Polish J. of Environ. Stud. Vol. 20, No. 2 (2011), 417-427

Original Research

Seasonal Variation of Particulate Matter Mass Concentration and Content of Metals

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Received: 30 June 2010
Accepted: 9 November 2010

Abstract

In this paper, an attempt is made to characterize PM_{10} imission field in the area of Warszawa with regard to PM content of the metals As, Cd, and Ni. Particulate matter concentration measurements were performed within this agglomeration with the use of many measuring methods, different not only in respect of the sampler operation rules, but also of the accuracy, sampling frequency, and separation of the particulate matter fractions. Since 1 October 2003, Warszawa agglomeration has had an extended measurement network consisting of 4 automatic stations and 7 manual ones. This paper attempts to estimate the influence of the prevailing meteorological conditions on PM_{10} imission and also to determine those parameter groups that enable the best description of monthly and seasonal variability of particulate matter. The data considered in this paper were collected in 2004-08.

Based on the performed analysis, it could be concluded that air quality in the area of Warszawa agglomeration is still unsatisfactory. The main cause of high PM concentration in Warszawa is the dynamic development of vehicular traffic and ever-increasing number of cars; both factors cause the PM concentration to be several times higher. The second important source of particulate matter in the Warszawa area is so-called “low emission”, occurring in the heating season, generated mainly by the processes of combustion in the communal and housing sectors. In 2004-08 the meteorological conditions prevailed 22.4% to 76.2% of the decadal variability of PM concentration in the individual months and 9.5% to 56.8% of seasonal variability. The most significant influence of the meteorological conditions was during the winter, especially in January. The regression analysis has found evidence for statistically vital relationships of PM_{10} concentration and meteorological parameters, especially maximum air temperature, wind speed, and precipitation.

Research on the chemical composition of PMs presented in this paper confirms that the target values of arsenic, cadmium, and nickel concentration in PM_{10}, determined by Directive 2004/107/WE, were not exceeded at the network stations in 2006-08 and the recorded concentration of these heavy metals were low. Analyzing the tendency of air quality changes for the last five years in the area of Warszawa, it was found that there was danger of not complying with the requirements set by the European Union. The time limit by which the member countries have to adjust the PM_{10} concentration limits in their territories to the EU norms is June 2011.

Keywords: particulate matter PM_{10}, content of metals, meteorological conditions, Warszawa, Poland

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Introduction

Long-term research has proved that there are such quantities of many substances in the air that can threaten human health or even life [1]. Moreover, these substances are harmful to animals and plants, and they are also considered to evoke climatic changes on Earth. They have been specified by council directives 96/62 WE, 1999/30/WE, and 2008/50/WE. The most dangerous substances include ozone, particulate matter, PM_{10}, and especially $PM_{2.5}$.

In Poland, as well as in many European countries, particulate matter pollution occurs mostly in bigger agglomerations. In recent decades high PM emissions in large cities of Poland was caused by industry, while emissions by vehicles were low due to little traffic congestion. At present, the situation is the opposite as higher PM emission takes place due to the significant increase of vehicular transport, while industrial emission is low because of the installation of air purification systems in factories. In many cities, however, the occurrence of particulate matter is determined by low emission, particularly coming from fossil fuel combustion in households and local power and heat generating plants. Additionally, the big traffic load in main roads causes a significant increase of particulate matter concentration, which is a dangerous situation for the health of the city center inhabitants. This problem concerns many cities in every voivodeship of Poland, especially the biggest Polish agglomerations of Kraków, Łódź, Bydgoszcz, etc., including the Warszawa agglomeration, which takes the leading position with respect to the highest mean yearly PM_{10} concentration. The reason for this situation is the structure of fuel utilization, which has not changed much in Poland recently. Hard coal is still the basic energy source in Poland, and its share of national primary energy consumption is about 50%, while brown coal has a share of 14%. The disadvantageous coal-based structure of fuel utilization is the basic cause for high emissions of fine particulate matter and others [2]. In consequence, it creates the need for the implementation of high-cost air quality conservation programs aimed at reducting the threat to human health in many areas of Poland.

The research that has been carried out for the last years in many countries has proved that contemporary particulate matter pollution is still related to increases of disease and death rates, despite the registered decrease of PM concentration [3-7]. Epidemiological research, in particular, has found evidence for the relationship of particulate matter with lungs dysfunction, increased frequency of respiratory disease symptoms, and increases in morbidity and mortality. This relationship has been found already for PM concentration levels currently occurring in many urbanized areas [8-12].

The most important factor that directly influences volatile properties, density, reactivity, and toxicity of atmospheric aerosol is its chemical composition, which also determines the degree of its impact on the human organism [13]. From the point of view of human impact, the composition of fine aerosol molecules-$PM_{2.5}$ is essential, because at first these molecules penetrate into lungs and bronchial tubes [14], and secondly it is exactly $PM_{2.5}$ that includes most chemical compounds, including trace elements and heavy metals [15, 16].

The harmfulness of atmospheric air pollutants depends not only on pollutant emission rates, but also on prevailing meteorological conditions. Meteorological parameters, which most significantly influence particulate matter concentration, are wind direction and speed, air relative humidity and precipitation, air temperature and solar radiation rates [17-24].

