Meteorological variations of $PM_{2.5}$/PM_{10} concentrations and particle-associated polycyclic aromatic hydrocarbons in the atmospheric environment of Zonguldak, Turkey

Mehmet Akyüz*, Hasan Çabuk

Zonguldak Karaelmas University, Faculty of Arts and Sciences, Department of Chemistry, 67100 Zonguldak, Turkey

ABSTRACT

Airborne particulate matter ($PM_{2.5}$ and PM_{10}) concentrations were measured in Zonguldak, Turkey from January to December 2007, using dichotomous Partisol 2025 sampler. Collected particulate matter was analyzed for 14 selected polycyclic aromatic hydrocarbons (PAHs) by high-performance liquid chromatography with fluorescence detection (HPLC-FL). The seasonal variations of $PM_{2.5}$ and PM_{10} concentrations were investigated together with their relationships with meteorological parameters. The maximum daily concentrations of $PM_{2.5}$ and PM_{10} reached 83.3 $\mu g\,m^{-3}$ and 116.7 $\mu g\,m^{-3}$ in winter, whereas in summer, they reached 32.4 $\mu g\,m^{-3}$ and 66.7 $\mu g\,m^{-3}$, respectively. Total concentration of PM_{10}-associated PAHs reached 492.4 $ng\,m^{-3}$ in winter and 26.0 $ng\,m^{-3}$ in summer times. The multiple regression analysis was performed to predict total $PM_{2.5}$- and PM_{10}-associated PAHs and benzo(a)pyrene-equivalent (BaPE) concentrations with respect to meteorological parameters and particulate mass concentrations with the determination coefficients (R^2) of 0.811, 0.805 and 0.778, respectively. The measured mean values of concentrations of total $PM_{2.5}$- and PM_{10}-associated PAHs were found to be 88.4 $ng\,m^{-3}$ and 93.7 $ng\,m^{-3}$ while their predicted mean values were found to be 92.5 $ng\,m^{-3}$ and 98.2 $ng\,m^{-3}$, respectively. In addition, observed and predicted mean concentration values of $PM_{2.5}$-BaPE were found to be 14.1 $ng\,m^{-3}$ and 14.6 $ng\,m^{-3}$. The close annual mean concentrations of measured and predicted total particulate related PAHs imply that the models can be reliably used for future predictions of particulate related PAHs in urban atmospheres especially where fossil fuels are mainly used for heating.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Ambient air pollution has adverse effects on respiratory and cardiovascular systems coming up as acute reduction in lung function, aggravation of asthma, increased risk of pneumonia in the elderly and low birth weight and high death rates in newborns [1]. Moreover, the concentration of respirable particulate matter (PM) in ambient air has become a topic of considerable importance over recent years in relation to public health [2] since epidemiological studies have shown that exposure to particulates with aerodynamic diameters <10 μm (PM_{10}) and especially <2.5 μm ($PM_{2.5}$) induces an increase of lung cancer, morbidity and cardiopulmonary mortality [3–5]. Although there is still a fundamental lack of understanding the underlying mechanisms of their toxicity, one of the widely accepted hypotheses is that toxicity of particulates depends not only on their size but also on their composition both of which

depend on location, time of year and meteorological conditions [6]. Studies performed on airborne particulates revealed that organic compounds like PAHs adsorbed by particulate matter probably play an important role on the generation of adverse health effects [7,8]. There are limited studies reported in the literature [9] for future predictions of particulate related PAHs in urban atmosphere for epidemiologic studies based on available meteorological and $PM_{2.5}$ data.

Therefore, the monitoring of seasonal concentrations of respirable PM together with their PAH content and determination of the effects of meteorological parameters on concentrations of these pollutants are important to control the factors which produce or disperse these pollutants to protect human health due to exposure to these pollutants through inhalation. This study has numerous purposes such as the determination of seasonal variations of $PM_{2.5}$ and PM_{10} concentrations, total PM-associated PAHs and the effects of meteorological parameters on concentrations of these pollutants. The study also presents an attempt to predict the particle-associated PAHs and $PM_{2.5}$-associated benzo(a)pyrene-equivalent (BaPE) carcinogenicity in the study area by utilizing multiple linear regression models which include mass concentra-

* Corresponding author. Tel.: +90 372 257 40 10x1371; fax: +90 372 257 41 81.
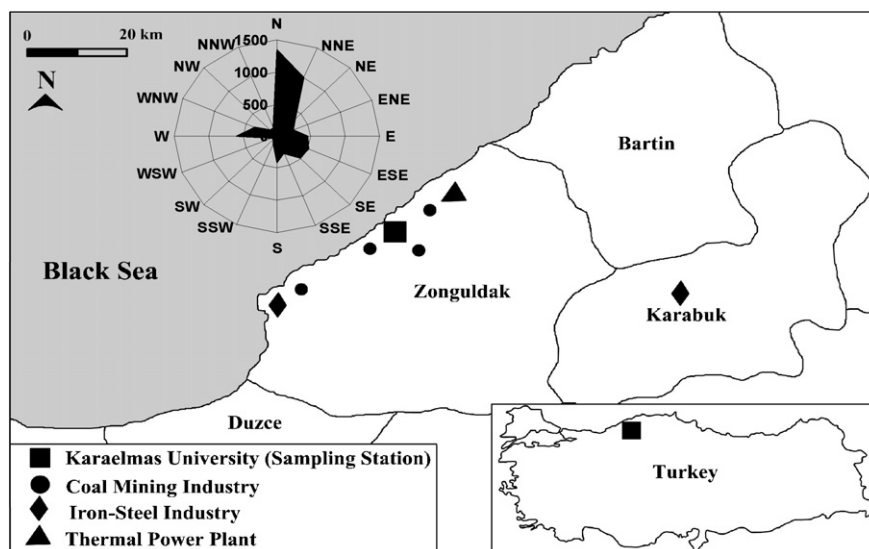*E-mail address:* makyuz2004@yahoo.co.uk (M. Akyüz).

Fig. 1. Location map of the sampling site in Zonguldak, Turkey.

tion, temperature, wind speed and relative humidity as explanatory variables.

2. Experimental

2.1. Sampling site

The study has been carried out in Zonguldak province (41°27′03″ N, 31°45′81″ E). This area is a centre for coal mining with the associated steel industry being located on the Northwest coast of the Black Sea in Turkey (Fig. 1). The area is surrounded by low mountains at three sides which cause poor dispersion of air masses especially during stagnant conditions and the Black Sea is the only way out open to the north. The total area of the city is about 3480 km^2 with a population of more than 600,000 and the area of the city centre is about 637 km^2. Coal is mainly used as fuel for domestic and central heating. A Walter–Lieth climate diagram for Zonguldak over the period of 1975–2005 is shown in Fig. 2 [10]. Its climate is predominantly temperate and rainy and approximate temperature over the year is 13.5 °C. During the sampling period, the mean temperature was 14.6 °C in the range of 1.3–31.7 °C, the mean air relative humidity was 70% in the range of 28–97%, the mean wind speed was 2.6 m s^{-1} in the range of 0.9–5.3 m s^{-1} and the accumulated rainfall was 1258 mm. The predominant wind direction was from the north in the sampling period as can be seen in Fig. 1.
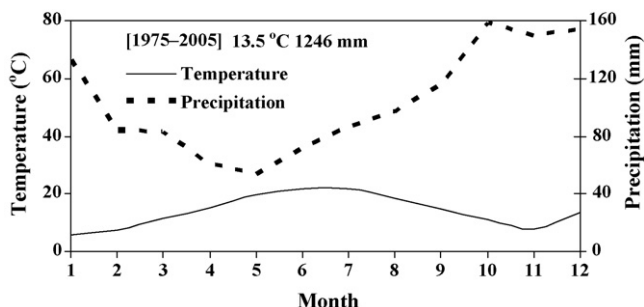

Fig. 2. Climate diagram for Zonguldak over the period of 1975–2005.

