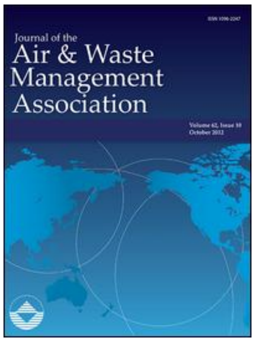

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Effect of Meteorological Parameters on Fine and Coarse Particulate Matter Mass Concentration in a Coal-Mining Area in Zonguldak, Turkey

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ABSTRACT
In this work, the effect of meteorological parameters and local topography on mass concentrations of fine ($PM_{2.5}$) and coarse ($PM_{2.5-10}$) particles and their seasonal behavior was investigated. A total of 236 pairs of samplers were collected using an Anderson Dichotomous sampler between December 2004 and October 2005. The average mass concentrations of $PM_{2.5}$, $PM_{2.5-10}$, and particulate matter less than 10 μm in aerodynamic diameter (PM_{10}) were found to be 29.38, 23.85, and 53.23 μg/m^3, respectively. The concentrations of $PM_{2.5}$ and PM_{10} were found to be higher in heating seasons (December to May) than in summer The increase of relative humidity, cloudiness, and lower temperature was found to be highly related to the increase of particulate matter (PM) episodic events. During non-rainy days, the episodic events for $PM_{2.5}$ and PM_{10} were increased by 30 and 10.7%, respectively. This is a result of the extensive use of fuel during winter for heating purposes and also because of stagnant air masses formed because of low temperature and low wind speed over the study area.

INTRODUCTION
Globally, anthropogenic air pollutants have intensified in the atmosphere of metropolitan cities and downtown locations. It is known that air pollutants have adverse effects on humans as well as the environment.[1–11] The close relationship between unfavorable health conditions and urban air pollution has increased the interest in studies aimed to improving the air quality of urban areas. The European Council (EC) renewed the daily and annual air quality limits (Directive 1999/30/EC). Because of the adverse effects of air quality, especially atmospheric particulate matter (PM), there are numerous studies on temporal and seasonal variations[12–14] and also on the effects of meteorological factors on PM.[15,16] European researches on air quality carried out within the Forecasting Urban Meteorology, Air Pollution, and Population Exposure (FUMAPEX) and the European Cooperation in the Field of Scientific and Technical Research (COST) 715 projects[17–19] employed air quality modeling systems for long-term air quality evaluation to minimize public health risk. The outcomes of these studies were used for urban planning and the design and management of transportation of industrial and residential areas

PM is a complex mixture of dry, solid particles, solid cores with liquid coatings, and small liquid droplets. These particles vary greatly in their physical and chemical properties, which are shape, size, solubility, residence time, reactivation, toxicity, and chemical composition and structure. In addition to the definition of these properties, determination of pollution reduction strategies also depends on the definition of their pollution sources. The local and regional meteorology, wind speed, wind direction, atmospheric stability, long-range transport, and pollution dispersion are all factors that play an important role in PM concentration reduction strategies. Analysis of local and regional meteorology is important to fully understand the processes responsible for the spatial and temporal distribution of PM.[15,16,20–24]

There is an increasing demand on energy related to the rapid growth rate of industries and the population in Turkey. Although there was an increase in the use of natural gas during the last decade, coal remains a primary source of energy production in Turkey. Turkey produces a considerable amount of coal (1.5 to 2 million t/yr) for its national usage, and of its cities Zonguldak is the major coal-mining city located in the Black Sea region. In addition to the utilization of coal as an energy source, the emission of PM from various mining operations deteriorate the air quality.[17–19] Sources of air pollution because of

IMPLICATIONS
This study was conducted in the city of Zonguldak, which is a city where a large reservoir of coal is located and its economy mainly depends on the coal-mining industry. The coal-mining activities have been criticized because they adversely affect both human health and air quality in the city. In Zonguldak, chronic respiratory, asthma, and chronic bronchitis patients are considered above normal prevalence in Turkey. This study is the first to be conducted in the city of Zonguldak.

coal-mining activities generally include drilling, blasting, coal loading and unloading, road transport, coal handling plants, and exposed pit faces.

This study was carried out in Zonguldak, a city where a large reservoir of coal is located and its economy mainly depends on the coal-mining industry. Coal-mining activities have been criticized because they adversely affect both human health and air quality in the city.[25,26] In Zonguldak, chronic respiratory, asthma, and chronic bronchitis patients are considered above the normal prevalence in Turkey.[27] To our knowledge, there are no other studies considering the effects of Turkish coal-mining activities along with coal combustion on urban air quality to date; therefore this study carried out in Zonguldak, Turkey is the first of its kind.

The aims of this work include the evaluation of:

(1) seasonal and temporal variations of fine ($PM_{2.5}$), coarse ($PM_{2.5-10}$), and PM less than 10 μm in aerodynamic diameter (PM_{10}) mass concentrations;
(2) correlations between PM fractions,
(3) the effects of meteorology over PM fractions; and
(4) Turkish coal-mining activities and coal combustion-related air quality of the city.

EXPERIMENTAL METHODS AND DATA ARCHIVING

Sampling Site

Zonguldak is a city located in the western Black Sea region of Turkey (41 °27′ N, 31 °46′ E). The city has rough ground with an area consisting of approximately 56% mountains, 31% level ground, and 13% valley area. The population of the city is approximately 110,000. The city has produced coal since 1948; accordingly, its economy is related to coal and coal-production industries. The State-owned coal company Turkish Hardcoal Enterprise produces, processes, and distributes hard coal (1.5–2 million t/yr) at the Kozlu, Uzulmez, and Karadon coal-mining sites located 5 km west, 7 km south, and 12 km east of Zonguldak city center, respectively (Figure 1). Produced coal, which is used mainly for power generation (66% utilized by Çates), steel production (Erdemir), and domestic heating, is generally of poor quality with low calorific value, containing 0.8% sulfur, 13 ± 2% ash, and 2% moisture. Erdemir is a steel company that has a high production capacity (3 million t/yr) and is considered the largest energy utilization steel production facility in Turkey.