In this paper an attempt is made to characterize PM_{10} imission field in the area of Warszawa with regard to PM chemical composition. Particulate matter concentration measurements were performed within this agglomeration with the use of many measurement methods, different not only in respect to the sampler operation rules, but also of the accuracy, sampling frequency and separation of the particulate matter fractions. Since 1 October 2003, Warszawa agglomeration has an extended measurement network consisting of 4 automatic stations and 7 manual ones. This paper is also an attempt to estimate the influence of main meteorological parameters on PM_{10} imission and also to determine those parameter groups that enable the best description of monthly and seasonal variability of particulate matter.

Material and Methods

Warszawa is located within two wide morphological units: the Warszawa Plain and the Wisła Valley. It is the largest city in Poland, with a population of about 1.7 million and an area of 517.24 km^2.

The most vital element of Warszawa's natural environment is the Wisła River, which serves as an ecological corridor of international importance.

Warszawa is situated in a moderately warm, transitional climate zone. Mean annual air temperature is 8.2ºC. Mean annual precipitation ranges from 550 mm to 650 mm. In Warszawa, the influence of the large agglomeration on the climate becomes visible in the form of the urban heat island [25]. It is demonstrated by higher air temperatures in the city centre as well as higher precipitation, and by a lower wind speed. Moreover, the urban heat island is associated with high air pollution, which increases cloudiness and diminishes air transparency, resulting in the decline of direct solar radiation and, at the same time, increasing scattered radiation.

Measurements used for PM dynamics analysis were collected from all 11 existing air quality monitoring stations that register PM_{10} imission in the area of the city of Warszawa:
MzWarszSGGW,
MzWarszBernWoda,
MzWarszZeganWSSE,
MzWarszBorKomWSSE,
MzWarszKrucza,
MzWarszZelazWSSE,

MzWarszAKrzWSSE,
MzWarszUrsynów,
MzWarszNiepodlKom,
MzWarszBielany,
MzWarszTarKondra,

and from four stations located outside the city limits:
MzLegionZegIMG,
MzPiastowPulask,
MzOtwockBrzozWSSE,
MzPiaseczDworWSSE.

The measurement methods used to determine the PM_{10} concentration are reference ones that comply with the norm EN12341, and are adequate to the demand included in the ordinance of the Ministry of the Environment concerning the estimation of substance levels in the air (Ordinance of the Ministry of Environment, 3rd March 2008).

This paper also presents results of the analysis for arsenic, cadmium and nickel compounds contained in PM_{10}. This analysis was based on the results of the measurements executed at permanent monitoring points. Arsenic, cadmium, and nickel concentrations were determined using a reference method that includes manual sampling of particulate matter followed by sample mineralization and sample analysis by absorption atomic spectrometry with inductively activated plasma. The determined heavy metal concentrations were compared with their target values established by the Directive 2004/107/WE of the European Parliament and Council on 15th December 2004. The data were made available by the Voivodship Inspectorate of Environmental Protection in Warszawa, which functions within the framework of State Environmental Monitoring. The data considered in this paper were from 2004-08.

Meteorological conditions are represented as decade values of solar radiation; minimum, mean, and maximum air temperature; wind speed; air relative humidity; and precipitation rates. All parameter values were collected at the meteorological station of the Department of Meteorology and Climatology of WULS.

The influence of meteorological conditions on PM_{10} concentration was determined through applying regression analysis at confidence levels equal to α=0.05 and α=0.01 for individual months, and separately for the seasons of the year, where all correlated variables were decade values of meteorological parameters (average for a decade or sums for a decade).

Results

Descriptive Statistics

Mean annual and seasonal PM_{10} concentration values calculated for the monitoring stations considered in this paper for 2004-08 are shown in Tables 1 a-c. These tables also show minimum and maximum concentration values, number of values that exceed the allowable limits, and their relative differentiation. Mean yearly and daily concentrations of PM were compared to allowable limits published by the Ministry of the Environment and adjusted to European standards. The current allowable limit for mean annual PM concentration in Poland is equal to D_a=40 $\mu g\cdot m^{-3}$, and for mean daily concentration D_{24}=50 $\mu g\cdot m^{-3}$ with an acceptable frequency of exceedance not higher than 35 days per year at random. Mean yearly PM_{10} concentration in the study area ranged from 20.4 $\mu g\cdot m^{-3}$ to 43.6 $\mu g\cdot m^{-3}$, except for MzWarszNiepodlKom(9) station. Mean yearly PM_{10} concentration at the "heavy traffic" station (MzWarszNiepodlKom, located in the direct centre of Warszawa) was much higher and ranged from 47.1 $\mu g\cdot m^{-3}$ to 58.7 $\mu g\cdot m^{-3}$. Comparing the recorded concentration values with allowable for mean yearly concentration limits, it can be concluded that in 2004 at almost 40% of the measurement locations (6 out of 15), the mean yearly concentration was over 80% of Da value (in 2005 it amounted to 73% of D_a, in 2006 it reached 86% of D_a, 33% in 2007, and 35% in 2008). The exceedance of the allowable limit of D_a=40 $\mu g\cdot m^{-3}$ was recorded in 2004 only at the "heavy traffic" station – MzWarszNiepodlKom. In 2005 the exceedance of D_a value took place at four stations (MzWarszNiepodlKom, MzWarszSGGW, MzWarszKrucza, and MzWarszBielany), whereas in 2006 it occurred at 3 stations (MzWarszNiepodlKom, MzWarszKrucza, and MzWarsz Bielany). In 2007 and 2008, similarly to 2004, the exceedance of D_a was recorded at the MzWarszNiepodlKom station only.