2.2. Sample collection and mass measurement

The fine (PM$_{2.5}$) and coarse (PM$_{2.5-10}$) particle samples were collected from January to December in 2007 onto Whatman PTFE filter with a diameter of 46.2 mm, using Rupprecht and Patashnick Dichotomous Partisol-Plus Model 2025 Sequential Air Sampler compatible with the European Union directives. The dichotomous configuration of the sampler splits a PM$_{10}$ sample stream into a 15 l/min flow containing fine particles and a 1.67 l/min flow with coarse particles. The sampler was positioned on the roof (5 m in height) of a building in the Karaelmas University Campus and samples were collected during 24-h periods, approximately twice in a week, with filter exchange taking place at 00:00 GTM. Before and after sample collection equilibrated filter papers were weighed by a microbalance (Precisa XB 220A) to calculate particle mass concentrations. After weighing, the filter papers were packed with aluminum foil and stored in a freezer (−18 °C) for PAH determination and the collected samples were analyzed as soon as they were prepared.

2.3. Analysis of particle-associated PAHs

The filters were extracted with 50 ml of *n*-hexane–acetone (1:1, v/v) in an ultrasonic bath for 30 min at room temperature. The extracts were concentrated to 1 ml using a rotary evaporator (300 mbar, 40 °C), and 100 μl of dimethylformamide was added as a keeper and evaporated again under gentle steam of nitrogen to 100 μl. Final volume was adjusted to 500 μl by adding 400 μl of acetonitrile and then analyzed [11].

The chromatographic analysis was performed by Thermo Finnigan HPLC system (San Jose, USA) consisting of a P1000 pump equipped with a Rheodyne injection valve (20 μl injection loop), a SCM 1000 degasser and a FL3000 fluorescence detector. The system was controlled by a Specta System Controller SN 4000 and a software package Chromquest 4.0. Separation was performed by means of a Phenomenex Max-RP column (250 mm × 4.6 mm, 4 μm) protected by a C$_{18}$ guard column (4 mm × 3 mm, Phenomenex). Fluorescence excitation and emission wavelengths were programmed according to elution times to obtain better sensitivity [12–14]. HPLC system was calibrated using an external standard method with a mixture of 16 PAHs (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, pyrene, flu-

Table 1
Maximum, minimum, median, mean concentration and standard deviation values for each fraction of the particulate matter and related PAHs collected during the sampling period.

	$PM_{2.5}$	PM_{10}		$PM_{2.5}$-PAH	PM_{10}-PAH
Minimum ($\mu g/m^3$)	4.6	12.5	Minimum (ng/m^3)	0.3	0.4
Maximum ($\mu g/m^3$)	83.3	116.7	Maximum (ng/m^3)	464.0	492.4
Median ($\mu g/m^3$)	23.1	41.7	Median (ng/m^3)	28.0	32.6
Mean ($\mu g/m^3$)	28.1	44.1	Mean (ng/m^3)	88.4	93.7
Standard deviation	18.7	21.4	Standard deviation	115.9	121.6
Sample number	93	93	Sample number	93	93
Sampling period	January–December 2007	January–December 2007	Sampling period	January–December 2007	January–December 2007

oranthene, benzo[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, dibenzo[*a,h*]anthracene, indeno[1,2,3-*cd*]pyrene, benzo[*ghi*]perylene) in HPLC grade acetonitrile containing 10 μg/ml of each compound (47940-U Supelco, USA). Acenaphthylene, although it was present in the mixture, was only weakly fluorescent and thus could not be detected. The separation was performed at room temperature with a constant flow-rate of 1.2 ml/min. by employing the elution program as follows; 0–5 min acetonitrile–water 75:25 (v/v) and then a linear gradient elution from 75% acetonitrile at 5 min to 100% acetonitrile at 30 min, followed by isocratic elution with acetonitrile for 5 min. Finally, 10 min were necessary to re-establish the initial conditions. Naphthalene could not be accurately quantified because of interference of co-eluted substances. Method validation parameters such as linearity, recovery and limit of detection were given in our previous study [11].

3. Results and discussions

3.1. Seasonal variations of $PM_{2.5}$ and PM_{10} concentrations

The concentrations of $PM_{2.5}$ and PM_{10} fractions of ambient airborne particulates were measured approximately twice a week during the period of January to December throughout the year of 2007 in Zonguldak province. The daily concentrations of $PM_{2.5}$ and PM_{10} reached 83.3 $\mu g\,m^{-3}$ and 116.7 $\mu g\,m^{-3}$ in winter, whereas in summer, they reached 32.4 $\mu g\,m^{-3}$ and 66.7 $\mu g\,m^{-3}$, respectively. Table 1 shows maximum, minimum, median and mean concentration with standard deviation values for each fraction of the particulate matter collected during the sampling period. In addition, the seasonal variation of particulate concentrations and results of linear regression analysis between $PM_{2.5}$ and PM_{10} concentrations in winter and summer are shown in Fig. 3.

As expected, the high average mass concentration of $PM_{2.5}$ was found in winter (37.3 $\mu g\,m^{-3}$), which was most likely associated with high burning of fossil fuels for heating purpose, whereas the

low $PM_{2.5}$ level was observed in summer (15.9 $\mu g\,m^{-3}$) due to the absence of combustion sources. $PM_{2.5–10}$ levels (14.8 $\mu g\,m^{-3}$ in winter and 17.6 $\mu g\,m^{-3}$ in summer) did not exhibit a marked seasonal trend although slightly higher levels were obtained in summer. Annual mean concentrations of particulate matter found in this study were similar to the results reported by Tecer et al. [15] for the sampling period of 2004–2005 in Zonguldak.

The fine and coarse particles are relatively different in their physical and chemical compositions. They generally originate from different sources or by different activities within the same source [16]. Relationships between $PM_{2.5}$ and PM_{10} mass concentrations were analyzed in terms of linear regression and the results revealed that coefficients of determination (R^2) were 0.6257 and 0.9042 in summer and winter times, respectively. The relatively high coefficients especially in winter imply that $PM_{2.5}$ and PM_{10} have some similar emission sources, and they were being influenced by the same local conditions [17]. In general, the contribution of combustion sources is much more in the $PM_{2.5}$ fraction. In our study, the increase in PM_{10} concentrations during the heating seasons was mainly driven by an increase in the $PM_{2.5}$ concentrations. Furthermore, the coefficient of determination between $PM_{2.5}$ and PM_{10} was found to be 0.6257 in summer suggested that nearly half of the mass of PM_{10} consists of soil-originated particles.