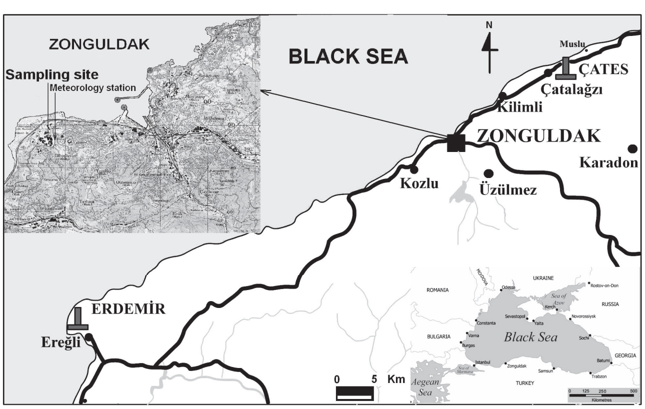

Figure 1. Study area and sampling station.

Settlement in the city has increased and developed as metallurgical workers settle in the city center. The coal-mining industry; the electric power plant (Çates), which is located 13 km northeast of the city center; the Demir-Çelik steel factory (Erdemir), which is located at 40 km to the southwest of the city center; and a paper factory (Seka), which is located 35 km to the southwest of the city center, have all contributed to the problem of local industrial air pollution in the city. In addition, domestic heating and mobile sources have also made an important contribution to the increased problem of PM.

An emission inventory of the region in terms of major PM source categories are defined and in Table 1. They are classifieds as (1) the combustion-related emissions of the important industrial point sources, Çates and Erdemir; (2) combustion-related emission sources; (3) domestic space-heating-related emissions; and (4) traffic-related tailpipe emissions. In the calculation of the amount of the emissions for each category, the U.S. Environmental Protection Agency (EPA) emissions factors were used.[28–31] In these calculations some parameters such as the daily coal usage, total number of houses, yearly fuel consumption, and the shares of the fuel types (coal, fuel, oil), registered number of cars and vehicles, their engine types, and estimated mileages were collected and/or calculated from related authorities like the management at the factories, city management, and the Turkish Statistical Institute.[32]

Sampling, Analyzing, Method, and Period

A total of 236 pairs of $PM_{2.5}$ and $PM_{2.5-10}$ samples were collected between December, 25, 2004, and October 9, 2005. The selection of the sampling site was done following the EPA guidelines.[33]

The PM sampling station selection was decided after a careful evaluation of the meteorological, topographical, land-use, and PM potential sources affecting the area. Accordingly, the selected sampling site represents an urban background. Consequently, a Dichotomous sampler was placed in the city center of Zonguldak, specifically at the campus of Karaelmas University. The site is approximately 4 m above sea level at coordinates 41.4508 ° N, 31.7726 ° E as seen in Figure 1. The site was not under significant influence from nearby stationary fossil fueled combustion sources. Furthermore, the sampler was 100 m away from the nearest motorway and away from human curiosity and vandalism.

The collection of $PM_{2.5}$ and $PM_{2.5-10}$ was performed using an Anderson automatic Dichotomous sampler (series 245). The sampler has a cutoff for PM greater than 10 μm; the mass of the entered particles was divided into $PM_{2.5}$ aerodynamic size and collected on a separate 37-mm diameter ringed Teflon filter (pore size equivalent to 2.5 μm) and $PM_{2.5-10}$ was collected on another filter. The sampler has a total volume flow of 1 m^3/hr.

The filter was conditioned in a desiccator for 24 hr before weighing with an accurate four-digit balance. The filters were placed in pre-acid-washed standard filter ring holder and situated in the sampler carousel to be ready for sampling. To prevent contamination of the filters during transportation, the carousel was covered with a special covering tray. After a 24-hr sampling period, the filters carousel was brought to the laboratory and the filters were

Table 1. PM emission inventory for Zonguldak, Turkey.

Source	Explanation	PM_{10} (t/yr)
Industry		5,500
Çates (power plant)	2 million t/yr coal consumption	
Erdemir (steel industry)	1 million t/yr coal utilization; 750,000 t/yr fuel oil consumption	11,000
Residential	55,000 homes and workplaces; 95% coal, 5% fuel oil utilization	355
Traffic	98,897 registered cars; 18% gasoline cars, 55% diesel cars, 4% minibuses, 2% buses, 15% small lories, 6% trucks	315
Total		17,170

placed in the desiccator again for 24 hr before determining the weight of the filter with the sample. For accuracy of the PM mass determination, the method of weighing was repeated three times until constant weight (uncertainty ± 0.0002) was gained. The method used by Karaca et al.[34] was followed for the collection of the mass concentrations of $PM_{2.5}$, $PM_{2.5-10}$, and PM_{10} (total of $PM_{2.5}$ and $PM_{2.5-10}$) and the gravimetric measurements.

Meteorological Data

The Zonguldak area is typified by temperate atmospheric conditions near the Black Sea. However, going inland from the coastal area the weather becomes colder. The city is affected by marine and terrestrial winds of 2.4 m/sec on average. The dominant meteorological conditions are high humidity (82% relative humidity [RH]) and foggy weather. The meteorological parameters such as wind speed and direction, temperature, humidity, rain volume, and cloudiness were obtained from the nearby governmental meteorology station for the study period and are given in Figure 2.

Statistical Analysis

The correlation between the observed PM concentration and meteorological parameters were investigated utilizing different tools including descriptive statistics, correlation analysis, classification, and cross-table tools. The annual, monthly, and daily variation and correlations between $PM_{2.5}$ and PM_{10} were investigated in particular. To elucidate these relationships multiple correlation methods were applied.

