actual black carbon (soot) while BC_{UV} is indicative of the presence of other non-black organic compounds (such as the Polycyclic Aromatic Hydrocarbons–PAHs) in the sample. The overall proportion of BC in $PM_{2.5}$ aerosol was represented by a signal at BC_{IR} which explained 3.4% of the total $PM_{2.5}$. BC had a moderate correlation with $PM_{2.5}$ ($r = 0.47$, p -value $< .0001$), SO_4^{2-} ($r = 0.42$, p -value $< .0001$) and NH_4^+ ($r = 0.3$, p -value $< .0001$) and a weak correlation with NO_3^- ($r = 0.16$, p -value = 0.0081). This shows that the sources of BC including but not limited to vehicular and industrial emissions contributed significantly to the overall $PM_{2.5}$.

Daily $PM_{2.5}$ measurements in Rabigh were compared with those from other cities worldwide. Only those measurements done over summer were considered for comparison since Rabigh $PM_{2.5}$ sampling was done over the period of May 6th through June 17th 2013. The mean $PM_{2.5}$ measured in Rabigh ($37 \mu g m^{-3}$) did not only exceed the WHO guideline ($20 \mu g m^{-3}$), but was also noticeably higher than measurements

observed for most cities used for comparison (Fig. 3). This is an indication of poor air quality in Rabigh and the neighboring areas. We compared the observed daily levels of $PM_{2.5}$ in Rabigh with the WHO guideline, which is international and applies to all member countries.

Furthermore, we computed an Air Quality Index (AQI) based on daily levels of fine particulate matter ($PM_{2.5}$) as shown in Fig. 4. We used an AQI tool provided by United States Environmental Protection Agency (US EPA) since this tool is only available from US EPA. The health risk associated with various levels of ambient $PM_{2.5}$ was categorized as per the specifications of US EPA. Good air quality (0–50; 0.0 – $12.0 \mu g m^{-3}$), Moderate (51–100; 12.1 – $35.4 \mu g m^{-3}$), Unhealthy for Sensitive Sub-Groups (101–150; 35.5 – $55.4 \mu g m^{-3}$), Unhealthy (151–200; 55.5 – $150.4 \mu g m^{-3}$), Very Unhealthy (201–300; 150.5 – $250.4 \mu g m^{-3}$) and Hazardous air quality (301–400; 250.5 – $350.4 \mu g m^{-3}$). In the brackets are the index values with the corresponding breakpoints for the 24-h mean $PM_{2.5}$ (U.S.EPA, 2012). Based on the AQI, there were 57% days of moderate air quality, 28% days of unhealthy air quality for sensitive groups, and 15% days of unhealthy air quality during the entire study period (Fig. 4). We did not observe any single day with good air quality throughout the entire study period. Results clearly indicate that air quality related to particulate air pollution in Rabigh is a significant issue.

The AQI as a tool is not an air quality guideline or regulation and thus should not be compared to either US EPA, WHO or any other ambient air quality guidelines. The analysis of AQI simplifies the presentation and communication of air quality data in the simplest terms possible as relates to how any given level of ambient $PM_{2.5}$ would affect the health of different categories of people that are exposed.



1 – (Zhao et al., 2009); 2 – (Kulshrestha et al., 2009); 3 – (Yatkin and Bayram, 2008); 4 – This Study; 5 – (Degobbi et al., 2011); 6 – (Akyuz and Cabuk, 2009); 7 – (Hueglin et al., 2005); 8 – (Pateraki et al., 2013); 9 – (Khan et al., 2010); 10 – (Bell et al., 2007); 11 – (Anderson et al., 2001); 12 – (Sillanpää et al., 2005)

Fig. 3. A bar graph showing the comparison of $PM_{2.5}$ levels measured at Rabigh site with other cities worldwide.

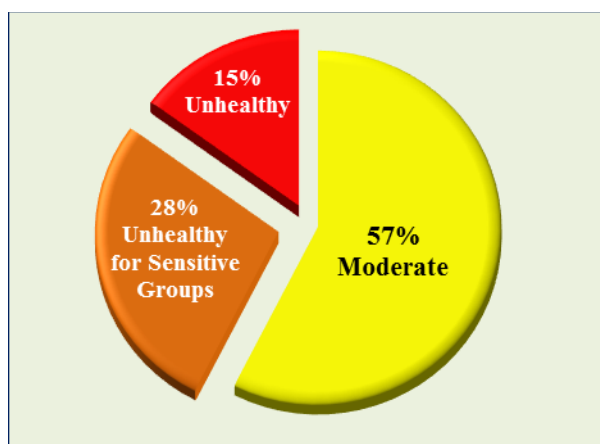


Fig. 4. Pie chart showing the air quality index (AQI) at Rabigh during the study period.

PM_{2.5} Mass Reconstruction

We performed a PM_{2.5} chemical mass reconstruction by re-grouping the various chemical species in the overall PM_{2.5} aerosol under six different categories (e.g., crustal material, anthropogenic trace elements, secondary ions, sea sprays, elemental carbon and organic matter) so as to determine the proportion of overall PM_{2.5} aerosol explained by the measured constituents in our analyses (Chow *et al.*, 2015). The reconstructed PM_{2.5} mass was calculated as shown in Eq. (3).

$$\text{Reconstructed-PM}_{2.5} = \text{Crustal Material [CM]} + \text{Trace Elements [TE]} + \text{Sea Spray [SS]} + \text{Secondary Ions [SI]} + \text{Elemental Carbon [EC/ or BC]} + \text{Organic Matter [OM]} \quad (3)$$

$$[\text{CM}] = 1.89[\text{Al}] + 1.21[\text{K}] + 1.43[\text{Fe}] + 1.4[\text{Ca}] + 1.66[\text{Mg}] + 1.67[\text{Ti}] + 2.14[\text{Si}] \quad (4)$$

$$[\text{TE}] = 1.31[\text{V}] + 1.46[\text{Cr}] + 1.29[\text{Mn}] + 1.27[\text{Ni}] + 1.13[\text{Cu}] + 1.24[\text{Zn}] + 1.32[\text{As}] + 1.41[\text{Se}] + 1.40[\text{Br}] + 1.37[\text{Sr}] + 1.12[\text{Ba}] + 1.08[\text{Pb}] \quad (5)$$

(Macias *et al.*, 1981; Solomon *et al.*, 1989)

$$[\text{SS}] = [\text{Cl}^-] + \text{ss} [\text{Na}^+] + \text{ss} [\text{Mg}^{2+}] + \text{ss} [\text{K}^+] + \text{ss} [\text{Ca}^{2+}] + \text{ss} [\text{SO}_4^{2-}] \quad (6)$$

where

$$\begin{aligned} \text{ss} [\text{Na}^+] &= 0.556 [\text{Cl}^-]; \text{ss} [\text{Mg}^{2+}] = 0.12 \text{ss} [\text{Na}^+]; \\ \text{ss} [\text{K}^+] &= 0.036 \text{ss} [\text{Na}^+]; \\ \text{ss} [\text{Ca}^{2+}] &= 0.038 \text{ss} [\text{Na}^+]; \text{ss} [\text{SO}_4^{2-}] = 0.252 \text{ss} [\text{Na}^+] \end{aligned} \quad (7)$$

(Seinfeld and Pandis, 2012).

$$[\text{SI}] = \text{nss}[\text{SO}_4^{2-}] + [\text{NO}_3^-] + [\text{NH}_4^+] + [\text{C}_2\text{O}_4^{2-}] \quad (7)$$

where $\text{nss} [\text{SO}_4^{2-}] = [\text{SO}_4^{2-}] - \text{ss} [\text{SO}_4^{2-}]$; ss and nss denote sea spray and non-sea spray, respectively.