The lowest yearly PM_{10} concentration in the study period occurred at MzWarszBernWoda and MzLegionZegrzIMGW stations.

Tables 1 a-c indicate that the allowable limits for the mean yearly concentration was exceeded at the stations located in the city centre, close to the main roads and in the densely populated districts of Warszawa. The further from the city centre, the lower the yearly concentration, so the allowable limit was not exceeded. The number of daily allowable limit exceedance was also smaller. Mean yearly concentrations reached the highest value at MzWarszNiepodlKom station for all analyzed years.

At all stations in the research period, exceedance of the daily PM_{10} concentrations occurred. The number of exceedance of the daily allowable limit ranged from 3 to 211 days at the considered stations, while this limit cannot be exceeded by 35 days in a year.

In 2004-08 the highest PM_{10} concentration at most of the monitoring stations was recorded in the cold season (covering the heating season). In this period, except for the increased PM emission from both: the sources of energetic fuel combustion and low emission sources, there occur meteorological conditions causing high PM_{10} concentration in the down-to-earth layer of the atmosphere. Such a situation was present in January 2006 when in the whole research area there was one of the most serious and long-lasting episodes of high PM concentration. The cause for this episode was the synoptic situation, demonstrated by the stagnation of cold air mass, related with high pressure over Central Europe. Very low air temperatures in this episode

Table 1a. Descriptive statistics of PM_{10} concentrations from the Warszawa area stations in 2004-08.

		MzWarszSGGW (1)					MzWarszBernWoda (2)					MzWarszZegWSSE (3)					MzWarszBorKom (4)			
I	Year	2004	2005	2006	2007	2008	2004	2005	2006	2007	2008	2004	2005	2006	2007	2008	2004	2005	2006	2007
II	Annual average:	36.9	42.2	34.7	25.5	22.5	20.4	21.6	30.5	26.8	32.3	37.6	39.2	36.2	25.7	26.0	25.7	35.2	38.9	33.0
III	Cold season average (S_z):	40.2	45.8	41.4	28.0	24.3	20.6	22.5	35.8	29.2	31.9	39.9	45.9	44.9	25.1	31.6	26.2	37.0	43.7	41.3
IV	Warm season average(S_l):	33.7	38.6	28.0	23.1	20.7	16.8	20.6	25.2	24.0	32.9	34.8	32.5	27.4	21.4	19.3	25.4	33.4	34.1	27.5
V	S_{24} Min.	3.9	7.8	2.0	1.9	1.9	4.0	2.0	2.0	4.0	5.0	4.0	8.0	8.0	5.0	6.0	4.0	2.0	9.0	8.0
VI	S_{24} Max.	140.2	158.8	320.8	115.9	102.4	109.0	78.0	294.0	102.0	128.0	178.0	155.0	237.0	89.0	112.0	90.0	111.0	224.0	147.0
VII	Number S_{24}> D_{24}	60	84	50	22	16	10	12	39	21	30	45	79	58	16	23	16	50	72	48
VIII	Relative differentiation - Z_w (%)	8.8	8.5	19.2	9.7	8.0	10.1	4.4	17.4	9.7	-1.5	6.8	17.0	24.1	7.9	24.2	1.6	5.1	12.3	20.0

S_{24} – daily average concentration [μg·m^{-3}]; D_a – yearly average permissible concentration [μg·m^{-3}]; D_a = 40 μg·m^{-3}. D_{24} – daily average permissible concentration [μg·m^{-3}]. D_{24} = 50 μg·m^{-3}.

$$S_Z(\%) = \frac{S_Z}{S_L + S_Z} \cdot 100\% \qquad S_L(\%) = \frac{S_L}{S_L + S_Z} \cdot 100\% \qquad Z_W(\%) = S_Z(\%) - S_L(\%)$$

where: S_Z – mean PM_{10} concentration [μg·m^{-3}] in cold season, S_L – mean PM_{10} concentration [μg·m^{-3}] in warm season, Z_w – relative differentiation of PM_{10} concentration between cold and warm half-years [%].

Table 1b.

	MzWarszKrucza (5)					MzWarszZelazWSSE (6)					MzWarszAKrzWSSE(7)				MzWarszUrsynow (8)					MzWarszNiepodlKom (9)				
I	2004	2005	2006	2007	2008	2004	2005	2006	2007	2008	2004	2005	2006	2007	2004	2005	2006	2007	2008	2004	2005	2006	2007	2008
II	31.0	41.7	43.6	34.1	31.7	31.4	32.9	37.7	27.2	26.2	23.9	31.1	34.3	17.2	35.5	32.8	36.5	27.1	27.8	57.3	51.6	58.7	47.1	47.4
III	37.1	49.2	53.5	41.0	33.8	36.8	36.8	47.2	31.9	28.1	29.0	38.0	47.3	19.8	37.5	33.6	41.9	29.3	30.5	58.5	50.6	64.7	47.2	50.0
IV	25.0	34.3	33.7	27.2	29.7	26.1	29.1	28.2	22.5	24.3	19.7	24.3	25.6	15.1	33.4	32.0	31.1	20.4	25.2	56.1	52.7	52.7	47.0	44.7
V	5.1	7.0	3.7	7.3	7.3	9.0	11.0	8.0	6.0	7.0	5.0	7.0	7.0	2.0	6.3	6.3	6.9	7.4	7.1	16.1	12.8	14.4	14.9	16.1
VI	143.0	162.0	289.0	135.5	168.9	128.0	89.0	372.0	106.0	89.0	94.0	120.0	226.0	63.0	156.4	102.6	312.0	91.4	123.3	179.3	125.1	260.4	128.7	150.9
VII	48	107	104	60	52	36	44	47	20	18	10	55	47	3	60	57	55	22	24	211	148	193	136	133
VIII	19.6	17.9	22.8	20.3	6.5	17.0	11.7	25.3	17.2	7.2	19.0	22.1	29.8	13.4	5.8	2.4	14.9	17.9	9.5	2.2	-2.0	10.2	0.2	5.6