Since different sizes of atmospheric particles probably originate from different sources, the mean $PM_{2.5}/PM_{10}$ ratios have been used for identifying the sources of $PM_{2.5}$ and PM_{10} [18–22]. Higher ratios (e.g., larger than 0.6) are generally ascribed to relatively high contributions from secondary particles and the combustion sources, while lower ratios indicate significant contributions from primary sources such as re-suspended soil/road dust (unpaved roads), and other mechanical activities [23–25]. $PM_{2.5}/PM_{10}$ ratios (mean + SD) were found to be 0.70 ± 0.13 in winter which indicated significant contributions from combustion sources and 0.47 ± 0.17 in summer which indicated significant contributions from re-suspended soil/road dust, coal mining and processing industries, and other mechanical activities. The mean ratio of $PM_{2.5}/PM_{10}$ varies widely from one location to another due to the differences in the sampling site characteristics. In general, $PM_{2.5}/PM_{10}$ ratios exhibit seasonal variation with the highest values during the winter months and the lowest values in the summer months. The obtained results showed similar seasonal variations when compared to other urban pollution studies. Gomiscek et al. [26] published winter ratio of 0.72 and summer ratio of 0.67 in Vienna, Austria. Sun et al. [19] found that the average ratio of $PM_{2.5}/PM_{10}$ in winter was 0.73, 0.52 and 0.61 at traffic, industrial and residential sites in Beijing, China, and in summer was 0.45, 0.48 and 0.47, respectively. Conversely, higher $PM_{2.5}/PM_{10}$ ratios were observed in summer in Barcelona, Spain by Viana et al. [27] and it was stated that photochemical formation of secondary fine particulates by the effect of sunlight increased the ratio of $PM_{2.5}/PM_{10}$ in summer. Similarly, Chan and Kwok [28] found the $PM_{2.5}/PM_{10}$ ratio of 0.69 in winter and 0.84 in summer in heavily trafficked area of Hong Kong. They concluded that frequent rains in the studied area diminished
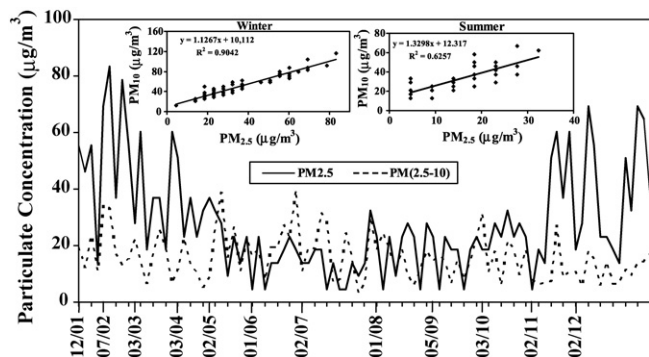

Fig. 3. Seasonal variations of particulate concentrations and results of linear regression analysis between $PM_{2.5}$ and PM_{10} concentrations. Winter: 25 September–7 May (central heating on); Summer: 8 May–24 September (central heating off).
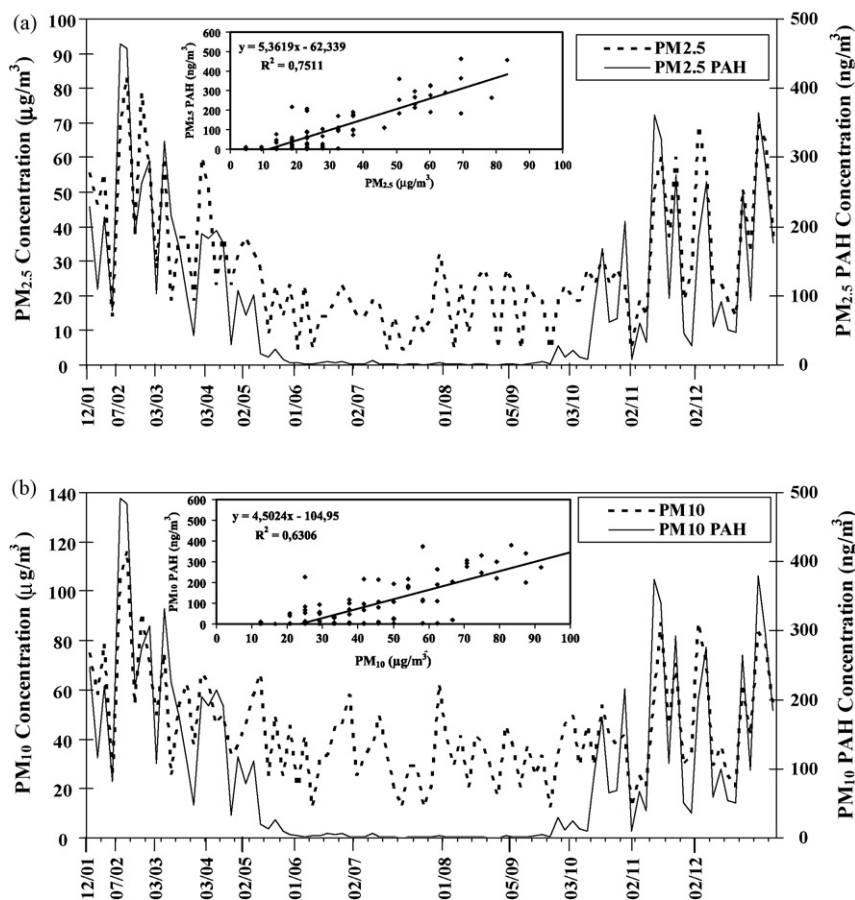
Fig. 4. Seasonal variations of PM and related PAHs and results of linear regression analysis between (a) $PM_{2.5}$ and related PAHs (b) PM_{10} and related PAHs.

the large size particulates and this caused small size particulates to be higher proportion with respect to total particulate mass in summer.

3.2. Relationships between concentrations of particulate matter and total particle-associated PAHs

The total concentrations of PAHs reached $464.0 \, \text{ng m}^{-3}$ in $PM_{2.5}$ and $492.4 \, \text{ng m}^{-3}$ in PM_{10} fractions in winter, whereas in summer times reached $22.9 \, \text{ng m}^{-3}$ and $26.0 \, \text{ng m}^{-3}$, respectively. Maximum, minimum, mean, median concentrations and standard deviation values of total PAHs determined in each fraction of the particulate matter are shown in Table 1. The seasonal variations of PM and PAHs and results of linear regression analysis are shown in Fig. 4.

The concentration levels of PM and related PAHs fluctuated significantly in winter times with higher means and peak concentrations, due to residential fuel combustion for heating (coal burning and central heating), compared to summer times [11]. In winter, the fluctuations in concentration levels of PAHs in PM are generally dominated by winds and frequent rains, which wash out these pollutants from the ambient air. The concentration of PM and related PAHs in ambient air generally decrease with increasing wind speed and frequency of the rain [29,30]. The lower PAHs concentrations in summer are likely due to not using fossil fuels for heating, washout effects, and, to a lesser extent, photo-degradation and higher percentage of PAHs in the gas phase [31,32]. As it has been reported before, the major sources of atmospheric emissions of $PM_{2.5}$ and particulate-bound PAHs were due to vehicle emission and fossil fuel combustion processes, primarily for residential heating [11,33–35].