The relationship between PM mass concentrations and meteorological parameter characteristics were determined using classification and cross-table techniques. These methods were used to:

(1) classify sampling days from December 2004 to October 2005 according to $PM_{2.5}$ and PM_{10} concentrations;
(2) classify episode days and meteorological characteristics; and
(3) determine key relationships and parameters that lead to different $PM_{2.5}$ and PM_{10} concentrations.

Percentile range of dependent ($PM_{2.5}$, PM_{10}) and independent (meteorological parameters) variables were used to separate and group days into classes. This analysis provides information about the conditions that are associated with episodes days of $PM_{2.5}$, PM_{10} concentrations, as well as the frequency of occurrence of different types of conditions. Classification categories of $PM_{2.5}$, PM_{10}, and meteorological parameters defined by percentiles are given in Table 2.

The direction of the maximum wind speed was assigned a number between 1 and 16, it was arranged into order and numbered as north = 1 and north-northwest = 16. The rainy days were classified as wet and non-rainy days as dry ("rainy day" is defined as a day on which any rainfall was recorded, i.e., >0.8 mm/day).

RESULTS AND DISCUSSION

PM Mass Concentrations

The average mass concentration of $PM_{2.5}$ and $PM_{2.5-10}$ particles during the study period was found as 29.38 $\mu g/m^3$ and 23.85 $\mu g/m^3$, respectively. General descriptive statistics results for PM mass concentration are given in Table 3. The results given include all data collected during the sampling period. The annual average value for PM_{10} was calculated as 53.23 $\mu g/m^3$.

For the year 2005, European urban background value for PM_{10} was calculated as 16.9 $\mu g/m^3$, with the averages of PM_{10} concentrations of 32 European countries showing considerable differences. For the year 2004, European PM_{10} yearly average concentration was calculated using data from 742 urban background sites and reported as 26 $\mu g/m^3$.[35,36] However, the highest urban background concentrations were reported in cities in central eastern and southern European countries. EPA's yearly average limit value of 60 $\mu g/m^3$ was exceeded in the cities of Sofia, Milano, Provdiv, and Rybrile during 2005.[35] In this study, the measured concentrations of PM fractions were higher than many European cites. In addition, $PM_{2.5}$ and PM_{10} mass concentrations were 38 and 105% higher than the European urban background value but not higher than the limit value. The comparisons of the measured mass concentrations of this study with other literature values are given in Table 4.

The annual average value for PM_{10} was less than the EPA annual average limit of 60 $\mu g/m^3$. However, the annual average European Union (EU) limit value for PM_{10} (40 $\mu g/m^3$) is lower than the corresponding measured values at the sampling site. Our value is 33% higher than the limit value. In some European countries (Bulgaria, Poland, Italy, and the Czech Republic) the limit value was exceeded in 69 and 89 stations during 2004 and 2005, respectively.[35] EPA annual average limit for $PM_{2.5}$ is 15 $\mu g/m^3$, and the measured $PM_{2.5}$ value at Zonguldak was 29.38 $\mu g/m^3$, approximately twice the EPA limit value.

Figure 3 shows the histogram of the collected data, and the corresponding percentiles of the exceeding number of the daily EU limits was calculated. During the study period, 62% of PM_{10} concentrations were under the 50-$\mu g/m^3$ limit value whereas this limit value was exceeded in 38% of the cases. The EU daily limit value for PM_{10} (50 $\mu g/m^3$) was exceeded 89 times in Zonguldak during the study period. Larssen et al.[35] reported that the EU PM_{10} daily limit was exceeded 99 times in Ispra, Italy and 40 times in Illmitz, Austria during 2005.

EC set up a target value for yearly average of atmospheric $PM_{2.5}$ of 25 $\mu g/m^3$ to be operative in 2012, but