Table 1c.

Station	I	II	III	IV	V	VI	VII	VIII
MzLegionZegrzMGW (12)	2004	22.1	26.1	18.0	2.0	113.0	15	18.3
	2005	22.5	25.3	19.6	2.0	108.0	16	12.7
	2006	31.1	33.9	28.2	4.0	219.0	44	9.2
	2007	26.3	30.1	22.5	4.0	97.0	24	14.5
	2008	32.3	35.8	28.9	4.0	183.0	46	10.7
MzPiastowPulask (13)	2004	22.7	27.0	18.5	4.0	102.0	11	18.7
	2005	24.4	26.9	21.9	4.0	91.0	21	10.3
	2006	34.6	38.1	31.1	4.0	135.0	50	10.1
	2007	28.5	22.2	20.6	5.0	75.0	13	3.9
	2008	38.4	38.7	38.1	4.0	188.0	79	0.8
MzOtwockBrzozWSSE14	2004	27.0	30.4	23.7	3.0	142.0	36	12.5
	2005	35.5	35.2	35.9	6.0	208.0	71	-1.0
	2006	32.2	36.3	28.1	3.0	227.0	65	12.8
	2008	28.8	35.9	21.7	2.0	158.0	54	24.6
MzPiaseczDworWSSE (15)	2004	29.5	39.8	25.7	8.0	212.0	29	21.4
	2005	37.2	44.5	37.3	4.0	203.0	79	8.8
	2006	37.1	43.1	31.2	7.0	243.0	65	15.9
	2007	35.2	44.5	33.4	6.0	121.0	67	14.3
	2008	33.4	36.6	29.4	6.0	175.0	48	10.9
MzWarszTarKondra (11)	2004	37.0	39.7	34.3	11.1	180.9	62	7.3
	2005	32.1	33.5	30.7	4.8	131.4	41	4.4
	2006	38.8	45.2	32.4	9.0	296.3	73	16.6
	2007	31.7	33.1	30.4	8.5	130.9	53	4.3
	2008	31.9	33.6	30.3	8.9	256.8	34	5.1

($T_{min.}$-26.0ºC, $T_{avg.}$ -8.0ºC) and low wind speed [25] contributed to a significant increase of PM_{10} concentration. Mean daily PM_{10} concentrations at analyzed stations ranged from 135 µg·m^{-3} at MzWarszPiastPulask (station located in the suburbs of the city) to 320.8 µg·m^{-3} at MzWarszSGGW station. Episodes that took place in January 2006 had a vital influence on the number of exceedances of the daily allowable concentration limit (Tables 1 a-c). The number of exceedances of the daily allowable limit (D_{24}=50 µg·m^{-3}) ranged from 39 at MzWarszBernWoda station to 193 at MzWarszNiepodlKom station.

Since 2007 there has been noticeable improvement of air quality. This improvement was manifested at most stations by a decrease of the number of days with daily allowable limit of exceedance. This situation can be explained by an exceptionally mild winter. Mean air temperature in the heating seasons of 2006/07 and 2007/08 was higher than the mean multi-year temperature by 3.1ºC and 1.2ºC, respectively [26]. This was the cause for lower consumption of fuels than in the previous heating seasons and, therefore, lower emission of pollutants related with energy-production. In consequence, the registered PM concentration was lower in comparison to the previous seasons. The number of days with exceedance of the daily allowable concentration limit decreased by about 50% on average at most of the analyzed stations.

At the stations located in the city centre, the relative differentiation of PM concentration was smaller than at the stations located farther from the city centre and especially away from it. Nevertheless, at the "heavy-traffic" station, located in the middle of the centre of Warszawa (MzWarszNiepodlKom) there was in general no differentiation of PM concentration between the warm and the cold half-years, with Z_w values ranging from -2.04% to +10.2%, and with considerable particulate matter content in the air occurring there through the whole year (this station is situated in a zone with main avenues).

Epidemiological research has shown that an increase of PM concentration by 10 µg·m^{-3} may cause a several percent (2-5%) increase of upper respiratory tract diseases [27]; then a 4 or 10 percent increase in this type of disease may be expected among the inhabitants of Warszawa, who live near large, heavy-traffic roads with big traffic congestion (in comparison to people living in housing located far from such roads) [28].