It was found that the strong relationship occurring between $PM_{2.5}$ and related PAHs ($R^2 = 0.7511$) indicated that the concentrations of PAHs increased effectively with increasing $PM_{2.5}$ mass concentrations. In general, smaller particles have a higher PAH content. This is due to the fact that combustion and other high temperature sources create primarily fine particulates carrying a high PAH content. Their small size, high number concentration, and relatively large surface area per unit mass make them an excellent adsorbent for harmful organic and inorganic compounds [36]. No relationship was found between $PM_{2.5-10}$ and related PAHs ($R^2 = 0.01$), which indicated that they were originated from different emission source. Coarse particles are normally generated by mechanical activities and wind action on soils [16,37]. In addition, the coefficient of determination between PM_{10} and related PAHs was even high ($R^2 = 0.6306$) as a result of strong relationship between $PM_{2.5}$ and PM_{10} ($R^2 = 0.8591$ for the whole year) and more PAH adsorption capacity of $PM_{2.5}$.

3.3. Relationships between PM, particle-associated PAHs and meteorological parameters

The relationships between PM, particle-associated PAHs and meteorological parameters (temperature, wind speed, relative humidity and pressure) in winter and summer periods were investigated by Pearson's correlation analysis. The meteorological data, which were found to be significant in describing the variation in the 24-h averaged PM concentrations [9,31,38,39] utilized in the present work, are: (1) wind speed (m s^{-1}), (2) relative humidity (%), (3) surface temperature (°C) and (4) pressure (mbar). The correlation coefficients (r) between daily average (24-h) PM, particle-associated PAHs and meteorological parameters are shown

Table 2
Correlation matrix of particulate matter, related PAHs and meteorological parameters in (a) winter ($n = 53$) and (b) summer ($n = 40$).

	$PM_{2.5}$	$PM_{2.5-10}$	PM_{10}	$PM_{2.5}$-PAH	$PM_{2.5-10}$-PAH	PM_{10}-PAH
(a) Winter ($n = 53$)						
$PM_{2.5}$	1					
$PM_{2.5-10}$	0.327[*]	1				
PM_{10}	0.951[**]	0.604[**]	1			
$PM_{2.5}$-PAH	0.845[**]	0.371[**]	0.834[**]	1		
$PM_{2.5-10}$-PAH	0.665[**]	0.357[**]	0.679[**]	0.775[**]	1	
PM_{10}-PAH	0.845[**]	0.375[**]	0.836[**]	0.999[**]	−0.796[**]	1
Temperature	−0.324[*]	0.361[**]	−0.155	−0.395[**]	−0.354[**]	−0.398[**]
Wind speed	−0.350[*]	−0.349[*]	−0.409[**]	−0.367[**]	−0.225	−0.364[**]
Humidity	−0.108	−0.448[**]	−0.237	−0.094	−0.160	−0.098
Pressure	0.172	−0.115	0.108	0.208	0.027	0.201
(b) Summer ($n = 40$)						
$PM_{2.5}$	1					
$PM_{2.5-10}$	0.306	1				
PM_{10}	0.791[**]	0.824[**]	1			
$PM_{2.5}$-PAH	0.267	0.367[*]	0.394[*]	1		
$PM_{2.5-10}$-PAH	0.205	0.394[*]	0.375[*]	0.902[**]	1	
PM_{10}-PAH	0.263	0.374[*]	0.396[*]	0.999[**]	0.375[*]	1
Temperature	0.225	0.220	0.275	−0.497[**]	−0.480[**]	−0.497[**]
Wind speed	−0.266	0.183	0.040	−0.164	−0.254	−0.179
Humidity	−0.053	−0.115	−0.104	0.043	0.154	0.058
Pressure	−0.338[*]	−0.497[**]	−0.521[**]	0.010	−0.033	0.005

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

in Table 2. The correlation coefficients were marked in the table to indicate the significance levels ($P < 0.01$ or <0.05).

Correlations between PM variables and meteorological characteristics have shown a clear seasonal pattern. In winter, correlation coefficients between temperature and PM variables are negative and reasonably high ($PM_{2.5} = −0.324$, $PM_{2.5}$-PAH $= −0.395$, $PM_{2.5-10}$-PAH $= −0.354$ and PM_{10}-PAH $= −0.398$), suggesting that lower temperature causes a higher rate of local heating. In summer, although there is no obvious correlation between mass concentrations and temperature, PM-associated PAHs and temperature are negatively correlated ($PM_{2.5}$-PAH $= −0.497$, $PM_{2.5-10}$-PAH $= −0.480$ and PM_{10}-PAH $= −0.497$) due to greater volatilization from particulates into the gas phase [31]. In addition, photochemical transformation of particulate PAHs by the impact of sunlight in summer might partly explain the cause of negative correlations observed between PM-associated PAHs and temperature [32,40]. Wind speed has long been recognized as an important controlling factor on concentrations of air pollutants [37,41–43]. Correlations between PM variables and wind speed were investigated in winter and summer. It is obvious that the concentrations of pollutants decrease effectively with increasing wind speed. There is a significant negative relationship between particulate mass concentrations and wind speed in winter ($PM_{2.5} = −0.350$, $PM_{2.5-10} = −0.349$ and $PM_{10} = −0.409$), similar to that between particle-associated PAHs and wind speed ($PM_{2.5}$-PAH $= −0.367$ and PM_{10}-PAH $= −0.364$). Correlations between PM variables and relative humidity are negative and remain weak in both seasons. Among these variables, $PM_{2.5-10}$ shows a significant negative correlation

($P < 0.01$) with relative humidity in winter ($r = −0.448$). Hien et al. [38] similarly found negative relationship between coarse particulates and relative humidity and suggested that relative humidity remove atmospheric particulates and diminish the amount of re-suspended soil dust by making the soil humid. Particulate concentrations exhibit significant negative correlations with atmospheric pressure in summer ($PM_{2.5} = −0.338$, $PM_{2.5-10} = −0.497$, $PM_{10} = −0.521$), whereas no correlation is observed between particulate PAHs and atmospheric pressure in both seasons. Re-suspended soil dust under unstable atmospheric conditions (low pressure and high wind speed) in summer might explain the cause of negative correlations observed between particulate concentrations and atmospheric pressure. Atmospheric pressure influences pollutant concentrations indirectly by affecting the atmospheric stability conditions. In general, high atmospheric pressure is often related to low wind speed and stable stratification, limiting dispersion of pollutants within the atmosphere [39,44]. Although stable atmospheric conditions with high pressure and low wind speeds are most unfavorable in terms of air pollution, low pressure with high wind speeds in the summer months apparently leading to high coarse particle concentrations due to re-suspension processes [37].

The effects of rainfall on concentrations of particulate mater and particle-associated PAHs were investigated separately by comparison of mean concentrations of pollutants in rainy and non-rainy days. As can be seen in Table 3, the scavenging of pollutants by precipitation is an important removal mechanism from the atmosphere in both winter and summer [45,46].

Table 3
Mean concentrations of particulates and particulate-associated PAHs in rainy and non-rainy days.