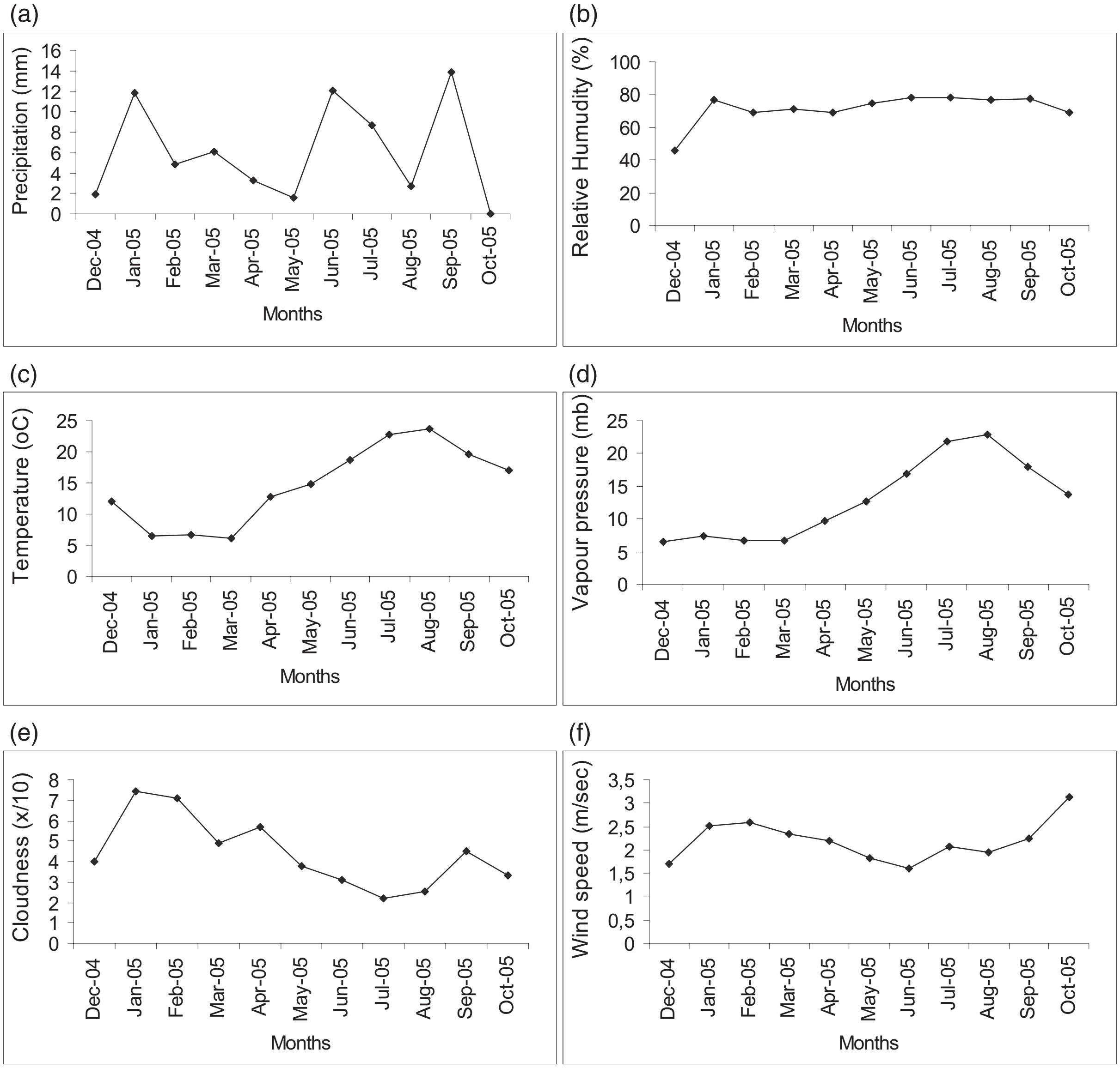

Figure 2. Monthly average values of meteorological parameters affecting the study area: (a) precipitation, (b) RH, (c) temperature, (d) vapor pressure, (e) cloudiness, and (f) wind speed.

this limit is now in use in the World Health Organization (WHO) criteria for a 24-hr $PM_{2.5}$ daily limit. This target value was also not fulfilled in Zonguldak. During the study period, the average mass of $PM_{2.5}$ particles was 29.38 $\mu g/m^3$, which is 18% higher than the target value. This limit value was exceeded 122 times, which accounts for almost half of our sampling days (Figure 3). Similar results were reported for the stations located in Ispra, Italy (162 times) and in Illmitz, Austria (104 times) for 2005.[42]

Table 2. Classification categories of $PM_{2.5}$, PM_{10}, and meteorological parameters defined by percentiles.

Percentiles	$PM_{2.5}$, PM_{10}	RH, Temperature, Vapor Pressure, Cloudiness, and Wind Speed
<25th	Low (background)	Low
>25th and <75th	Medium (impacted)	Medium
>75th	High (episode)	High

Seasonal, Monthly, and Daily Variations

To understand the general trend of the measured mass concentration, the seasonal, monthly, and daily variations of $PM_{2.5}$, $PM_{2.5-10}$, and PM_{10} were graphically investigated. To understand the change of PM concentration throughout a whole year, seasonal mean concentrations were calculated. The mean mass concentrations of $PM_{2.5}$ and PM_{10} during the heating season, which includes both winter and spring, were 34.17 and 63.59 $\mu g/m^3$ for winter and 29.84 and 59.16 $\mu g/m^3$ for spring, respectively. Consequently, the mean mass concentrations of $PM_{2.5}$ and PM_{10} for summer and autumn were 25.03 and 41.83 $\mu g/m^3$, and 23.03 and 39.66 $\mu g/m^3$, respectively. When compared with studies given in Table 5, our values are in accordance with research conducted by other researchers. Our results were slightly higher

Table 3. Descriptive statistical analysis of PM concentrations.

	$PM_{2.5}$	$PM_{2.5-10}$	PM_{10}	$PM_{2.5}/PM_{10}$
N	236	236	236	236
Mean	29.382	23.851	53.234	0.570
Median	26.087	20.833	45.817	0.580
Standard Deviation	15.329	19.882	29.898	0.121
Minimum	4.55	4.00	12.00	0.18
Maximum	95.65	154.17	200.00	0.86
Percentiles				
10	13.458	8.695	25.760	0.426
25	20.833	13.043	36.090	0.500
50	26.087	20.833	45.817	0.580
75	34.782	29.166	62.993	0.666
90	50.000	39.130	88.073	0.714

than those measured in Büyükçekmece, Vienna, and Oslo, but lower than those found in Beijing.

The seasonal changes of mass concentration values are shown in Figure 4. The winter/spring mass concentrations of $PM_{2.5}$ and PM_{10} during the study period show significant differences from summer/autumn, where the former are higher than the later. This clearly shows the effect of local domestic heating due to utilizing coal in the study region. The PM mass concentration could be increased and affected by different factors, including traffic congestion, domestic heating, population intensity, topography, and meteorology. Some workers suggested there is significant amount of long-range transport inputs to the region from eastern Europe, the Mediterranean, and the Middle East during winter, as well as spring and summer.[34,45–48] Long-range transportation may be another factor that affects the region. However, this was not possible to confirm in this study because at a site affected by high local emissions, especially during the heating season, it is very difficult to identify long-range transport inputs due to high local contributions.

High-level PM winter mass concentrations can be related to specific thermal inversions and domestic heating emissions. We believe that the observed high levels of PM mass concentrations in the Zonguldak region were mostly related to the low-quality coal used locally. During fall and winter the region has many long-lasting inversions. Topography also has a significant effect on the regional inversions

Table 4. Average PM concentrations measured from different regions.