Spatial Distribution of Particulate Matter Concentration in the Area of Warszawa

Spatial distribution of PM_{10} concentration values is presented in Fig. 1. This spatial distribution of PM, divided into the warm and the cold half-years, shows that the concentration of PM_{10} is characterized by significant variation during a year. This variation is related to the high input from so-called "low emission" in the area of Warszawa agglomeration, generated mostly by processes of combustion in the communal and housing sectors, and related to prevailing climatic conditions.

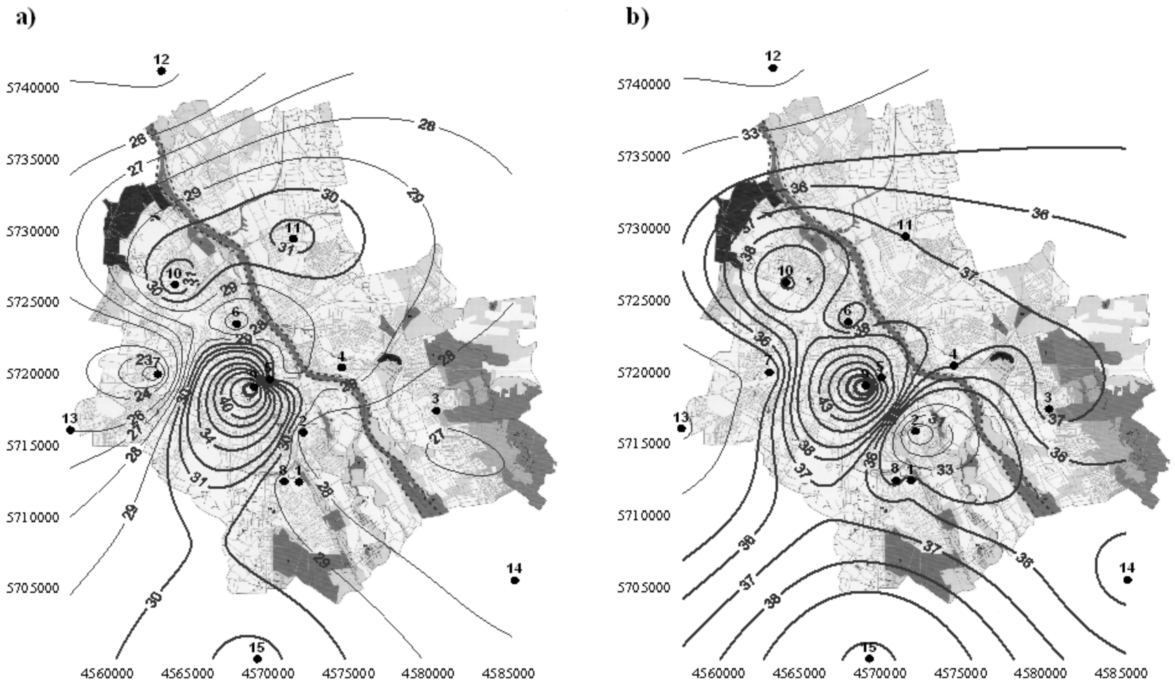

Fig. 1. Isolines of mean PM_{10} [$\mu g \cdot m^{-3}$] concentration in the area of Warszawa agglomeration in 2004-08; 1,2..15 – station number a) warm half-year b) cold half-year.

In the warm half-year the highest PM concentration occurs in the centre of Warszawa at the western side of the Wisła River; however, moving farther from the city centre to the city suburbs, the concentration decreases. In the centre of Warszawa, covered by the isolines of the highest concentration – over 40 $\mu g \cdot m^{-3}$, though there is lack of industrial emission sources, the most dangerous and highest pollution comes from traffic (linear emission sources).

In the cold half-year there is much higher PM_{10} concentration in the whole area of Warszawa. It is particularly visible in these districts where low emission from energetic fuel combustion occurs. These districts have considerable problems with individual heating, and they include: Ursus and fragments of Praga Północ, Praga Południe, and Targówek, as well as on Wawer district due to the large number of single houses. A linear (traffic-related) and a surface source of emission from low emittors (local heat and power plants, household stoves and fire places) occur in the above-mentioned city districts, where they combine with the emission from energetic fuels combustion generated by the Warszawa Heat and Power Plant Group: Vattenfall Heat Poland S.A. – heat and power plant EC Siekierki, EC Żerań, Kawęczyn, and Wola. When all the kinds of emission join together there appear situations of exceedence of the allowable PM_{10} concentration limit. Such situations occur mainly in the cold half-year, when there is higher emission of contaminants from fuels combustion for heating purposes.

Meteorological Conditions – Statistical Analysis

The results of the analysis of regression between PM_{10} concentration and selected meteorological parameters are presented in Table 2. The results show statistically vital relationships particularly between PM_{10} concentration and maximum air temperature, wind speed, and precipitation.

The role of air temperature in the development of particulate matter is reflected well by extreme air temperatures; however, in winter months, a better description of the PM changes is provided by minimum air temperature, while in spring and summer months maximum air temperature is used. The increase of air temperature in the winter period, which resulted in lower intensity of heat- generating processes, directly decreased PM imission; but in the summer the increase of air temperature increased PM imission.