Oxide factors used in Eqs. (4–5) were computed using the most stable oxides (Al₂O₃, K₂O, Fe₂O₃, CaO, MgO, SiO₂, TiO₂, VO, Cr₂O₃, MnO, NiO, Cu₂O, ZnO, BrO₂, Rb₂O₃, SrO₂, Er₂O₃, Lu₂O₃, and PbO) of these elements (Macias *et al.*, 1981; Solomon *et al.*, 1989). Elemental and water-soluble

ionic species concentrations were obtained from ED-XRF and ion exchange chromatography analyses respectively as described earlier.

In summary, crustal material explained 51.5%, secondary ions 31.8%, sea spray 4.5%, black carbon 3.4% and anthropogenic trace elements 0.64% of the overall observed PM_{2.5}. Altogether, these PM_{2.5} chemical species including BC, trace elements, water soluble anions and cations explained 91.9% of the total observed PM_{2.5}. However, it should be noted that we had no estimates on organic matter (OM). Also, converting the total S mass (3.18 μg m⁻³) from ED-XRF analysis gives 9.54 μg m⁻³ of total SO₄²⁻. The PM mass closure on secondary aerosols shown in Eqs. (6–7) uses total SO₄²⁻ obtained from the IC analysis (7.01 μg m⁻³). This represents only the water-soluble portion of total S. The remaining water-insoluble portion (i.e., 2.53 μg m⁻³) of total S together with OM may account for the unexplained portion (8.1%) of the overall PM_{2.5} mass. The proportion of explained daily PM_{2.5} from individual samples ranged from 79.3%–103.1%. The overall variations in observed and reconstructed daily levels of PM_{2.5} over the entire sampling period are shown in a radar graph in Fig. 5.

Sources of PM_{2.5} in Rabigh — Enrichment Factor (EF) Analysis

Essentially, the trace elements in air particulate samples originate from either earth-crust/soil through weathering, decomposition and soil re-suspension processes or anthropogenic activities. Soil and anthropogenic sources were delineated using computations of enrichment factor (EF) as described previously. A summarized distribution of anthropogenic as well as crustal/soil derived elements is provided in a bar graph in Fig. 6. Anthropogenic sources as indicated by EF values greater than 10 contributed significantly for measurements of Ni, V, Zn, Pb, Cl, S, Lu and Br; while the earth-crust/soil derived elements included Si, Rb, Ti, Fe, Mn, Mg, K, Sr, Cr, Ca, Cu, Na and Al.

From the relative mean concentrations of trace elements shown in Table 2, soil contributed a large proportion of trace elements measured in this study. Overall, anthropogenic sources had a relatively small trace elemental contribution with exception of sulfur (S). The relatively high EF values for

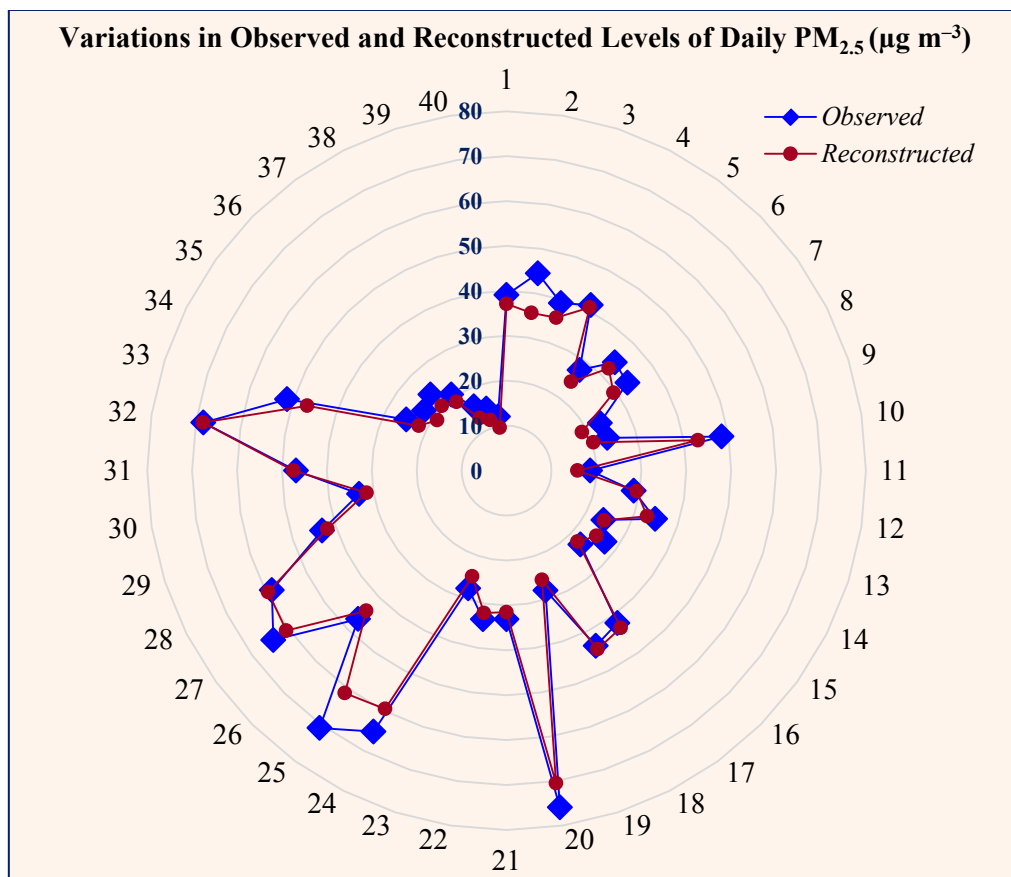


Fig. 5. Radar graph showing the variations in observed and reconstructed the daily PM_{2.5} during the study period.