Region	Measured Concentrations (μg/m³) $PM_{2.5}$	PM_{10}
Zonguldak (this work)	29.38 ± 15.32	53.23 ± 29.89
Büyükçekmece, Istanbul [34]	32.56 ± 13.60	47.11 ± 20.76
Rajshahi, Bangladesh[37]	22.465 ± 10.413	41.131 ± 21.979
Vienna, Austria[38]	18.6 ± 10.7	26.5 ± 13.3
Salzburg, Austria (urban traffic, 2005)	26	33
Innsbruck, Austria[d] (urban, 2005)[35]	21	29
Bern, Switzerland[39]	20.7	32.5
Nontelibretti, Italy (semi-rural, 2006)-Italy[40]	17.6	29.2
Urban background in Spain[41]	19–29	28–47

(typical of the Black Sea region city with high elevations closest to the sea). Throughout the whole year, the $PM_{2.5}$ mass concentration in each season was higher than $PM_{2.5-10}$. The chief portion of the sudden increase in winter and spring PM_{10} mass concentration is attributed to the increase of $PM_{2.5-10}$ due to local meteorological conditions triggered by the urban structures and transportation activities, whereas another part is attributed to the increase of $PM_{2.5}$ mass concentration generated from domestic heating and fuel combustion for energy production. The prevailing winds blow from the northwest and northeast locations, where the two biggest industrial plants, Erdemir and Çates are located. This meteorological situation makes these plants more significant as PM sources affecting the region. The most important anthropogenic $PM_{2.5-10}$ sources are the coal processing and mining industries located in Kozlu, Üzülmez, and Karadon, which are located close to the study area and are operated during all seasons. Pinto et al.[49] studied ambient $PM_{2.5,}$ sulfate, organic and elemental carbon, and polyaromatic hydrocarbons, with a focus on the effect of sulfur dioxide measurements to estimate the relative contributions to aerosol samples collected at the Teplice site in the Czech Republic. Modeling results from a chemical mass balance were evaluated to estimate the emissions from various sources (chimney of home heating, power plants, hospital incinerator, and motor vehicle traffic). They reported that residential space heating was the major source of fine PM, whereas power plants, motor vehicles and incinerators were less important.

Figure 5 shows monthly concentrations of $PM_{2.5}$, $PM_{2.5-10,}$ and PM_{10}. PM_{10} concentrations during January, February, March, and April were higher than other months. The highest monthly PM_{10} concentration was observed during February (77.78 μg/m³), whereas the lowest was observed during May (37.61 μg/m³). The highest $PM_{2.5}$ monthly mean concentration of 43.47 μg/m³ was found in January, whereas the lowest value of 19.84 μg/m³ was found in May. The highest $PM_{2.5-10}$ monthly mean concentration value of 39.68 μg/m³ was found in February, whereas the lowest value of 15.34 μg/m³ was found in August.

In this study, $PM_{2.5}$, $PM_{2.5-10}$, and PM_{10} concentrations were parallel to seasonal and monthly mean changes, the daily mean concentrations show higher values in winter and spring compared with summer and autumn because of the utilization of fuel in domestic heating, industrial activities, coal-mining production, transportation, and traffic.

Correlations between $PM_{2.5}$ and PM_{10}

For further understanding the possible sources, annual and seasonal correlations of summer and winter mass concentrations of PM samples and their ratio were investigated. The correlation between annual mean values of $PM_{2.5}$ and PM_{10} particles is 0.80 (*R* value). Statistically, when the number of the samples was considered (>50), this value indicates a strong relationship at Çates. A similar result was reported for some northern European countries. This correlation value was higher (0.88) than our average value of all European Monitoring and Evaluation Programme (EMEP) countries, and lower than some Nordic countries such as Denmark, Finland, Ireland, Norway, and Sweden.[35]

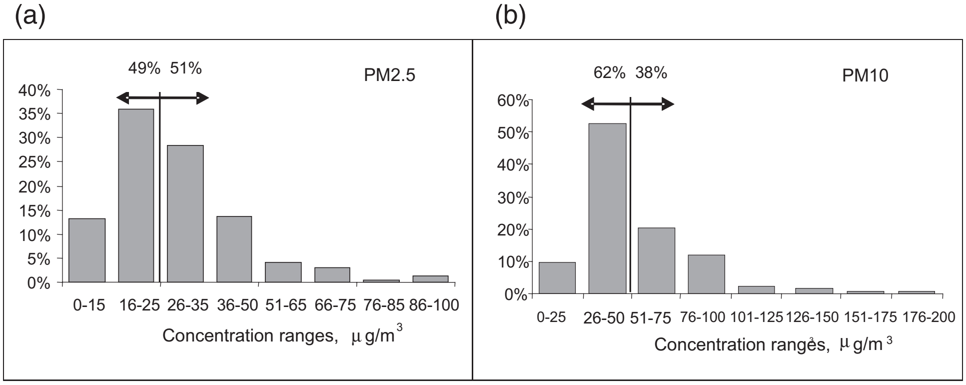

Figure 3. Exceedance days of EU limit values for (a) $PM_{2.5}$ and (b) PM_{10}.

Inspection of the correlations between $PM_{2.5}$ and PM_{10} mass concentration values indicates that at Çates, summer has higher correlations than winter. The correlation coefficients for winter and summer are 0.70 and 0.90, respectively. Two possible effects that generate seasonal differences in the ratio of $PM_{2.5}$ to PM_{10} can be attributed to (1) the absence of residential burning, which has a decreasing effect on the relative amount of fine fraction in PM_{10}; and (2) resuspension of surface dust in summer, which increases the relative amount of the coarse fraction in PM_{10}. The relatively high correlation observed in summer could be an indication of common sources[44] or particles carried to the receptor site by similar transportation mechanisms.[34] We believe that the latter option is the most possible one in our case. Thus, surface winds, which carry $PM_{2.5}$-sized anthropogenic particles from their emission sources along with $PM_{2.5–10}$-sized resuspended surface dust, were the main governing meteorological factor on the transportation of atmospheric particles in the region during the study period.