The mean air temperature in January and February had a positive influence on air purity, while in June, July, and August its influence was negative. The most significant relationship between PM_{10} concentration and mean air temperature was found in January both at MzWarszSGGW and MzWarszUrsynow stations, where the R^2 reached 0.71 and 0.73, respectively. The increase of maximum air temperature in January and February caused the decrease of PM concentration but, on the other hand, this increase contributed to the increase of PM imission in May, June, July, and August, which is proved by statistical analysis. The most significant relationship, similarly to mean air temperature, was found for maximum temperature and PM concentration at both considered stations, with determination coefficient values R^2 equal to 0.65 and 0.67. However, minimum air temperature had a positive impact on the decrease of PM_{10} concentration in January and February. The most significant relationship similar to the mean and maximum temperatures, was found for minimum air temperature in January at both considered stations, with R^2 equal to 0.74 and 0.76, respectively.

Table 2. Coefficients of determination (R^2) for the relationship between the linear relationship of particulate matter PM_{10} concentration and meteorological parameters.

Month/ Season	Station	Meteorological elements							
		t	t_{min}	t_{max}	v	P	f	C	T
January	MzWarszSGGW (1)	**- 0.71	**- 0.74	**- 0.65				**+ 0.38	
	MzWarszUrsynow (8)	**- 0.73	**- 0.76	**- 0.67		*- 0.33		**+ 0.50	*+ 0.37
February	MzWarszSGGW (1)								
	MzWarszUrsynow (8)	*- 0.38	**- 0.41	*- 0.31					
March	MzWarszSGGW (1)				*- 0.30				
	MzWarszUrsynow (8)				**- 0.60	*- 0.35			
April	MzWarszSGGW (1)								
	MzWarszUrsynow (8)								
May	MzWarszSGGW (1)			*+ 0.30	**- 0.66		*- 0.31		
	MzWarszUrsynow (8)								
June	MzWarszSGGW (1)								
	MzWarszUrsynow (8)	*+ 0.31		*+ 0.31					
July	MzWarszSGGW (1)								
	MzWarszUrsynow (8)	*+ 0.35		*+ 0.39	**- 0.54			*+ 0.36	*+ 0.32
August	MzWarszSGGW (1)			*+ 0.333	*- 0.29	*- 0.27			**+ 0.60
	MzWarszUrsynow (8)				**- 0.42	*- 0.27			
September	MzWarszSGGW (1)	*+ 0.27		*+ 0.34	*- 0.29		*- 0.28		*+ 0.27
	MzWarszUrsynow (8)			**+ 0.44	**- 0.44	*- 0.36	**- 0.44		**+ 0.52
October	MzWarszSGGW (1)					*- 0.38			
	MzWarszUrsynow (8)					**- 0.52			
November	MzWarszSGGW (1)				*- 0.33	*- 0.29		*+ 0.37	
	MzWarszUrsynow (8)					*- 0.35		*+ 0.22	
December	MzWarszSGGW (1)								
	MzWarszUrsynow (8)								
Winter	MzWarszSGGW (1)	**- 0.52	**- 0.55	**- 0.47					
	MzWarszUrsynow (8)	**- 0.53	**- 0.57	**- 0.46	*- 0.11	**- 0.22		**+ 0.15	
Spring	MzWarszSGGW (1)				**- 0.16				
	MzWarszUrsynow (8)		*- 0.13		**- 0.21	*- 0.15			

Table 2. Continued.

Month/ Season	Station	Meteorological elements							
		t	t_{min}	t_{max}	v	P	f	C	T
Summer	MzWarszSGGW (1)				*- 0.11	**- 0.17			*+ 0.10
	MzWarszUrsynow (8)	**+ 0.15		**+ 0.20	**- 0.37	**- 0.16			
Autumn	MzWarszSGGW (1)				*- 0.14	**- 0.19		*+ 0.10	
	MzWarszUrsynow (8)			*+ 0.10	**- 0.26	*- 0.13		**+ 0.22	*+0.11

-/+ – negative/positive relationship
** – significant at α≤0.01.
* – significant at α≤0.05.
t – mean air temperature (ºC), t_{max} – maximum air temperature (ºC), t_{min} – minimum air temperature (ºC), v – mean wind speed [$m \cdot s^{-1}$], P – total precipitation [mm], f – relative air humidity (%), C – atmosheric pressure [hPa], T – solar radiation [$W \cdot m^{-2}$]

The correlation of PM_{10} concentration and precipitation rate, at both considered stations, shows a positive role of precipitation in purification of the atmosphere. Statistically vital values of determination coefficients ranged from 0.27 in August to 0.52 in October at MzWarszUrsynow station, and from 0.27 in August to 0.38 in October at MzWarszSGGW station.

The increase of air pressure contributed to the increase of PM_{10} concentration. Here, the most significant relationship was found for January at both MzWarszSGGW and MzWarszUrsynow stations. The R^2 values estimated for the relationship of air pressure and PM concentration at those stations in January were equal to 0.38 and 0.50, respectively.

On the other hand, the regression analysis of PM_{10} concentration and mean wind speed has proved a positive role of wind as a basic factor of natural air ventilation. The most significant relationship was found here for March at MzWarszUrsynow station; R^2 was equal to 0.60 and it was also significant for May at MzWarszSGGW station, with a value of 0.66.

The correlation of PM_{10} concentration and relative air humidity proved the positive influence of that parameter on diminishing air pollution, similar to wind speed. Significant relationships of PM_{10} concentration and relative air humidity were found for May at MzWarszSGGW – with R^2 value amounting to 0.31; in August for both analyzed stations R^2 were 0.28 (station MzWarszSGGW) and 0.43 (station MzWarszUrsynow).