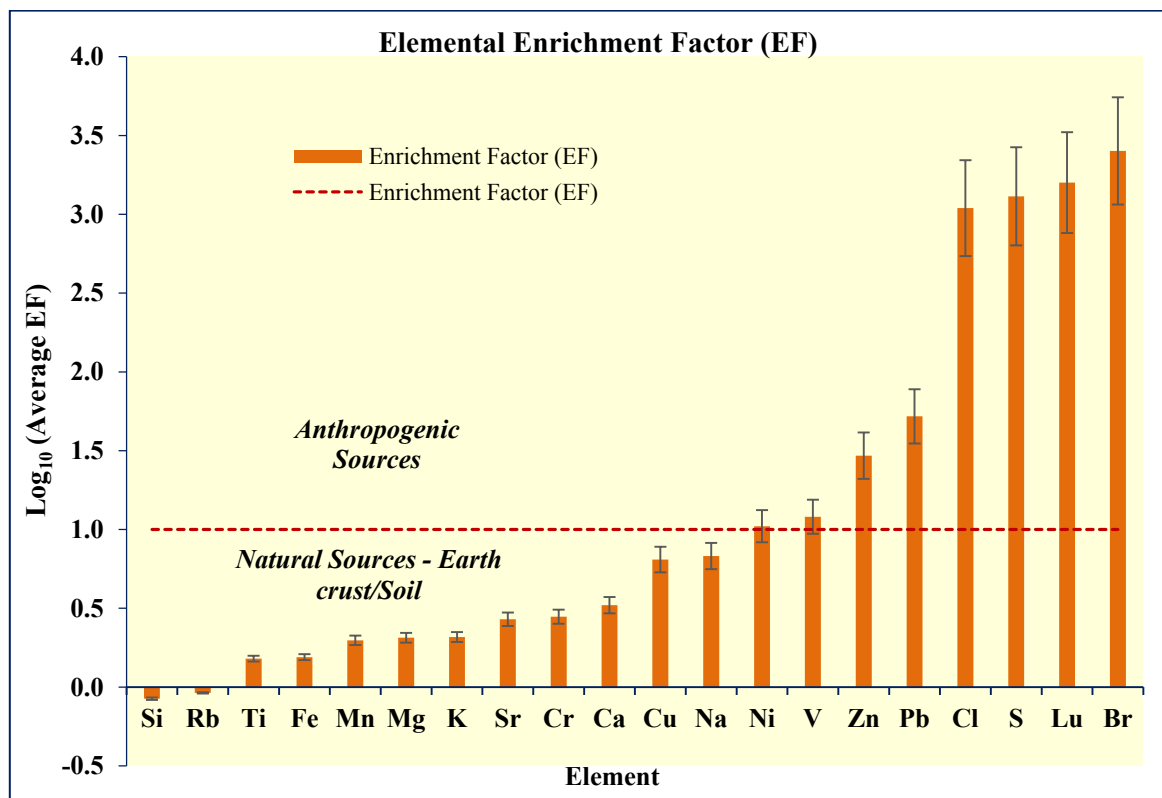


Fig. 6. Plot of log transformed values of enrichment factor (EF).

Na and Cl may not necessarily be indicative of a significant anthropogenic contribution but rather may be attributable to marine input (sea-spray) since Rabigh is located at the eastern coast of the Red Sea. Silicon (Si), Rb, Cr, Ti, Mn, and Fe had consistently the lowest EF values in all the samples ($EF \leq 2$), suggesting a common source (soil/earth crust) for these elements.

The high EF values for Ni, V, Zn, Pb, Cl, S, Lu and Br further help to point out the most significant anthropogenic sources of $PM_{2.5}$ in Rabigh. Vanadium (V) and S mostly come from fossil-fuel/or oil combustion; while Cu, Zn, Ni and Pb come from vehicular emissions. Lutetium (Lu) being a rare earth metal, has very few commercial applications. However, its stable isotopes (^{175}Lu and ^{176}Lu) can be used as catalysts in petroleum cracking in refineries, alkylation, hydrogenation, and polymerization processes. These observations are very consistent with results from previous studies (Nasrallah and Seroji, 2008; Khodeir et al., 2012; Munir et al., 2013).

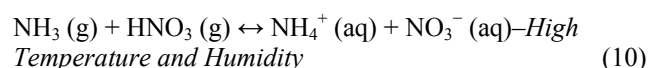
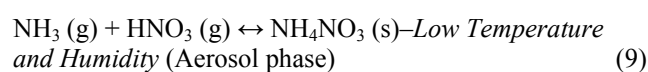
Sources of Rabigh $PM_{2.5}$ — Positive Matrix Factorization (PMF)

PMF model has been widely used in air pollution research to generate constructs for source apportionment and describe the various sources of measured air pollutants (Gianini et al., 2012; Mansha et al., 2012). We set our PMF base model at 20 runs with 5 source factors. Overall the model had a 100% convergence rate with all the Q-robust and Q-true values being within a very close range. Results for the model run with the lowest Q-value are presented. Residual analysis indicated that all the parameters/variables input into the model had a Gaussian or close enough to Gaussian distribution with some variables having a correlation of $r = 1$ on observed versus predicted values from the PMF model. Overall, the correlation between observed and predicted values for each variable entered in the model was greater than 0.8 ($r > 0.8$) which further validates the results obtained from our PMF source apportionment and the identification of the different sources/factors for $PM_{2.5}$.

The factor contributions for each source type are shown in Fig. 7. We interpreted the factors to determine the sources by comparing the factor loadings of each aerosol specie used in the PMF model. Different sources of $PM_{2.5}$ will emit characteristic chemical species in the overall $PM_{2.5}$ aerosol. Thus, the chemical species measured in $PM_{2.5}$ aerosol can be used as markers for specific sources. V, S and Ni normally originate from fossil-fuel combustion (oil refineries) and diesel. Ni may also come from several industrial processes and soil; Cu and Zn are typically used in engine oil due to their antioxidant property and thus may be related to automobile/vehicular emissions if measured in $PM_{2.5}$ aerosol; Al, Si, Ca, Fe, Mn, Ti, Na, Ba, and K normally have crustal origin. Na may also come from marine contribution as sea salt while K originates from bio-mass burning. Chloride (Cl^-) normally originates from the sea sprays as sea-salt.

Total S from ED-XRF and the water-soluble SO_4^{2-} from IC analysis were highly correlated ($r = 0.94$, $p\text{-value} < .0001$) (Fig. 8). The results for source apportionment from PMF model were similar when either S or SO_4^{2-} was used.

Particulate sulfate (SO_4^{2-}), nitrate (NO_3^-), ammonium (NH_4^+) and oxalate ($\text{C}_2\text{O}_4^{2-}$) form the secondary aerosol portion of $PM_{2.5}$ (Hueglin et al., 2005; Park et al., 2013). Nitrate (NO_3^-) and SO_4^{2-} are formed by gas-phase oxidation of the primary gaseous oxides of nitrogen and sulfur (NO_x and SO_2) into nitric acid (HNO_3 gaseous) and sulfuric acid (H_2SO_4 aqueous) respectively (Panis, 2008). Ammonium (NH_4^+) typically exists as ammonium salts formed through the neutralization of H_2SO_4 and HNO_3 acids by atmospheric ammonia (NH_3) (Harrison and Yin, 2000) as shown in Eqs. (8–10).



NO_x and SO_2 are predominantly from vehicular and industrial emissions respectively. While NH_3 is predominantly of an agricultural origin, a significant proportion of it can be from industrial and vehicular emissions and other biogenic processes such as volatilization from soils and oceans (Behera et al., 2013). SO_4^{2-} and NH_4^+ were highly correlated ($r = 0.94$, $p\text{-value} < .0001$) and this could either be due to the fact that these particle species are both predominantly formed in fine aerosol mode or that they have a common emission source in Rabigh. Strong correlations between SO_4^{2-} and NH_4^+ have also been observed in previous studies where measurements were done over summer (Bell et al., 2007). NO_3^- was moderately correlated with NH_4^+ ($r = -0.29$, $p\text{-value} < .0001$) and not significantly correlated with SO_4^{2-} ($r = -0.072$, $p\text{-value} = 0.2252$).