However, the heating season $PM_{2.5}$ and PM_{10} concentrations (December–May) show weak correlation. In this case, the increased emissions of winter-related activities like space heating and strong ground-level inversions were observed frequently during the season in the region. Under these winter meteorological conditions such as strong inversions, wet ground due to increased precipitation, and stagnant atmospheric conditions, it is well possible to have more anthropogenic PM directly dispersed from its source and less natural PM due to ongoing conditions.

Special attention was given to winter concentrations. The observed high winter PM_{10} concentration is due to the increase in $PM_{2.5}$ during January, whereas in $PM_{2.5–10}$ mass concentration during February, March, and April $PM_{10.}$ This situation during winter and spring months can be explained by regional and/or local meteorological factors. The presence of high humidity during spring in the study area in addition to an increase in evaporation in marine and crustal regions causes the increase of coarse-sized crustal elements such as sodium in the $PM_{2.5–10}$ particle size range. Another possible effect that increases the anthropogenic fine particles over the city is winter inversions related to atmospheric stability. The typical features of the weather of Zonguldak, rainy with very high humidity, are the governing factor over the $PM_{2.5–10}$ mass concentration during the whole year, especially in spring and winter months, where it has a significant correlation with PM measurements.

$PM_{2.5}/PM_{10}$ Ratio

As seen from Table 3, the average and median ratio values of $PM_{2.5}$ to PM_{10} are 0.57 and 0.58, respectively. The 75th percentile is given as 0.66. The ratio is almost equal during heating and nonheating times (0.57 and 0.56), but with detailed monthly inspection it has higher values during summer (Figure 6). The situation was possibly caused by the decrease of $PM_{2.5–10}$ mass concentration during summer. The results of these analyses show that the seasonal averages of the $PM_{2.5}/PM_{10}$ ratio during a year are greater than 0.5. This is an indication that coarse

Table 5. PM winter and summer average concentration from different regions.

	Concentration (μg/m³)					
	Winter			Summer		
Region	$PM_{2.5}$	PM_{10}	$PM_{2.5}/PM_{10}$	$PM_{2.5}$	PM_{10}	$PM_{2.5}/PM_{10}$
Zonguldak (this work)	34.17	63.59	0.53	25.03	41.83	0.59
Bÿkçekmece, Istanbul[34]	24.77	47.1		18.11	47.54	
Vienna, Austria[38]	19.5 (13)	26.9 (16.6)	0.72 (0.14)	17.5 (7.3)	26.1 (10.5)	0.67 (0.09)
Beijing, China [43]	140.8 (73.9)	287.7 (155.7)		82.2 (49)	170 (66.7)	
Oslo, Norway	14	32		11	20	
Trondheim, Norway[44]	11	21		7.7	15	

Notes: Numbers in parentheses are standard deviation values.

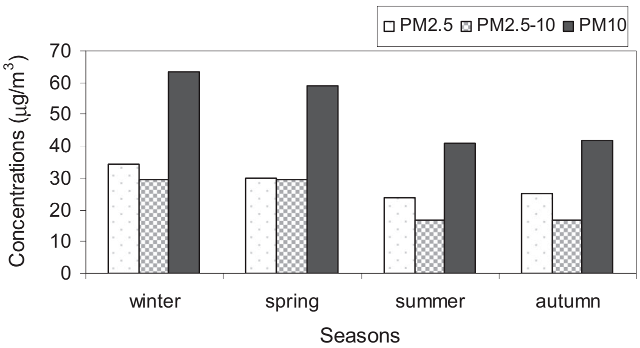

Figure 4. PM mass concentration seasonal change.

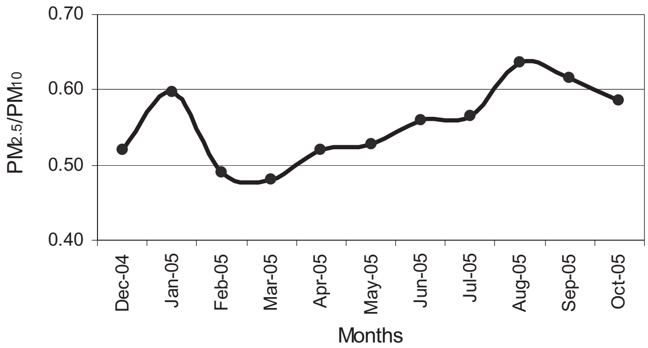

Figure 6. $PM_{2.5}/PM_{10}$ monthly variation.

particles are more available in the atmosphere than fine particles in this region of Turkey.

Winter and summer histogram graphs for the ratio are given in Figure 7. These figures show that no clear difference in the graphs, but the summer profile is more symmetrical, has a thinner left tail, and a more leptokurtic distribution peaked at 0.6. These results indicate summer concentrations fit normal distribution. Coal mining, transportation, and coal-processing activities can contribute significantly to $PM_{2.5}$ emissions in the atmosphere.[25,26] The conveyed left tail between 0.4 and zero in Figure 7 during winter indicates that the $PM_{2.5}$ has a constant share in PM_{10}. This may be a clear indication of fine-sized PM contribution from sources such as industrial coal burning, coal-related mining, transportation, and coal-processing activities in the region. Some similar results are reported. In the north, northwest, and central/eastern Europe there is a clear tendency toward higher ratios of 0.46, 0.61, and 0.70, respectively.[35]

Relationship between Meteorological Parameters and PM Measurements

The temporal patterns of meteorological parameters were analyzed to establish a consistent description for Zonguldak during the study period. The aim of the analysis conducted in this aspect was to discuss the effect of the meteorological conditions, especially during the occurrence of pollution episodes

Accordingly, the increase of RH and cloudiness is associated with an increase in episodic values of $PM_{2.5}$ and PM_{10}. Cloudiness is also found to be directly related to PM episodes. The maximum episode occurrence was observed in the range of 62–83% RH, compared with the ranges of 0–62% and 83–100%. This can be explained by