Parameters	Winter		Summer	
	Rainy days ($n = 25$)	Non-rainy days ($n = 28$)	Rainy days ($n = 6$)	Non-rainy days ($n = 34$)
$PM_{2.5}$ ($\mu g/m^3$)	33.5	40.7	6.2	17.7
$PM_{2.5-10}$ ($\mu g/m^3$)	11.5	17.8	16.7	17.7
PM_{10} ($\mu g/m^3$)	45.0	58.5	22.9	35.4
$PM_{2.5}$-PAH (ng/m^3)	134.1	169.2	1.2	3.7
$PM_{2.5-10}$-PAH (ng/m^3)	8.3	9.5	0.2	0.6
PM_{10}-PAH (ng/m^3)	142.4	178.7	1.5	4.3

Table 4
The performance statistics of the models for PM$_{2.5}$-PAHs, PM$_{10}$-PAHs and PM$_{2.5}$-BaPE.

Statistical indicators	Model for PM$_{2.5}$-PAHs	Model for PM$_{10}$-PAHs	Model for PM$_{2.5}$-BaPE
R^2	0.811	0.805	0.778
IA	0.945	0.944	0.934
MAE (ng m^{-3})	37.4	40.7	5.7
MBE (ng m^{-3})	0.015	−0.046	0.018
RMSE (ng m^{-3})	50.4	53.6	7.8

3.4. The multiple regression analysis

Multiple linear regression analysis was performed by Statistical Package of Social Sciences (SPSS 13.0) to investigate relationships between PM, PAHs and meteorological parameters. In addition, total PM$_{2.5}$-associated benzo(a)pyrene-equivalent (BaPE) carcinogenicity was evaluated by multiplying the concentrations of each PAH with their toxic equivalent factors (TEFs) [47]. This can also be used to calculate the relative carcinogenicity of ambient PM$_{2.5}$ samples with a known distribution of PAHs. The relationship between PM$_{2.5}$, total PM$_{2.5}$-associated BaPE concentrations and meteorological parameters were also investigated. Explanatory variables in multiple regression analyses were selected according to their significance and ability to contribute to prediction of the dependent variable. The precipitation and pressure produced the weakest significance, and therefore they were excluded from the regression analysis. Resulting equations are given below:

$$PM_{2.5}\text{-PAHs} = 146.240 + 4.076\,[PM_{2.5}] - 5.914\,[\text{temperature}]$$
$$-11.107\,[\text{wind speed}] - 0.747\,[\text{humidity}] \quad (R^2 = 0.811)$$

$$PM_{10}\text{-PAHs} = 155.773 + 3.311\,[PM_{10}] - 8.950\,[\text{temperature}]$$
$$-11.065\,[\text{wind speed}] - 0.581\,[\text{humidity}] \quad (R^2 = 0.805)$$

$$PM_{2.5}\text{-BaPE} = 20.042 + 0.564\,[PM_{2.5}] - 0.860\,[\text{temperature}]$$
$$-1.549\,[\text{wind speed}] - 0.079\,[\text{humidity}] \quad (R^2 = 0.778)$$

Considering the above equations, the measured and predicted total concentrations of PM$_{2.5}$-PAHs, PM$_{10}$-PAHs and PM$_{2.5}$-BaPE were compared by using the data set during the period of January–December in 2007. The comparison of predicted and observed concentrations of PM$_{2.5}$-PAH, PM$_{10}$-PAHs and PM$_{2.5}$-BaPE is shown in Fig. 5a–c. As shown in Fig. 5a–c, predicted values are generally able to reflect well the measured ones with the strong coefficients of determination of 0.811 for PM$_{2.5}$-PAHs, 0.805 for PM$_{10}$-PAHs and 0.778 for PM$_{2.5}$-BaPE.

Five statistical indicators applied by several authors [48–51] were used to provide a general indication of the relationship between the observed and the predicted data. These statistical indicators are coefficients of determination (R^2), index of agreement (IA), mean absolute error (MAE), mean bias error (MBE) and root mean square error (RMSE). The performance statistics of the models for PM$_{2.5}$-PAHs, PM$_{10}$-PAHs and PM$_{2.5}$-BaPE are shown in Table 4.

The index of agreement (IA) is an alternative of R^2 and if the IA is closer to 1, then the model is more appropriate to simulate the observed data [52]. The MAE and the RMSE measure residual errors which gives a global idea of the difference between the observed and predicted values. RMSE indicates the difference between observed and predicted concentrations. Smaller MAE and RMSE mean that the model is more appropriate. MBE with lower values is the degree of correspondence between the mean predict

and the mean observation. The MBE indicates whether the observed concentrations are over or under estimated [51]. The obtained results show smaller values of RMSE, MAE, MBE and higher values of R^2, IA underlying the correct behavior of the developed models.

The models follow seasonal behavior, and give acceptable results although they have some difficulties in predicting the summer time concentrations. As the models are strongly dependent on the mass concentrations, the predicted concentrations tend to deviate more from measured concentrations due to lesser correlations between PM and related PAH concentrations in summer as compared to winter. The models produced negative concentrations for several days in summer which they were considered as 0 values.
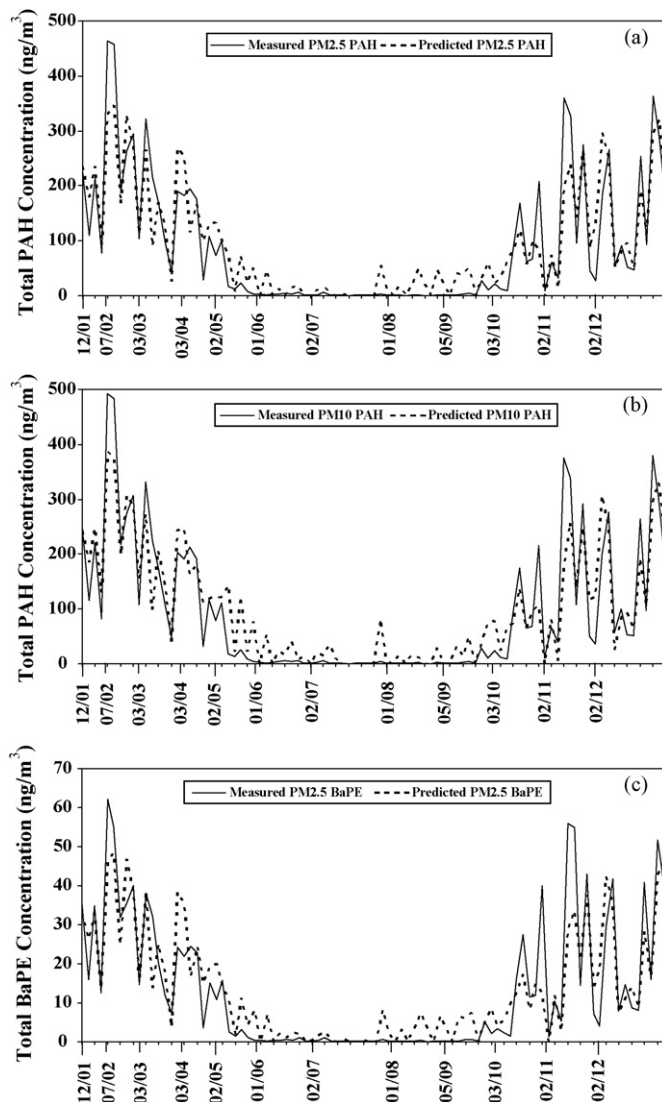