Compared to SO_4^{2-} and NH_4^+ , the chemistry of NO_3^- is quite unique. While SO_4^{2-} and NH_4^+ are predominantly formed in fine aerosol mode ($PM_{2.5}$), NO_3^- can be formed in both the coarse and fine aerosol modes depending on sampling location and weather conditions (Zhuang et al., 1999a, b). Since we sampled at the coastal region (Eastern Coast of the Red Sea) with strong influence of sodium from sea salt, it is possible that most of the NO_3^- was in the form of sodium nitrate (NaNO_3) which for most part forms as a coarse aerosol. A minor proportion if any of the total NO_3^- in the fine aerosol mode would be ammonium nitrate (NH_4NO_3). It is also possible that we lost some of the NO_3^- since the entire sampling period had relatively high temperature (32.4°C) and moderate humidity (50.4%) (Table 2). Under these meteorological conditions NH_4NO_3 will either evaporate or undergo photolytic decomposition upon its formation (Zhuang et al., 1999b; U.S.EPA, 2000) as shown in Eqs. (9–10). Loss of NO_3^- from air filter samples during and after field sampling has been shown in number of studies especially where sampling was done during warmer seasons (Ashbaugh and Eldred, 2004; Chow et al., 2005).

Since we measured significant amounts of NO_3^- in our samples but with limited amounts of NH_4^+ to neutralize all

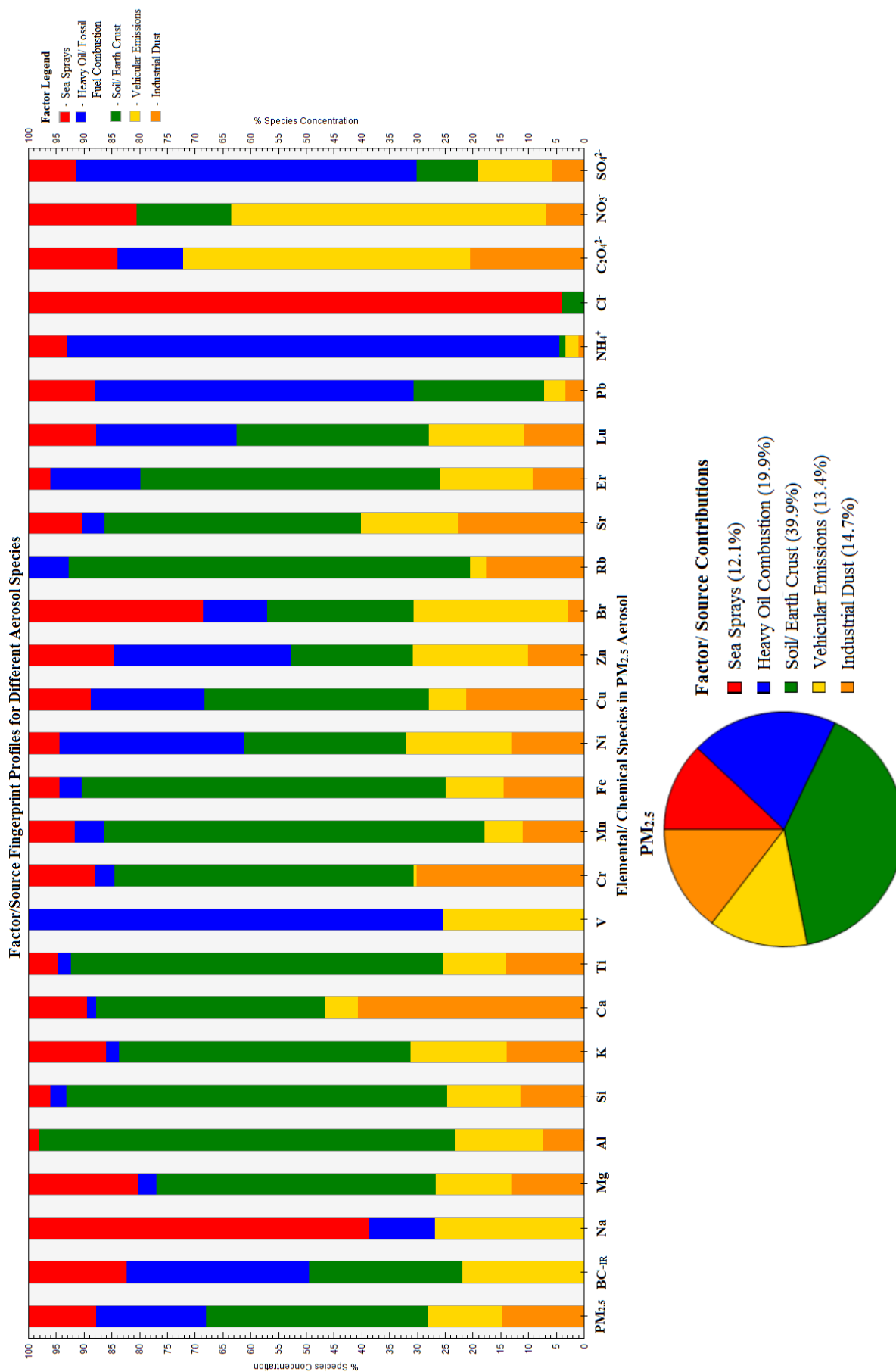


Fig. 7. Fingerprint Profiles for Emission Sources of PM_{2.5} in Rabigh and the Relative Percentage Contribution of each Identified Source to the Overall PM_{2.5} Measurement.

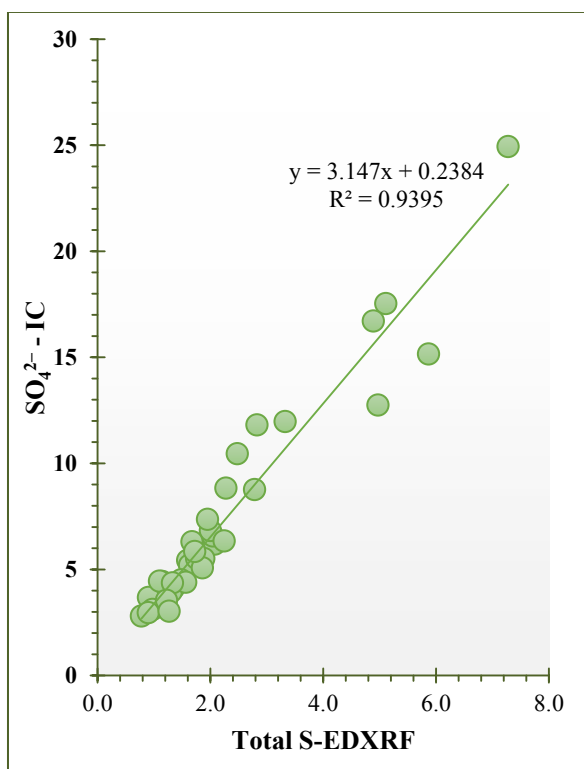


Fig. 8. A plot of water-soluble SO_4^{2-} from IC analysis against total S from ED-XRF analysis.

the available SO_4^{2-} , it is possible that the existence of NH_4NO_3 was less likely in our samples. However, significant correlations were observed between NO_3^- and Na ($r = 0.682$, p -value $< .0001$), Mg ($r = 0.394$, p -value $< .0001$), K ($r = 0.403$, p -value $< .0001$), and Ca ($r = 0.326$, p -value $< .0001$), suggesting that a substantial proportion of our observed total NO_3^- was in the form of NaNO_3 , $\text{Mg}(\text{NO}_3)_2$, KNO_3 and $\text{Ca}(\text{NO}_3)_2$.