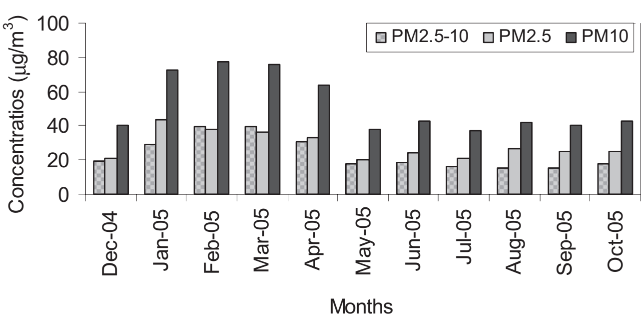

Figure 5. $PM_{2.5}$, $PM_{2.5–10}$, and PM_{10} monthly mean concentrations.

cloud scavenging characteristic of high RH levels (>83%), which result in low concentrations of gas and aerosols.[20]

The amount of rain had a decreasing effect on $PM_{2.5}$ and PM_{10} mass concentration, in which an atmospheric washout process takes place. During non-rainy days, the episodic events for $PM_{2.5}$ and PM_{10} were increased by 30 and 10.7%, respectively. Similar results were obtained in EMEP model scenarios during 2002 and 2003.[35] Under the conditions of low amount of rainfall, PM, especially naturally originated PM, tends to increase. It is reported by Frolova et al.[50] that on dry days (i.e., days without or with poor precipitation), the daily limit value of PM_{10} was exceeded in 94% of the cases in Latvia.

Temperature and PM have a significant effect on the occurrence of episodic events. The correlation between PM and temperature shows that there is a significant negative correlation. In the case of the 25th percentile of temperature (the lowest values of the temperature), the number of episodes of $PM_{2.5}$ and PM_{10} increased six and seven times, respectively. The effect of wind on the observed PM concentration over the city was not profound. This could be due the surface roughness and topography of the region. The other possible limiting effect over wind is the urban meteorology and the effects of structures. The city is located on a hilly area with unplanned, dense housing construction. This structure has a breaking, diluting, and diverging effect on the wind speed. When the wind speed increases from 1.39 to 2.80 m/sec, the number of polluted days increases. This may be an unexpected result, because of the dilution effects of wind, but it should be also be noted that buildings and trains have a marked influence on the behavior of plumes.[51] The results for PM_{10} show that for wind speeds higher than 2.80 m/sec, the number of episodic days decreased up to 40%.

High concentrations of PM are found in a mining area and the concentrations are gradually diminished with an increase in distance due to transportation, deposition, and dispersion of particles.[52–54] The dispersion of PM follows the annual predominant wind direction of an area. The prevailing winds, which may transport PM from nearby sources, play a significant role on the observation of PM episode in city. The major prevailing wind directions are westerly (south-southwest, southwest, west-northwest, north-northwest) and easterly (north-northeast, northeast) winds. The westerly and easterly prevailing winds have an increasing effect on the number of episodes over Zonguldak. This is thought to be because of nearby PM_{10} local sources, Kozlu (located at 5 km west)

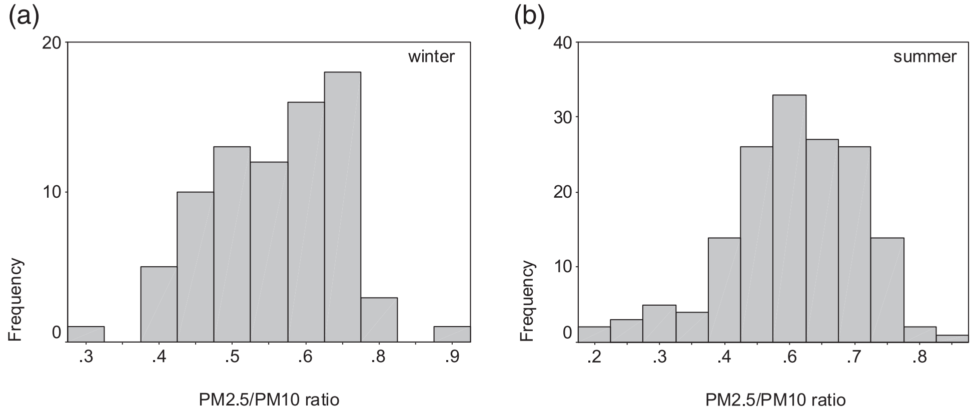

Figure 7. Frequency distribution of the $PM_{2.5}/PM_{10}$ ratio for Zonguldak city in (a) winter and (b) summer.