Analyzing the statistical relationships of PM_{10} concentration and solar radiation, it was found that solar radiation contributed to the increase of PM concentration. The most significant relationship was established here for August at MzWarszSGGW – R^2 totaled 0.60 and in September at MzWarszUrsynow station R^2 reached 0.52.

Metals in PM_{10}

Except for their concentration, PMs are also characterized by their chemical composition. According to Directive 2004/107/EC and to the Order of the Ministry of the Environment, dated 3 March 2008 (Journal of Laws, Poland, 2008/47/281), the target values for three heavy metals determined in particulate matter are equal to 6 $ng \cdot m^{-3}$ for arsenic, 5 $ng \cdot m^{-3}$ for cadmium, and 20 $ng \cdot m^{-3}$ for nickel.

The degree of air contamination by heavy metals was estimated on the base of mean-yearly concentrations, calculated with the use of daily or periodic measurements. All the concentrations of heavy metals were measured in the samples of PM_{10}, which were collected by filter-based gravimetric measurements.

The content of heavy metals in PM_{10} in the area of Warszawa is measured at four stations: MzWarBernWoda, MzWarszZeganWSSE, and MzWarszZelazWSSE (since 2007), and MzWarszSGGW (periodic measurements).

On the basis of the results of heavy metal concentrations in PM_{10} for 2006-08 in Warszawa agglomeration, it can be concluded that the level of all three measured metals didn't exceed the target levels of arsenic, cadmium, and nickel (Table 3). So the imission of heavy metals in the research area is not a major threat, due to lack of regional, well-developed metallurgic industry.

The range of cadmium concentration was from 0.01 $ng \cdot m^{-3}$ to 4.53 $ng \cdot m^{-3}$. Mean yearly concentrations of cadmium in PM_{10} ranged from 0.6 $ng \cdot m^{-3}$ to 2.07 $ng \cdot m^{-3}$. At MzWarszZelazWSSE station, located in the city center, the mean concentrations of cadmium reached 1.25 $ng \cdot m^{-3}$ in 2007 (25% of D_a) and 0.6 $ng \cdot m^{-3}$ in 2008 (12% of D_a). At MzWarszZeganWSSE station, located in the area of prevailing low emissions from the energetic fuels combustion, the mean yearly cadmium concentration amounted to 2.07 $ng \cdot m^{-3}$ in 2007 (over 41% of D_a) and 0.77 $ng \cdot m^{-3}$ in 2008 (15% of D_a).

The lowest yearly concentrations of cadmium in PM_{10} occurred at MzWarszBernWoda station (the southern part of the city), reaching 0.42 $ng \cdot m^{-3}$ in 2007 (about 8% of D_a) and 0.62 $ng \cdot m^{-3}$ in 2008 (which is 12% of D_a).

The yearly course of cadmium in PM_{10} is most significantly reflected by the areas of low emission from coal

Table 3. Mean yearly and seasonal concentrations of heavy metals [ng·m^{-3}] in PM_{10} at the stations located in Warszawa.

Station	MzWarszBernWoda			MzWarszZeganWSSE		MzWarszZelazWSSE	
Lear/parameter	2006	2007	2008	2007	2008	2007	2008
	As [ng·m^{-3}]						
Mean	0.08	0.14	0.18	0.18	0.07	0.12	0.15
Warm half-year	0.07	0.17	0.16	0.11	0.03	0.07	0.08
Cold half-year	0.10	0.10	0.20	0.29	0.11	0.19	0.24
Minimum	0.03	0.03	0.03	0.01	0.01	0.01	0.01
Maximum	0.55	0.60	1.18	0.67	0.72	0.35	0.59
Standard deviation	0.08	0.14	0.21	0.17	0.12	0.11	0.20
	Cd [ng·m^{-3}]						
Mean	0.57	0.42	0.62	2.07	0.77	1.25	0.60
Warm half-year	0.43	0.30	0.57	1.88	0.72	1.27	0.74
Cold half-year	0.71	0.55	0.68	2.30	0.83	1.23	0.44
Minimum	0.01	0.01	0.05	0.30	0.30	0.30	0.30
Maximum	4.50	1.60	3.10	4.00	2.78	2.60	3.69
Standard deviation	0.53	0.30	0.49	1.36	0.45	0.73	0.61
	Ni [ng·m^{-3}]						
Mean	4.54	5.61	5.64	2.85	3.07	1.49	2.57
Warm half-year	4.28	5.18	6.78	4.90	3.92	2.35	3.52
Cold half-year	4.79	6.12	4.14	0.80	2.24	0.80	1.44
Minimum	1.00	1.00	0.50	0.80	0.80	0.80	0.80
Maximum	27.00	22.00	19.70	11.00	11.60	7.00	10.63
Standard deviation	3.18	4.11	4.26	3.94	2.29	2.07	2.47

combustion. At the stations of MzWarszZeganWSSE and MzWarszBernWoda the concentrations of cadmium in PM_{10} were siginificantly higher in the cold half-year. However, in the area of the city centre, at MzWarszZelazWSSE station, the concentration of cadmium in PM_{10} was higher in the warm half-year (Table 3).