Fig. 5. Comparison of predicted and observed concentrations of (a) PM$_{2.5}$-PAH, (b) PM$_{10}$-PAH and (c) PM$_{2.5}$-BaPE for the period of January–December 2007.
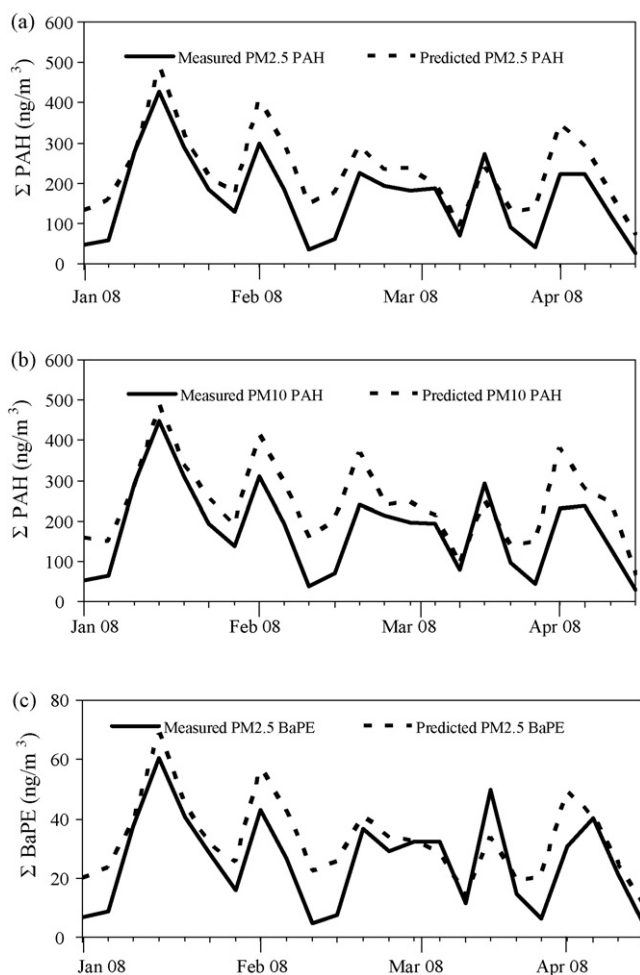
Fig. 6. Comparison of predicted and observed concentrations of (a) $PM_{2.5}$-PAHs, (b) PM_{10}-PAHs and (c) $PM_{2.5}$-BaPE for the period of January–April 2008.

Fig. 7. Relationships between observed and predicted concentrations of (a) $PM_{2.5}$-PAHs, (b) PM_{10}-PAHs and (c) $PM_{2.5}$-BaPE for the period of January–April 2008.

The maximum concentrations of total $PM_{2.5}$ and PM_{10}-associated PAHs predicted by the model were found to be 346.8 ng m^{-3} and 386.7 ng m^{-3}, respectively. The measured mean concentrations of total $PM_{2.5}$ and PM_{10}-associated PAHs were found to be 88.4 ng m^{-3} and 93.7 ng m^{-3} while their predicted mean concentrations were found to be 92.5 ng m^{-3} and 98.2 ng m^{-3}, respectively. In addition, observed and predicted mean concentrations of the $PM_{2.5}$-BaPE were found to be 14.1 ng m^{-3} and 14.6 ng m^{-3}, respectively.

In order to confirm viability of the predictive models developed, they were applied to predict $PM_{2.5}$-PAHs, PM_{10}-PAHs and $PM_{2.5}$-BaPE and validated against a dataset belonging to the period of January–April 2008. The comparison of predicted and observed concentrations of $PM_{2.5}$-PAHs, PM_{10}-PAHs and $PM_{2.5}$-BaPE is shown in Fig. 6a–c. In addition, relationships between measured and predicted concentrations are shown in Fig. 7a–c. The results of validation analysis indicate satisfactory predictions with R^2 values of 0.8422 for $PM_{2.5}$-PAHs, 0.7989 for PM_{10}-PAHs and 0.7387 for $PM_{2.5}$-BaPE.

The close annual mean concentrations of measured and predicted total particulate related PAHs and $PM_{2.5}$-BaPE imply that the models can be reliably used for future predictions of particulate related PAHs and their carcinogenic activities using widely available $PM_{2.5}$ measurements and meteorological data in urban atmospheres especially where fossil fuels is mainly used for heating.
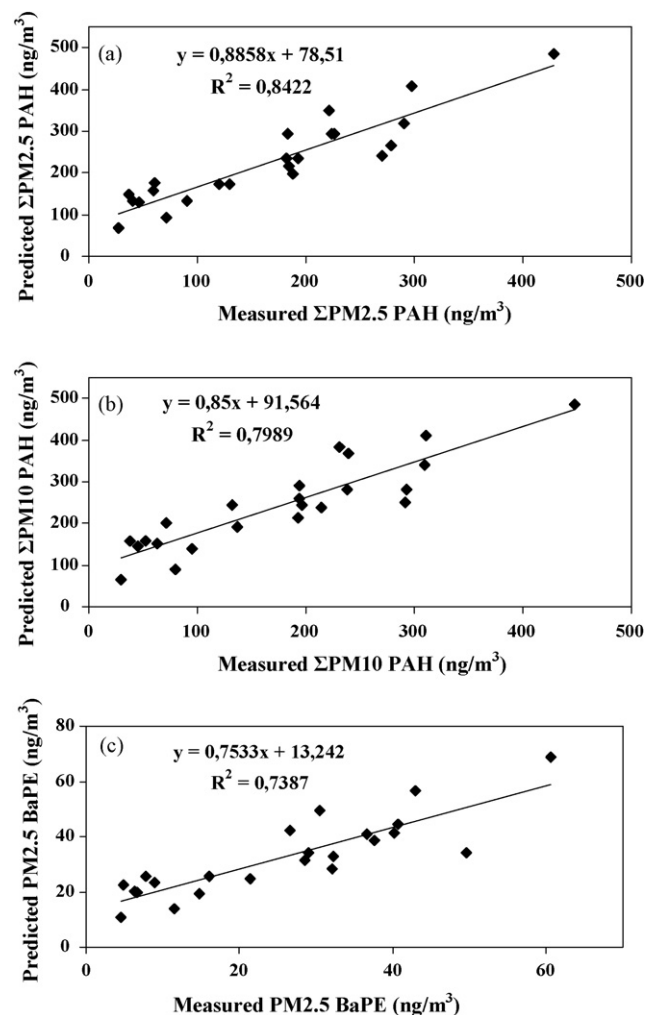
4. Conclusions

Measurement of $PM_{2.5}$ and PM_{10} fractions of ambient airborne particulates and the determination of particulate PAH concentrations were performed in Zonguldak province during heating and non-heating periods. A seasonal trend was observed for the particulates and related PAH concentrations with higher levels during the heating season influenced by increased fossil fuel usage. It could therefore be proposed that some effective control measures should be taken to reduce urban atmospheric pollution in Zonguldak to protect human health because of the exposure to those pollutants through inhalation. A strong correlation was found between $PM_{2.5}$ and related PAHs ($R^2 = 0.7511$) indicating that the concentrations of PAH increased effectively with increasing $PM_{2.5}$ mass concentrations. The relationships between PM, particle-associated PAHs and meteorological parameters (temperature, wind speed, relative humidity and pressure) in winter and summer periods were also investigated and among the meteorological parameters, the ambient temperature and local wind conditions were found to be the most important factors controlling the concentrations of pollutants. The relative humidity and atmospheric pressure were also weakly correlated with PM and related PAHs. The multiple linear regression analysis was performed to predict total concentrations of $PM_{2.5}$-PAHs, PM_{10}-PAHs and $PM_{2.5}$-BaPE with respect to meteorological parameters and particulate mass concentrations with

the determination coefficients (R^2) of statistical models of 0.811, 0.805 and 0.778, respectively. The determination of close annual mean concentrations of measured and predicted total particulate related PAHs imply that the multiple regression models can reliably be used for future predictions of especially $PM_{2.5}$-associated PAHs in urban atmosphere for epidemiologic studies based on publicly available meteorological and $PM_{2.5}$ data when PAH measurement is unavailable.