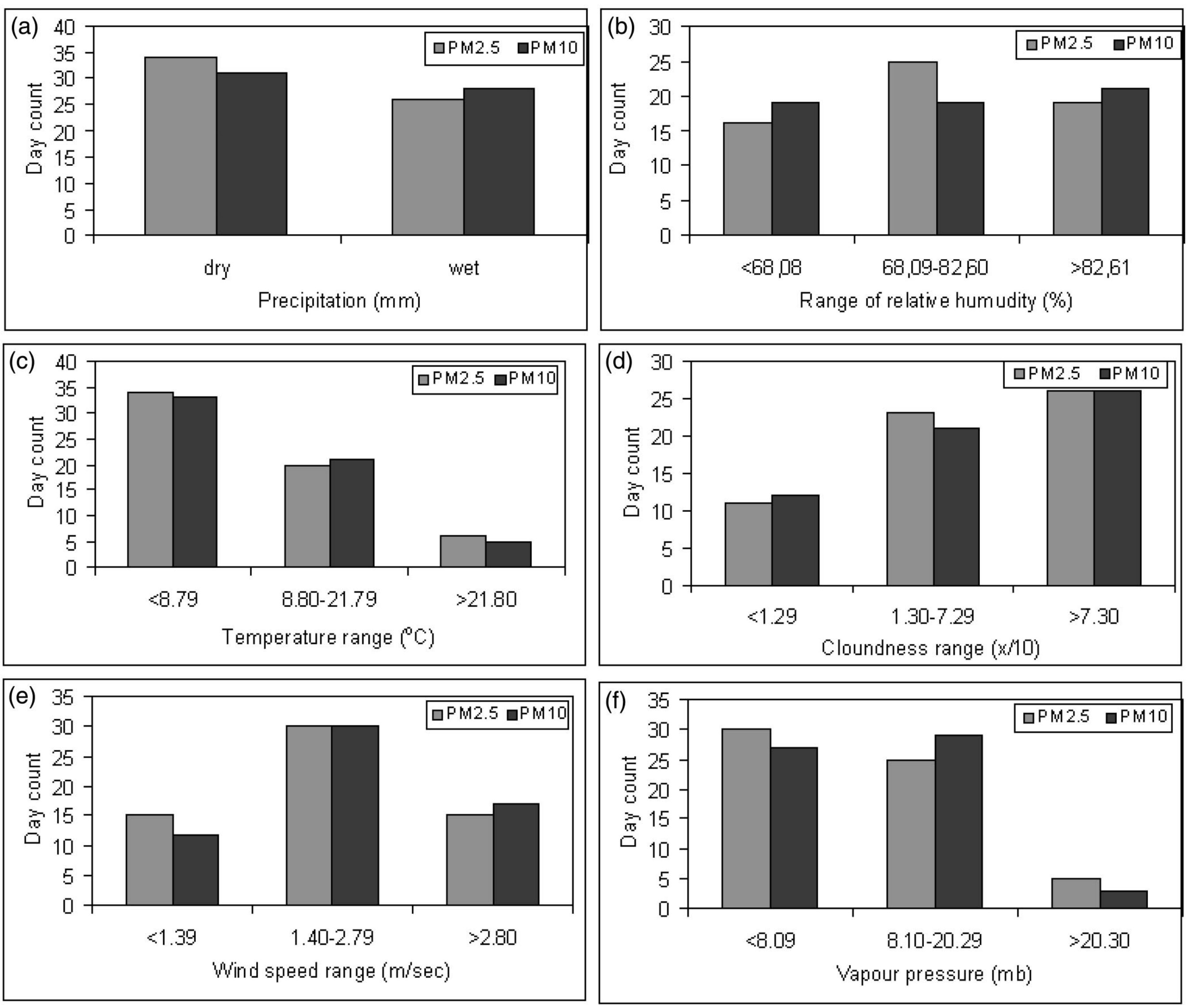

Figure 8. Relationship between meteorological parameters and PM episode days: (a) precipitation, (b) range of RH, (c) temperature range, (d) cloudiness range, (e) wind speed range, and (f) vapor pressure.

Table 6. Descriptive statistics of meteorological parameters and PM concentrations.

	$PM_{2.5}$ (μg/m^3)	PM_{10} (μg/m^3)	Rain (mm)	RH (%)	Temperature (°C)	Vapor Pressure (mb)	Cloudiness (x/10)	Wind Speed (m/sec)
n	236	236	97	236	236	235	236	236
Mean	29.38	53.23	6.90	73.87	15.01	13.83	4.43	2.15
Standard Deviation	15.32	29.89	8.98	13.64	7.39	6.52	3.30	1.08
Minimum	4.55	12	0.00	29.00	−0.10	4.10	0.00	0.30
Maximum	95.65	200	38.50	95.00	26.80	26.20	10.00	6.50
Percentiles								
10th	13.46	25.76	0.10	56.19	3.81	5.50	0.00	0.90
25th	20.84	36.09	0.80	68.08	8.80	8.10	1.30	1.40
50th	26.09	45.81	3.30	77.70	16.55	13.30	4.30	2.00
75th	34.79	62.99	8.80	82.60	21.80	20.30	7.30	2.80
90th	50.01	88.07	19.82	87.70	23.53	22.84	9.00	3.53

and Üzülmez (located 7 km northwest); for a regional perspective, Çates (located to the east) and Erdemir (located to the west) (Figure 1).

The number of PM episode occurrences (75th percentile) under specified meteorological conditions are given in Figure 8. The effect and correlation between $PM_{2.5}$ and PM_{10} episodic values and local meteorological parameters could be inferred easily from these figures.

CONCLUSIONS

Located in the western Black Sea region of Turkey, Zonguldak is a city of different industrial activities, mainly the coal-mining industry. This study related to PM and its fractions in the city center during December 2004 and October 2005 shows significant and meaningful correlations between meteorological parameters and PM mass concentration.

As a result, the mass concentration of $PM_{2.5}$ particle size is dominant in the atmospheric inhalable fraction (PM_{10}). Compared with many European cities, the measured concentrations are among the highest.[14–19] During the entire study the two particle sizes, $PM_{2.5}$ and PM_{10}, show a significant correlation. This study showed that in a region characterized by coal-mining activities, fine sized particles can represent a constant share of inhalable particles throughout the year. However, this is more applicable during summer. It is noted that high winter values are consistent with contributions from domestic heating sources and governing local and/or regional meteorological conditions. Also, coal-mining activities create wider air-quality deterioration due to PM in and around the mining complexes, which affects Zonguldak. There is a need to carry out additional campaigns to address these effects.

The analysis showed that the meteorological parameters have a major effect on the observed $PM_{2.5}$ and PM_{10} (Table 6). The increase of RH and cloudiness coincides with an increase of PM episodic events. As expected, low temperatures are associated with an increase in the number of episodic events. This is a result of the use of coal in space heating during winter and also because of stagnant air masses formed because of low temperature and low wind speed over the study area.

The roughness of the topography of the study area and the unplanned, crowded settlement in the city center along with a low wind speed (2.79 m/sec) hindered the distribution of PM air pollution over the city.

Serious health problems such as asthma, allergies, and other respiratory system problems in the study region could be attributed to the high concentrations of PM and meteorological conditions, especially the occurrence of episodic events in the study region. There is a need to spend a special effort in evaluating the health effects of air quality over the city. This will be addressed in detail in a separate paper.

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