Besides industrial and vehicular emissions, oxalate ($\text{C}_2\text{O}_4^{2-}$) may also originate from bio-mass burning more so if it is highly correlated with K (Jiang *et al.*, 2011). However, only 30% of the $\text{PM}_{2.5}$ samples had detectable levels of $\text{C}_2\text{O}_4^{2-}$ with an overall mean concentration of $0.22 \mu\text{g m}^{-3}$. In addition the daily estimates of Delta-C were very low with an overall mean of -0.16 ± 0.17 (Table 2). $\text{C}_2\text{O}_4^{2-}$ and Delta-C are strong markers for bio-mass burning as the major source of air particulate emissions (Wang *et al.*, 2011; Wang *et al.*, 2012; Rattigan *et al.*, 2013). Thus, bio-mass burning was ruled out as a possible source of $\text{PM}_{2.5}$ in Rabigh during our study period since the estimates on $\text{C}_2\text{O}_4^{2-}$ and Delta-C were very low.

Overall, five factors were identified as the main sources of $\text{PM}_{2.5}$ in Rabigh. These included; Soil, Fossil-Fuel (Heavy Oil) Combustion, Vehicular/automobile emissions, Industrial Dust, and Sea Sprays (Fig. 7). The identification of these factors/sources was entirely based on the relative abundances of different aerosol chemical species within each factor as obtained from the PMF model. The relative contribution of each identified factor to the overall $\text{PM}_{2.5}$ aerosol is shown in Fig. 7. We identified the first factor

that explained the largest proportion (39.9%) of the total variation in overall $\text{PM}_{2.5}$ as *Soil/Earth crust* since it was mostly dominated by Si, Al, Ti, Mn, Fe, Mg, Rb, K, Cr, Er, Sr, Ca, and Cu. From $\text{PM}_{2.5}$ mass reconstruction in Eq. (4), the crustal elements explained a larger proportion (51.5%) of the total $\text{PM}_{2.5}$ mass than the PMF model (39.9%). This is because the $\text{PM}_{2.5}$ mass re-construction assumes 100% of the crustal elements to originate from the earth-crust while the PMF model provides more details on any other sources that contributed to the overall observed levels of crustal elements. As shown in the PMF fingerprint (Fig. 7), the crustal elements (Al, K, Fe, Ca, Mg, Ti and Si) had some minor proportions coming from other sources other than the earth-crust. The difference (11.6%) between these two estimates from $\text{PM}_{2.5}$ mass re-construction and PMF analysis is accounted for by the other sources identified from the PMF model.

The second factor accounted for 19.9% of the total $\text{PM}_{2.5}$ and was identified as *Fossil-fuel (Heavy Oil) Combustion* due to high proportions of V, Ni, Pb, Lu, Cu, Zn, NH_4^+ , SO_4^{2-} and BC. The third factor explained 14.7% of the overall $\text{PM}_{2.5}$ and was identified as *Industrial Dust/Cement* due to high proportions of Ca, Fe, Al, Si and Cr. The elements (Ca, Fe, Al and Si) are mostly used in cement production. The fourth factor explained only 13.4% of the variation in total $\text{PM}_{2.5}$. We identified this factor as *Vehicular Emissions* due to high proportions of NO_3^- , $\text{C}_2\text{O}_4^{2-}$, V, Ni and BC. The fifth factor explained 12.1% of the total variation in $\text{PM}_{2.5}$. This was identified as *Sea Sprays* due to high relative abundances of Cl^- and Na. Sea-salt is usually predominantly NaCl and thus the high proportions of Na and Cl^- as shown on PMF fingerprint in Fig. 7.

Backward-in-Time Trajectories

We used plots of Backward-in-time Hybrid Single-Particle Lagrangian Integrated Trajectories (HYSPPLIT) to define the influence of regional and local sources' contribution to the daily $\text{PM}_{2.5}$ measurements. Trajectories help to explain some of the intricacies in the variations of $\text{PM}_{2.5}$ especially with the chemical composition as well as mass concentrations. Fig. 9 shows wind trajectories 72-hrs prior to sampling for the 2 days with the highest $\text{PM}_{2.5}$ measurements (75.9 and $70.8 \mu\text{g m}^{-3}$ on May 28th and June 2nd, 2013 respectively); and 2 days with lowest $\text{PM}_{2.5}$ measurements (14.5 and $12.2 \mu\text{g m}^{-3}$ on June 16th and June 17th, 2013 respectively). On all the 4 days, wind direction toward the sampling site in Rabigh, was mostly Northwesterly. However, on days with lowest $\text{PM}_{2.5}$ measurements the wind was blowing over the Red Sea into our sampling site. This had a dilution effect on the concentration of ambient particulates since the air over the sea has relatively low levels of particulates. Conversely, the days with the highest $\text{PM}_{2.5}$ measurements, the wind blew across the heavily industrialized areas carrying along all the particulate emissions into Rabigh. This helps to explain the regional as well local contributions towards the measured fine air particulate concentrations. Furthermore, with more stratified analyses we observed that, the chemical composition of the $\text{PM}_{2.5}$ varied significantly with different days having elemental species that characterized the wind