The recorded concentrations of nickel in PM_{10} were generally higher than of other metals. The range of nickel concentrations was from 0.5 ng·m^{-3} to 27.0 ng·m^{-3}. Mean yearly values of nickel concentration in PM_{10} ranged from 1.49 to 5.64 ng·m^{-3}. Mean yearly concentrations of nickel at MzWarszZelazWSSE station ranged from 1.49 ng·m^{-3} in 2007 (which is 7.5% of D_a) to 2.57 ng·m^{-3} in 2008 (which is 12.9% of D_a). At MzWarszZeganWSSE the mean yealy concentration of cadmium was 2.85 ng·m^{-3} in 2007 (14.3% of D_a) and 3.07 ng·m^{-3} in 2008 (15.4% of D_a). The highest yearly concentrations of nickel in PM_{10} occured at MzWarszBernWoda station, from 4.54 ng·m^{-3} in 2006 (22.7% of D_a) to 5.64 ng·m^{-3} (28.2% of D_a). Mean yearly concentration of arsenic in PM_{10} was 0.18 ng·m^{-3} (3% of D_a). However, the mean daily values of arsenic concentration in PM_{10} ranged from 0.01 ng·m^{-3} to 1.18 ng·m^{-3}. The highest concentrations of Arsenic were present at MzWarszBernWoda station.

Conclusions and Discussion

Based on the analysis performed in this paper, it could be concluded that the air quality in the area of Warszawa is still unsatisfactory. A positive occurrence is the tendency of the levels of contaminants to decrease in recent years, especially these of sulphur dioxide and carbon monoxide; however, there are still records of exceedence of the allowable PM_{10} limits. Although many activities were implemented in the frame of air conservation programs, a satisfactory result has not yet been achieved. It is, first of all, the result of the specific character of PM_{10} from many emission sources. The emission from large point sources was quite easily reduced. Then, the vital problem is the linear emission sources related to traffic and the scattered emissions from low sources. These types of emission are the most difficult to be controled.

The main cause of the existence of high PM concentration in Warszawa is the dynamic development of transportation and ever-increasing number of cars, which causes during rush hours the concentration to become several times higher than off rush hours or on weekends [26, 28]. A study performed in highly urbanized areas of California has shown that vehicles are at present the greatest source of PM_{10} emission [29]. Also, in European countries the emission form motor vehicles becomes the most vital source of air pollution [30]. Nowadays, in Europe the ratio of PM_{10} emissions from the transport sector to emissions from the energy sector (along with the communal and municipal sectors) reaches 0.8 [31]. The results of recently published scientific papers show that the process of a constant increase of vehicle intensity on the roads has a close correlation with an increasing threat for many people from the presence of PMs [8, 32, 33]. Such correlation causes the need to use means for limiting the impact of traffic particulate matter on human health, which requires extending the monitoring of air quality in the area of Warszawa, especially near streets of high traffic congestion (at present – there is one station MzWarszNiepodlKom). The construction of bypasses round the city is also vital, which would direct the transit outside the city limits. First of all two bypasses should be constructed, which have been planned for many years: the "city-centre bypass" and the "inner-city bypass"; also the upgrade of the transport system and the traffic management system ought to be realized.

The second important source of PM in the research area is the so-called "low emssion", occurring in the heating season, generated by the processes of combustion in the communal and housing sectors. This emission is conditioned by the quality of fuel used by individual inhabitants. The combustion of cheap and low-quality fuel and the combustion of litter in home fireplaces are the most difficult problems to be addressed. The priority is the elimination of individual house stoves and fireplaces, which concerns, in particular, such districts as Ursus, Praga Północ, Południe, Targówek, and Wawer.

In 2004-08 the meteorological conditions explained 22.4% to 76.2% of the decade variability of PM concentration in the individual months, and 9.5% to 56.8% in the seasons of the year. The most significant influence of meteorological conditions was present during the winter, especially in January.

The regression analysis has found evidence for statistically vital relationships of PM_{10} concentration and meteorological parameters, especially including maximum air temperature, wind speed, and precipitation.

High PM_{10} concentration was recorded most frequently for weather conditions characterized by low air temperature, low wind speed, and high atmospheric pressure without precipitation. Similar research results were achieved by Van der Wal and Jansen [19], Elminir [20], Turahoğli et al. [21], and Kalbarczyk et al. [24].

Research on the content of selected metals in PM, presented in this paper, confirms that the target values of arsenic, cadmium, and nickel concentrations in PM_{10}, determined by Directive 2004/107/WE, were not exceeded at all stations in 2006-08; the recorded concentrations of these heavy metals were low. The concentrations of the analyzed metals in the research area are much lower than in other cities of Poland and in other parts of the world, where there is a significantly higher content of metals in PMs [34-38].

The current state of knowledge on the negative impact of fine matter on various components of the environment, especially on living organisms [6, 7], along with the evidence of high PM_{10} concentrations in the area of Warszawa [23, 26], created the need to extend the measurements of particulate matter composition at other stations located near roads with big traffic congestion. Moreover, much stress is often laid even on small quantities of metals emitted in the atmosphere, which are contained in fine PMs and may have a negative influence on human health [39, 40].

Analyzing the tendency of air quality changes for the last five years in the area of Warszawa, it was found that there was a danger for not complying with requirements made by the European Union. The time limit, set for June 2011, until which the member countries have postponed the adjustment of PM_{10} concentration on their territories to the currently vital norms, may not be complied with.

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