Acknowledgements

References

[1] A.M. Wilson, J.C. Salloway, C.P. Wake, T. Kelly, Air pollution and the demand for hospital services: a review, Environ. Int. 30 (2004) 1109–1118.

[2] R.M. Harrison, A.M. Jones, R.G. Lawrence, Major component composition of PM_{10} and $PM_{2.5}$ from roadside and urban background sites, Atmos. Environ. 38 (2004) 4531–4538.

[3] R. Pozzi, B.D. Berardis, L. Paoletti, C. Guastadisegni, Winter urban air particles from Rome (Italy): effects on the monocytic–macrophagic RAW 264.7 cell line, Environ. Res. 99 (2005) 344–354.

[4] O.R.A. Chakra, M. Joyeux, E. Nerriere, M.P. Strub, D. Zmirou-Navier, Genotoxicity of organic extracts of urban airborne particulate matter: an assessment within a personal exposure study, Chemosphere 66 (2007) 1375–1381.

[5] WHO, Particulate Matter Air Pollution: How it Harms Health, World Health Organization Europe, 2005, pp. 1–4.

[6] R.M. Harrison, J. Yin, Particulate matter in the atmosphere: which particle properties are important for its effects on health? Sci. Total Environ. 249 (2000) 85–101.

[7] M. Skarek, J. Janosek, P. Cupr, J. Kohoutek, A. Novotna-Rychetska, I. Holoubek, Evaluation of genotoxic and non-genotoxic effects of organic air pollution using in vitro bioassays, Environ. Int. 33 (2007) 859–866.

[8] G. Gilli, C. Pignata, T. Schiliro, R. Bono, A.L. Rosa, D. Traversi, The mutagenic hazards of environmental $PM_{2.5}$ in Turin, Environ. Res. 103 (2007) 168–175.

[9] A.B. Lobscheid, T.E. McKone, D.A. Vallero, Exploring relationships between outdoor air particulate associated polycyclic aromatic hydrocarbon and $PM_{2.5}$: a case study of benzo(a)pyrene in California metropolitan regions, Atmos. Environ. 41 (2007) 5659–5672.

[10] Zonguldak Governorship, Environment and Forestry Management, Environment Situation Report, Zonguldak, 2007.

[11] M. Akyüz, H. Çabuk, Particle-associated polycyclic aromatic hydrocarbons in the atmospheric environment of Zonguldak, Turkey, Sci. Total Environ. 405 (2008) 62–70.

[12] F. Busetti, A. Heitz, M. Cuomob, S. Badoer, P. Traverso, Determination of sixteen polycyclic aromatic hydrocarbons in aqueous and solid samples from an Italian wastewater treatment plant, J. Chromatogr. A 1102 (2006) 104–115.

[13] K.S. Williamson, J.D. Petty, J.N. Huckins, J.A. Lebo, E.M. Kaiser, HPLC-PFD determination of priority pollutant PAHs in water, sediment, and semipermeable membrane devices, Chemosphere 49 (2002) 703–715.

[14] R.M. Harrison, D.J.T. Simith, L. Luhana, Source apportionment of atmospheric polycyclic aromatic hydrocarbons collected from an urban location in Birmingham, U.K., Environ. Sci. Technol. 30 (1996) 825–832.

[15] L.H. Tecer, P. Süren, O. Alagha, F. Karaca, G. Tuncel, Effect of meteorological parameters on fine and coarse particulate matter mass concentration in a coal-mining area in Zonguldak, Turkey, J. Air Waste Manage. Assoc. 58 (2008) 543–552.

[16] N.T.K. Oanh, N. Upadhyay, Y.H. Zhuang, Z.P. Hao, D.V.S. Murthy, P. Lestari, J.T. Villarin, K. Chengchua, H.X. Co, N.T. Dung, E.S. Lindgren, Particulate air pollution in six Asian cities: spatial and temporal distributions, and associated sources, Atmos. Environ. 40 (2006) 3367–3380.

[17] F. Karaca, O. Alagha, F. Ertürk, Statistical characterization of atmospheric PM_{10} and $PM_{2.5}$ concentrations at a non-impacted suburban site of Istanbul, Turkey, Chemosphere 59 (2005) 1183–1190.

[18] C.Y. Chan, X.D. Xu, Y.S. Li, K.H. Wong, G.A. Ding, L.Y. Chan, X.H. Cheng, Characteristics of vertical profiles and sources of $PM_{2.5}$, PM_{10} and carbonaceous species in Beijing, Atmos. Environ. 39 (2005) 5113–5124.

[19] Y. Sun, G. Zhuang, Y. Wang, L. Han, J. Guo, M. Dan, W. Zhang, Z. Wang, Z. Hao, The air-borne particulate pollution in Beijing—concentration, composition, distribution and sources, Atmos. Environ. 38 (2004) 5991–6004.

[20] A. Charron, R.M. Harrison, Fine ($PM_{2.5}$) and coarse ($PM_{2.5-10}$) particulate matter on a heavily trafficked London Highway: sources and processes, Environ. Sci. Technol. 39 (2005) 7768–7776.

[21] H. Bogo, M. Otero, P. Castro, M.J. Ozafran, A. Kreiner, E.J. Calvo, R.M. Negri, Study of atmospheric particulate matter in Buenos Aires city, Atmos. Environ. 37 (2003) 1135–1147.

[22] R. Gehrig, B. Buchmann, Characterising seasonal variations and spatial distribution of ambient PM_{10} and $PM_{2.5}$ concentrations based on long-term Swiss monitoring data, Atmos. Environ. 37 (2003) 2571–2580.

[23] N. Perez, J. Pey, X. Querol, A. Alastuey, J.M. Lopez, M. Viana, Partitioning of major and trace components in PM_{10}–$PM_{2.5}$–PM_1 at an urban site in Southern Europe, Atmos. Environ. 42 (2008) 1677–1691.

[24] X. Querol, A. Alastueya, C.R. Ruiz, B. Artinano, H.C. Hansson, R.M. Harrison, E. Buringh, H.M. Brink, M. Lutz, P. Bruckmann, P. Straehl, J. Schneider, Speciation and origin of PM_{10} and $PM_{2.5}$ in selected European cities, Atmos. Environ. 38 (2004) 6547–6555.