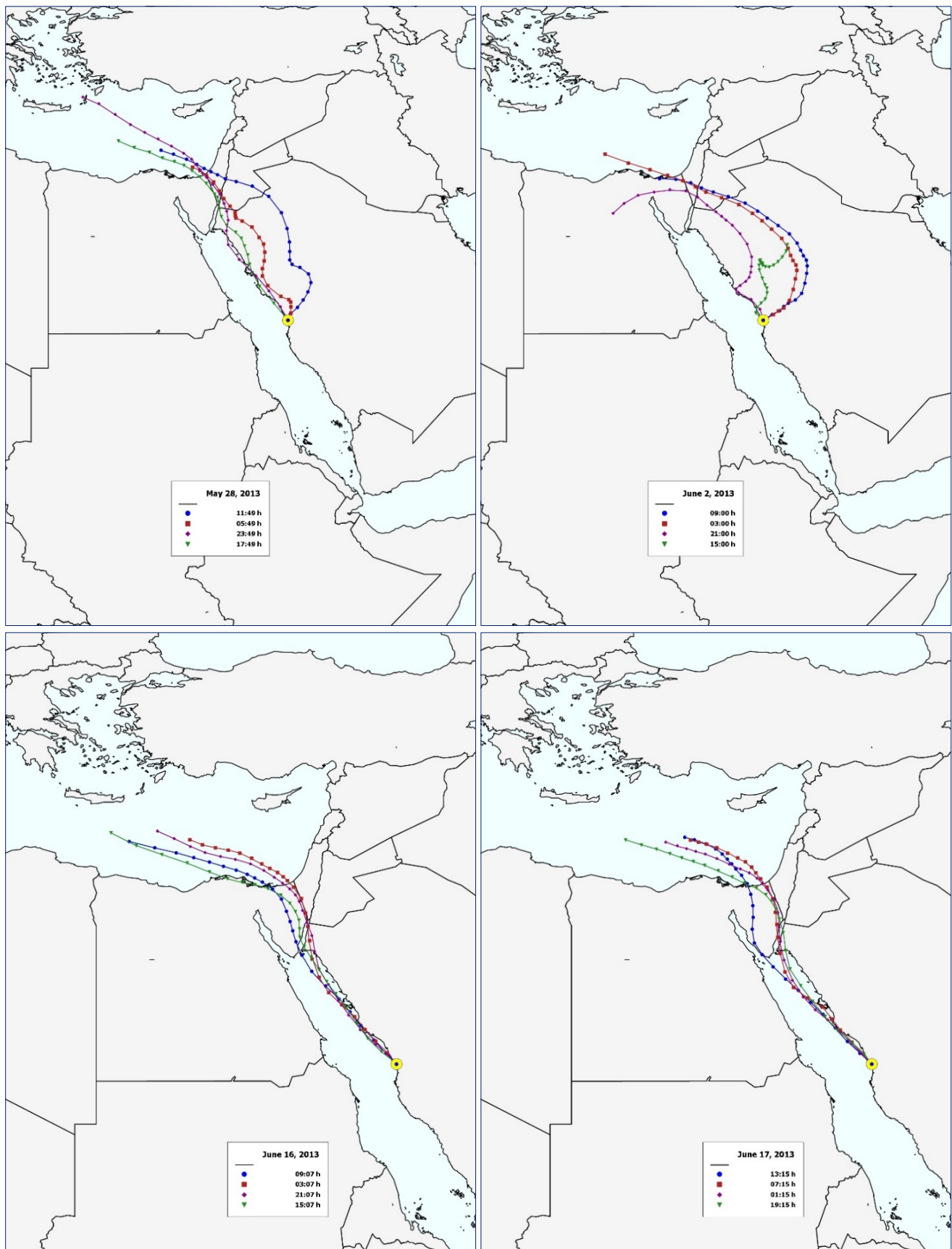


Fig. 9. Plots of Backward-in-time HYbrid Single-Particle Lagrangian Integrated Trajectories (HYSPLIT) Showing Wind Direction and its Influence on Daily $PM_{2.5}$ Levels Recorded at Rabigh Sampling Site.

trajectories. For example, the measurement of relatively higher concentrations of Na and Cl⁻ on days where the wind trajectories predominantly passed across the Red Sea into our sampling site.

CONCLUSION

This is the first study to assess fine particulate air pollution (PM_{2.5}) in Rabigh, Saudi Arabia and its possible sources. The daily PM_{2.5} levels ranged from 12.2–76 µg m⁻³ with an overall mean of 37 ± 16.2 µg m⁻³. Results show that fossil-fuel combustion, crustal and anthropogenic trace elements, sea-sprays, industrial and vehicular emissions contribute significantly to the overall air particulate emissions in Rabigh. Regional and Continental transport of fine aerosols cannot be excluded as a source of fine particulate air pollution in Rabigh, Saudi Arabia.

These findings are consistent with previous studies and highlight the need for more comprehensive research into air pollution to better understand the major source of particulate air pollutants in Rabigh and the neighboring areas. This is fundamental as per the formulation of more effective and sustainable control strategies on emission of PM_{2.5} so as to efficiently protect and preserve human health and the environment in Rabigh and the entire Middle East region.

ACKNOWLEDGMENTS

This work was supported by King Abdul-Aziz University, Jeddah, Saudi Arabia. We would like to acknowledge the support of Dr. Ahmed Ebrahim Hakora and Dr. Abdullah Sharif Alshamrani, Rabigh General Hospital for sampling. Additionally, the authors gratefully acknowledge the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model and/or READY website (<http://www.ready.noaa.gov>) used in this publication. More appreciation to Dr. Lung C. Chen, New York University School of Medicine for his great support analyzing the trace elements from PM_{2.5} samples using ED-XRF.

REFERENCES

- Ahmed, T., Dutkiewicz, V. A., Shareef, A., Tuncel, G., Tuncel, S. and Husain, L. (2009). Measurement of black carbon (BC) by an optical method and a thermal-optical method: Intercomparison for four sites. *Atmos. Environ.* 43: 6305–6311.
- Akyuz, M. and Cabuk, H. (2009). Meteorological variations of PM_{2.5}/PM₁₀ concentrations and particle-associated polycyclic aromatic hydrocarbons in the atmospheric environment of Zonguldak, Turkey. *J. Hazard. Mater.* 170: 13–21.
- Alharbi, B.H., Maghrabi, A. and Tapper, N. (2013). The March 2009 dust event in Saudi Arabia: Precursor and supportive environment. *Bull. Am. Meteorol. Soc.* 94: 515–528.
- Al-Jeelani, H.A. (2009a). Air quality assessment at Al-Taneem area in the Holy Makkah City, Saudi Arabia. *Environ. Monit. Assess.* 156: 211–222.
- Al-Jeelani, H.A. (2009b). Evaluation of air quality in the Holy Makkah during Hajj season 1425 H. *J. Appl. Sci. Res.* 5: 115–121.
- Anderson, H., Bremner, S., Atkinson, R., Harrison, R. and Walters, S. (2001). Particulate matter and daily mortality and hospital admissions in the west midlands conurbation of the United Kingdom: associations with fine and coarse particles, black smoke and sulphate. *Occup. Environ. Med.* 58: 504–510.
- Aprile, F.M. and Bouvy, M. (2008). Distribution and enrichment of heavy metals in the sediments at the Tapacurá River basin, Northeastern Brazil. *Braz. J. Aquat. Sci. Technol.* 12: 1–8.
- Ashbaugh, L.L. and Eldred, R.A. (2004). Loss of particle nitrate from teflon sampling filters: effects on measured gravimetric mass in California and in the IMPROVE network. *J. Air Waste Manage. Assoc.* 54: 93–104.
- Behera, S.N., Sharma, M., Aneja, V.P. and Balasubramanian, R. (2013). Ammonia in the atmosphere: a review on emission sources, atmospheric chemistry and deposition on terrestrial bodies. *Environ. Sci. Pollut. Res. Int.* 20: 8092–8131.
- Bell, M.L., Dominici, F., Ebisu, K., Zeger, S.L. and Samet, J.M. (2007). Spatial and temporal variation in PM_{2.5} chemical composition in the United States for health effects studies. *Environ. Health Perspect.* 115: 989–995.
- Bernstein, J.A., Alexis, N., Barnes, C., Bernstein, I.L., Nel, A., Peden, D., Diaz-Sanchez, D., Tarlo, S.M. and Williams, P.B. (2004). Health effects of air pollution. *J. Allergy Clin. Immunol.* 114: 1116–1123.
- Cançado, J.E.D., Saldiva, P.H.N., Pereira, L.A.A., Lara, L.B.L.S., Artaxo, P., Martinelli, L.A., Arbex, M.A., Zanobetti, A. and Braga, A.L.F. (2006). The impact of sugar cane-burning emissions on the respiratory system of children and the elderly. *Environ. Health Perspect.* 114: 725–729.
- Cheung, H.C., Wang, T., Baumann, K. and Guo, H. (2005). Influence of regional pollution outflow on the concentrations of fine particulate matter and visibility in the coastal area of southern China. *Atmos. Environ.* 39: 6463–6474.
- Chow, J.C., Watson, J.G., Lowenthal, D.H. and Magliano, K.L. (2005). Loss of PM_{2.5} nitrate from filter samples in central California. *J. Air Waste Manage. Assoc.* 55: 1158–1168.
- Chow, J.C., Watson, J.G., Mauderly, J.L., Costa, D.L., Wyzga, R.E., Vedal, S., Hidy, G.M., Altshuler, S.L., Marrack, D., Heuss, J.M., Wolff, G.T., Arden Pope III, C. and Dockery, D.W. (2006). Health effects of fine particulate air pollution: Lines that connect. *J. Air Waste Manage. Assoc.* 56: 1368–1380.
- Chow, J.C., Lowenthal, D., Chen, L.W.A., Wang, X. and Watson, J. (2015). Mass reconstruction methods for PM_{2.5}: A review. *Air Qual. Atmos. Health* 8: 243–263.
- Degobbi, C., Lopes, F.D.T.Q.S., Carvalho-Oliveira, R., Muñoz, J.E. and Saldiva, P.H.N. (2011). Correlation of fungi and endotoxin with PM_{2.5} and meteorological parameters in atmosphere of Sao Paulo, Brazil. *Atmos.*

- Environ.* 45: 2277–2283.
- Deng, X., Tie, X., Wu, D., Zhou, X., Bi, X., Tan, H., Li, F. and Jiang, C. (2008). Long-term trend of visibility and its characterizations in the Pearl River Delta (PRD) region, China. *Atmos. Environ.* 42: 1424–1435.
- Draxler, R.R. and Rolph, G.D. (2013) HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website. NOAA Air Resources Laboratory, College Park, MD. <http://www.arl.noaa.gov/HYSPLIT.php>.
- Fabretti, J.F., Sauret, N., Gal, J.F., Maria, P.C. and Schärer, U. (2009). Elemental characterization and source identification of PM_{2.5} using Positive Matrix Factorization: The Malraux road tunnel, Nice, France. *Atmos. Res.* 94: 320–329.
- Furman, H.K.H. (2003). Dust storms in the Middle East: Sources of origin and their temporal. *Indoor Built Environ.* 12: 419–426.
- Gianini, M.F.D., Fischer, A., Gehrig, R., Ulrich, A., Wichser, A., Piot, C., Besombes, J.L. and Hueglin, C. (2012). Comparative source apportionment of PM₁₀ in Switzerland for 2008/2009 and 1998/1999 by Positive Matrix Factorisation. *Atmos. Environ.* 54: 149–158.
- Harrison, R.M. and Yin, J. (2000). Particulate matter in the atmosphere: Which particle properties are important for its effects on health?. *Sci. Total Environ.* 249: 85–101.
- Hueglin, C., Gehrig, R., Baltensperger, U., Gysel, M., Monn, C. and Vonmont, H. (2005). Chemical characterisation of PM_{2.5}, PM₁₀ and coarse particles at urban, near-city and rural sites in Switzerland. *Atmos. Environ.* 39: 637–651.
- Hyslop, N.P. (2009). Impaired visibility: The air pollution people see. *Atmos. Environ.* 43: 182–195.
- Jiang, Y., Zhuang, G., Wang, Q., Liu, T., Huang, K., Fu, J. S., Li, J., Lin, Y., Zhang, R. and Deng, C. (2011). Characteristics, sources and formation of aerosol oxalate in an Eastern Asia megacity and its implication to haze pollution. *Atmos. Chem. Phys. Discuss.* 11: 22075–22112
- Karakatsani, A., Analitis, A., Perifanou, D., Ayres, J., Harrison, R., Kotronarou, A., Kavouras, I., Pekkanen, J., Hameri, K., Kos, G., de Hartog, J., Hoek, G. and Katsouyanni, K. (2012). Particulate matter air pollution and respiratory symptoms in individuals having either asthma or chronic obstructive pulmonary disease: A European multicentre panel study. *Environ. Health* 11: 75.
- Khan, M.F., Shirasuna, Y., Hirano, K. and Masunaga, S. (2010). Characterization of PM_{2.5}, PM_{2.5–10} and PM₁₀ in ambient air, Yokohama, Japan. *Atmos. Res.* 96: 159–172.
- Khodeir, M., Shamy, M., Alghamdi, M., Zhong, M., Sun, H., Costa, M., Chen, L.C. and Maciejczyk, P. (2012). Source apportionment and elemental composition of PM_{2.5} and PM₁₀ in Jeddah City, Saudi Arabia. *Atmos. Pollut. Res.* 3: 331–340.
- Kim, E., Larson, T.V., Hopke, P.K., Slaughter, C., Sheppard, L.E. and Claiborn, C. (2003). Source identification of PM_{2.5} in an arid Northwest U.S. City by positive matrix factorization. *Atmos. Res.* 66: 291–305.
- Kim, Y.J., Kim, K.W., Kim, S.D., Lee, B.K. and Han, J.S. (2006). Fine particulate matter characteristics and its impact on visibility impairment at two urban sites in Korea: Seoul and Incheon. *Atmos. Environ.* 40: 593–605.
- Klos, A., Rajfur, M., Waclawek, M. and Waclawek, M. (2011). Application of enrichment factor (EF) to the interpretation of results from the biomonitoring studies. *Ecol. Chem. Eng.* 18: 171–183.
- Korzova, E.N., Kuznetsova, O.V., Smagunova, A.N. and Stavitskaya, M.V. (2011). Determination of inorganic pollutants in atmospheric aerosols. *J. Anal. Chem.* 66: 222–240.
- Kulshrestha, A., Satsangi, P.G., Masih, J. and Taneja, A. (2009). Metal concentration of PM_{2.5} and PM₁₀ particles and seasonal variations in urban and rural environment of Agra, India. *Sci. Total Environ.* 407: 6196–204.
- Laden, F., Neas, L.M., Dockery, D.W. and Schwartz, J. (2000). Association of fine particulate matter from different sources with daily mortality in six U.S. cities. *Environ. Health Perspect.* 108: 941–947.
- Macias, E.S., Zwicker, J.O., Ouimette, J.R., Hering, S.V., Friedlander, S.K., Cahill, T.A., Kuhlmeier, G.A. and Richards, L.W. (1981). Regional haze case studies in the southwestern US—I. Aerosol chemical composition. *Atmos. Environ.* 15: 1971–1986.
- Mansha, M., Ghauri, B., Rahman, S. and Amman, A. (2012). Characterization and source apportionment of ambient air particulate matter (PM_{2.5}) in Karachi. *Sci. Total Environ.* 425: 176–83.
- Munir, S., Habeebullah, T.M., Seroji, A.R., Gabr, S.S., Mohammed, A.M.F. and Morsy, E.A. (2013). Modeling particulate matter concentrations in Makkah, applying a statistical modeling approach. *Aerosol Air Qual. Res.* 13: 901–910.
- Nasrallah, M.M. and Seroji, A.R. (2008). Particulates in the atmosphere of Makkah and Mina valley during Ramadhan and Hajj season of 1424 and 1425 H (2004–2005). *Arab Gulf J. Sci. Res.* 26: 199–206.
- Ozturk, F., Zararsiz, A., Kirmaz, R. and Tuncel, G. (2011). An approach to measure trace elements in particles collected on fiber filters using EDXRF. *Talanta* 83: 823–831.
- Panis, L. (2008). The effect of changing background emissions on external cost estimates for secondary particulates. *Open Environ. Sci.* 2: 47–53.
- Park, S.S., Jung, S.A., Gong, B.J., Cho, S.Y. and Lee, S.J. (2013). Characteristics of PM_{2.5} haze episodes revealed by highly time-resolved measurements at an air pollution monitoring supersite in Korea. *Aerosol Air Qual. Res.* 13: 957–976.
- Pateraki, S., Assimakopoulos, V.D., Maggos, T., Fameli, K.M., Kotroni, V. and Vasilakos, C. (2013). Particulate pollution over a Mediterranean urban area. *Sci. Total Environ.* 463–464: 508–524.
- Peden, D.B. (2005). The epidemiology and genetics of asthma risk associated with air pollution. *J. Allergy Clin. Immunol.* 115: 213–219.
- Peng, R.D., Chang, H.H., Bell, M.L., McDermott, A., Zeger, S.L., Samet, J.M. and Dominici, F. (2008). Coarse particulate matter air pollution and hospital admissions for cardiovascular and respiratory diseases among medicare