[25] C.K. Chan, X. Yao, Air pollution in mega cities in China, Atmos. Environ. 42 (2008) 1–42.

[26] B. Gomiscek, H. Hauck, S. Stopper, O. Preining, Spatial and temporal variations of PM_1, $PM_{2.5}$, PM_{10} and particle number concentration during the AUPHEP—project, Atmos. Environ. 38 (2004) 3917–3934.

[27] M. Viana, X. Querol, A. Alastuey, G. Gangoiti, M. Menendez, PM levels in the Basque Country (Northern Spain): analysis of a 5-year data record and interpretation of seasonal variations, Atmos. Environ. 37 (2003) 2879–2891.

[28] L.Y. Chan, W.S. Kwok, Roadside suspended particulates at heavily trafficked urban sites of Hong Kong-Seasonal variation and dependence on meteorological conditions, Atmos. Environ. 35 (2001) 3177–3182.

[29] J.S. Park, T.L. Wade, S. Sweet, Atmospheric distribution of polycyclic aromatic hydrocarbons and deposition to Galveston Bay, Texas, USA, Atmos. Environ. 35 (2001) 3241–3249.

[30] J. Mantis, A. Chaloulakou, C. Samara, PM_{10}-bound polycyclic aromatic hydrocarbons (PAHs) in the Greater Area of Athens, Greece, Chemosphere 59 (2005) 593–604.

[31] B.C. Panther, M.A. Hooper, N.J. Tapper, A comparison of air particulate matter and associated polycyclic aromatic hydrocarbons in some tropical and temperate urban environments, Atmos. Environ. 33 (1999) 4087–4099.

[32] T. Chetwittayachan, D. Shimazaki, K. Yamamoto, A comparison of temporal variation of particle-bound polycyclic aromatic hydrocarbons (pPAHs) concentration in different urban environments: Tokyo, Japan, and Bangkok, Thailand, Atmos. Environ. 36 (2002) 2027–2037.

[33] J.B. Dallarosa, E.C. Teixeira, M. Pires, J. Fachel, Study of the profile of polycyclic aromatic hydrocarbons in atmospheric particles (PM_{10}) using multivariate methods, Atmos. Environ. 39 (2005) 6587–6596.

[34] G.C. Fang, Y.S. Wu, C.N. Chang, T.T. Ho, A study of polycyclic aromatic hydrocarbons concentrations and source identifications by methods of diagnostic ratio and principal component analysis at Taichung chemical Harbor near Taiwan Strait, Chemosphere 64 (2006) 1233–1242.

[35] C. Schauer, R. Niessner, U. Pöschl, Polycyclic aromatic hydrocarbons in urban air particulate matter: decadal and seasonal trends, chemical degradation, and sampling artifacts, Environ. Sci. Technol. 37 (2003) 2861–2868.

[36] H.L. Sheu, W.J. Lee, S.J. Lin, G.C. Fang, H.C. Chang, W.C. You, Particle-bound PAH content in ambient air, Environ. Pollut. 96 (1997) 369–382.

[37] R.M. Harrison, J. Yin, D. Mark, J. Stedman, R.S. Appleby, J. Booker, S. Moorcroft, Studies of the coarse particle (2.5–$10\,\mu m$) component in UK urban atmospheres, Atmos. Environ. 35 (2001) 3667–3679.

[38] P.D. Hien, V.T. Bac, H.C. Tham, D.D. Nhan, L.D. Vinh, Influence of meteorological conditions on $PM_{2.5}$ and $PM_{2.5-10}$ concentrations during the monsoon season in Hanoi, Vietnam, Atmos. Environ. 36 (2002) 3473–3484.

[39] Y.I. Tsai, Atmospheric visibility trends in an urban area in Taiwan 1961–2003, Atmos. Environ. 39 (2005) 5555–5567.

[40] M. Rehwagen, A. Müller, L. Massolo, O. Herbarth, A. Ronco, Polycyclic aromatic hydrocarbons associated with particles in ambient air from urban and industrial areas, Sci. Total Environ. 348 (2005) 199–210.

[41] F.S. Turalıoğlu, A. Nuhoğlu, H. Bayraktar, Impacts of some meteorological parameters on SO_2 and TSP concentrations in Erzurum, Turkey, Chemosphere 59 (2005) 1633–1642.

[42] A. Chaloulakou, P. Kassomenos, N. Spyrellis, P. Demokritou, P. Koutrakis, Measurements of PM_{10} and $PM_{2.5}$ particle concentrations in Athens, Greece, Atmos. Environ. 37 (2003) 649–660.

[43] A. Motelay-Massei, D. Ollivon, B. Garban, M. Chevreuil, Polycyclic aromatic hydrocarbons in bulk deposition at a suburban site: assessment by principal component analysis of the influence of meteorological parameters, Atmos. Environ. 37 (2003) 3135–3146.

[44] T. Hussein, A. Karppinen, J. Kukkonen, J. Harkönen, P.P. Aalto, K. Hameri, K.V. Kerminen, M. Kulmala, Meteorological dependence of size-fractionated number concentrations of urban aerosol particles, Atmos. Environ. 40 (2006) 1427–1440.

[45] D.L. Poster, J.E. Baker, Influence of submicron particles on hydrophobic organic contaminants in precipitation. 2. Scavenging of polycyclic aromatic hydrocarbons by rain, Environ. Sci. Technol. 30 (1996) 349–354.

[46] S.K. Sahu, G.G. Pandit, S. Sadasivan, Precipitation scavenging of polycyclic aromatic hydrocarbons in Mumbai, India, Sci. Total Environ. 318 (2004) 245–249.

[47] P.J. Tsai, T.S. Shih, H.L. Chen, W.J. Lee, C.H. Lai, S.H. Liou, Assessing and predicting the exposures of polycyclic aromatic hydrocarbons (PAHs) and their carcinogenic potencies from vehicle engine exhausts to highway toll station workers, Atmos. Environ. 38 (2004) 333–343.

[48] P. Goyal, A.T. Chan, N. Jaiswal, Statistical models for the prediction of respirable suspended particulate matter in urban cities, Atmos. Environ. 40 (2006) 2068–2077.

[49] U. Brunelli, V. Piazza, L. Pignato, F. Sorbello, S. Vitabile, Two-days ahead prediction of daily maximum concentrations of SO_2, O_3, PM_{10}, NO_2, CO in the urban area of Palermo, Italy, Atmos. Environ. 41 (2007) 2967–2995.

[50] C.J. Lin, T.C. Ho, H.W. Chu, H. Yang, M.J. Mojica, N. Krishnarajanagar, P. Chiou, J.R. Hopper, A comparative study of US EPA 1996 and 1999 emission inventories in the west Gulf of Mexico coast region, USA, J. Environ. Manage. 75 (2005) 303–313.

[51] S.I.V. Sousa, F.G. Martins, M.C. Pereira, M.C.M. Alvim-Ferraz, Prediction of ozone concentrations in Oporto city with statistical approaches, Chemosphere 64 (2006) 1141–1149.

[52] H.C. Lu, T.S. Chang, Meteorologically adjusted trends of daily maximum ozone concentrations in Taipei, Taiwan, Atmos. Environ. 39 (2005) 6491–6501.