- patients. *JAMA* 299: 2172–2179.
- Pope, C.A., Burnett, R.T., Thurston, G.D., Thun, M.J., Calle, E.E., Krewski, D. and Godleski, J.J. (2004). Cardiovascular mortality and long-term exposure to particulate air pollution: Epidemiological evidence of general pathophysiological pathways of disease. *Circulation* 109: 71–77.
- Pope, C.A. and Dockery, D.W. (2006). Health effects of fine particulate air pollution: Lines that connect. *J. Air Waste Manage. Assoc.* 56: 709–742.
- Rattigan, O.V., Civerolo, K., Doraiswamy, P., Felton, H.D. and Hopke, P.K. (2013). Long term black carbon measurements at two urban locations in New York. *Aerosol Air Qual. Res.* 13: 1181–1196.
- Rolph, G.D. (2013) Real-time Environmental Applications and Display sYstem (READY) Website. NOAA Air Resources Laboratory, College Park, MD. <http://www.ready.noaa.gov>.
- Seinfeld, J.H. and Pandis, S.N. (2012) *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*. John Wiley & Sons.
- Shaltout, A.A., Boman, J., Al-Malawi, D.A.R. and Shehadeh, Z.F. (2013). Elemental composition of PM_{2.5} particles sampled in industrial and residential areas of Taif, Saudi Arabia. *Aerosol Air Qual. Res.* 13: 1356–1364.
- Sillanpää, M., Frey, A., Hillamo, R., Pennanen, A.S. and Salonen, R.O. (2005). Organic, elemental and inorganic carbon in particulate matter of six urban environments in Europe. *Atmos. Chem. Phys.* 5: 2869–2879.
- Solomon, P.A., Fall, T., Salmon, L., Cass, G.R., Gray, H.A. and Davidson, A. (1989). Chemical characteristics of PM₁₀ aerosols collected in the Los Angeles area. *JAPCA* 39: 154–163.
- Sunyer, J., Schwartz, J., Tobias, A., Macfarlane, D., Garcia, J. and Antó, J.M. (2000). Patients with chronic obstructive pulmonary disease are at increased risk of death associated with urban particle air pollution: A case-crossover analysis *Am. J. Epidemiol.* 151: 50–56.
- Taylor, S.R. (1964). Abundance of chemical elements in the continental crust: A new table. *Geochim. Cosmochim. Acta* 28: 1273–1285.
- Thermo-Scientific (2007) Analysis of Air Filters by ARL QUANT'X High Performance Energy Dispersive X-Ray Fluorescence Spectrometer (EDXRF). <http://www.thermoscientific.com/AN-41903-Analysis-of-Air-Filters-by-EDXRF.pdf>.
- U.S.EPA (2000) Atmospheric Ammonia: Sources and Fate: A Review of Ongoing Federal Research and Future Needs. U.S.EPA. <http://www.esrl.noaa.gov/csd/AQRS/reports/ammonia.pdf>.
- U.S.EPA (2012) The National Ambient Air Quality Standards for Particle Pollution. Revised Air Quality Standards for Particle Pollution and Updates to the Air Quality Index (AQI). U.S.EPA. <http://www.epa.gov/pm/2012/decfsstandards.pdf>.
- UNSD (2014). United Nations Statistics Data (UNSD) - Demographic Statistics, United Nations Statistics Division. <http://data.un.org>, Last Access: 10 November 10 2014.
- Wang, Y., Hopke, P.K., Rattigan, O.V., Xia, X., Chalupa, D.C. and Utell, M.J. (2011). Characterization of residential wood combustion particles using the two-wavelength aethalometer. *Environ. Sci. Technol.* 45: 7387–7393.
- Wang, Y., Hopke, P.K., Rattigan, O.V., Chalupa, D.C. and Utell, M.J. (2012). Multiple-year black carbon measurements and source apportionment using Delta-C in Rochester, New York. *J. Air Waste Manage. Assoc.* 62: 880–887.
- WHO (2014) Burden of Disease from Household Air Pollution for 2012. Summary of Results., WHO, 1211 Geneva 27, Switzerland. www.who.int/phe/health_topics/outdoorair/databases/FINAL_HAP_AAP_BoD_24March2014.pdf.
- Yatkin, S. and Bayram, A. (2008). Source apportionment of PM₁₀ and PM_{2.5} using positive matrix factorization and chemical mass balance in Izmir, Turkey. *Sci. Total Environ.* 390: 109–123.
- Yatkin, S., Gerboles, M. and Borowiak, A. (2012). Evaluation of standardless EDXRF analysis for the determination of elements on PM₁₀ loaded filters. *Atmos. Environ.* 54: 568–582.
- Zhao, X., Zhang, X., Xu, X., Xu, J., Meng, W. and Pu, W. (2009). Seasonal and diurnal variations of ambient PM_{2.5} concentration in urban and rural environments in Beijing. *Atmos. Environ.* 43: 2893–2900.
- Zhuang, H., Chan, C.K., Fang, M. and Wexler, A.S. (1999a). Formation of nitrate and non-sea-salt sulfate on coarse particles. *Atmos. Environ.* 33: 4223–4233.
- Zhuang, H., Chan, C.K., Fang, M. and Wexler, A.S. (1999b). Size distributions of particulate sulfate, nitrate, and ammonium at a coastal site in Hong Kong. *Atmos. Environ.* 33: 843–853.

Received for review, November 30, 2015

Revised, April 14, 2016

Accepted, April 14, 2016