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W. Trapp

Instytut Badań Systemowych
Polska Akademia Nauk

Systems Research Institute
Polish Academy of Sciences

POLSKA AKADEMIA NAUK

Instytut Badań Systemowych

ul. Newelska 6

01-447 Warszawa

tel.: (+48) (22) 3810100

fax: (+48) (22) 3810105

Kierownik Zakładu zgłaszający pracę:
Prof. dr hab. inż. Zbigniew Nahorski

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Air quality modeling for Warsaw agglomeration

Piotr Holnicki[a,1], Andrzej Kałuszko[a], Zbigniew Nahorski[a,b], Krystyna Stankiewicz[b], Wojciech Trapp[c]

[a] Systems Research Institute, Polish Academy of Sciences, Newelska 6, 01-447 Warsaw, Poland

[b] Warsaw School of Information Technology, Newelska 6, 01-447 Warsaw, Poland

[c] EKOMETRIA, Office of the Studies & Ecological Measurements, Elbląska 66, 80-761 Gdańsk, Poland

Abstract

The paper deals with the investigation of the air quality in the urban area of Warsaw, Poland. Calculations are carried out using the emissions and meteorological data from the year 2012. The modeling tool is the regional CALMET/CALPUFF system, which is used to link the emission sources with the distributions of the annual mean concentrations. Several types of polluting species that characterize the urban atmospheric environment, like PM_{10}, $PM_{2.5}$, NOx, SO_2, Pb, B(a)P, are included in the analysis. The goal of the analysis is to determine the most polluted districts and polluting compounds there, to check where the concentration limits of particular pollutants are exceeded. Then, emission sources (or emission categories) which are mainly responsible for violation of air quality standards and increase the adverse health effects, are identified. The modeling results show how the typical emission sources – the energy sector, industry, traffic and the municipal sector – relate to the concentrations calculated in receptor points, including the contribution of the transboundary inflow. The results indicate regions where the concentration limits are exceeded and action plans are needed. A quantitative source apportionment shows the emission sources which are mainly responsible for the violation of air quality standards. It is shown that the road transport and the municipal sector are the emission classes which substantially affect air quality in Warsaw. Also transboundary inflow contributes highly to concentrations of some pollutants. The results presented can be of use in analyzing emission reduction policies for the city, as a part of an integrated modeling system.

Keywords: urban air pollution, emission inventory, air quality standards, source apportionment

[1] Corresponding author, email: holnicki@ibspan.waw.pl, phone: +48608045344

1. Introduction

The problem related to urban air pollution is nowadays high in the priorities of atmospheric environmental concern. Cities and agglomerations are the most susceptible areas of air pollution due to high concentration of different human activities and related emissions, like industrial, municipal or transport. The main urban agglomerations are also considered in the European scale studies where the City Delta approach has been developed (Thunis et al. 2007) to identify and quantify the systematic differences (deltas) between urban and rural background air quality.

Warsaw, similarly as many other European agglomerations (Lim et al. 2005, Calori et al. 2006, Mediavilla-Sahagún and ApSimon 2006, Buchholz et al. 2013), has recently suffered from high concentrations of some air pollutants which characterize the urban atmospheric environment. These are usually particulate matter, sulfur- and nitrogen oxides, carbon monoxide, some heavy metals, as well as polycyclic aromatic hydrocarbons in some cases. In practice, the adverse impact of some particular pollutants of an urban air quality depends on several individual factors, such as the city location, topography, the structure of the emission field, meteorology, etc. In Warsaw, the composition of the main polluting species, their spatial distribution and the maximum values also reflect the peculiar structure of the local emission field, which is determined by two dominating factors.

The first one, of more general character, relates to coal, which is the main fossil fuel used by the Polish industry and power engineering, but also by the individual housing sector. The district heating system operates in the main part of Warsaw, but in the peripheral districts and the neighboring rural area coal fired is used in individual heating installations, which considerably contribute to the urban air quality. This category of emission sources is responsible for particulate matter pollution (especially $PM_{2.5}$), SO_2, some heavy metals and

B(a)P. The highly toxic B(a)P pollution, resulting from the sources of municipal sector, constitutes a serious general problem in Poland (EEA 2012), also apparent in Warsaw.

The second dominating pollution category relates to traffic-induced emission, due to the steadily increasing number of cars registered in Warsaw, by 80% in the last decade (//wawalove.pl/**Ile-samochodow**-jezdzi-po-**Warszawie**-a1268), as opposite to many other European cities. Traffic originated emission is mainly responsible for NO_X, Pb, CO, C_6H_6 concentrations, but it also contributes to PM_{10} pollutions via the re-suspended particles (Dimitriou and Kassomenos 2014, Kiesewetter et al. 2014). In particular, concentrations of NO_X and PM_{10} show increasing tendency.

An important part of the resulting air pollution in Warsaw is the transboundary inflow of some pollutants coming from distant sources.

Many of the earlier urban scale modeling studies addresses the road transport originated pollutants. Berkowicz et al. (2003) present modeling results of the traffic related NOx and CO pollution in Copenhagen. They consider the vehicle emission factor with differentiation between vehicle types (passenger cars, vans, trucks, buses, etc.), fuel used, engine capacity, emission legislation category. The same pollutants are considered by Buchholz et al. (2013) for Luxembourgh, aiming at reducing their annual mean concentrations. In the emission scenarios for the years 1998-2006, they consider only the most important sources, i.e. the road transport and nonindustrial combustion. A Gaussian dispersion model is used in simulation. An integrated analysis concerning NO_2 and CO concentration in the Turin agglomeration is presented in Calori et al. (2006). The Lagrangian particle model is applied to the simulation of emission and meteorological scenarios. Results are discussed as a base for possible improvements. The impact of the road transport on the urban air quality in London is discussed in Oxley et al. (2009). In this case NO_2, NOx and PM_{10} are considered as the main traffic-related pollutants. Integrated modeling assessment is applied to link emissions, pollution concentrations, human exposure and the possible emission abatement techniques. London air pollution is also discussed by Mediavilla-Shagún and ApSimon (2006), who consider integrated analysis of PM_{10} pollution. The aim of the study is to provide a tool to assess and select the most effective emission reduction scenarios.

Spatial and temporal patterns of air pollution are also studied. Dimitriou and Kassomenos (2014) apply a linear regression model to reconstruct daily PM10 and PM2.5 concentrations in Paris. They consider 4 local and 11 surrounding districts as emission sources affecting urban air quality. Patton et al. (2014) discuss the spatial and temporal patterns in traffic-related concentrations near the main roads in Boston, for NO_2, NOx, $PM_{2.5}$, and CO. In Poland air quality modeling studies for Mazovian Voivodship, containing Warsaw, as the main agglomeration have been performed by Trapp (2010). The gaseous and particulate matter pollutions are considered.

2. Warsaw case study implementation

2.1 The study area and spatial resolution

The results presented concern the analysis of air pollution in the Warsaw agglomeration, wherein for the simulation of pollutant dispersion processes Gaussian puff model CALPUFF v.5 was used (Scire et al. 2000). Meteorological fields are generated by the CALMET cooperating preprocessor, taking into account, among other factors, the impact of terrain topography, orography and aerodynamic roughness of the ground. The aim of simulation is to obtain the spatial maps of year average concentrations of the main urban pollutants, to show the regions where the pollution limits are exceeded and to identify emission sources responsible for these violations. The results, including the earlier uncertainty estimates (Holnicki and Nahorski 2015), may be useful in formulation of the respective regulatory actions and emission reduction strategy (compare e.g. Carnevale et al. 2012, Lim et al. 2005, Mediavilla-Sahagún and ApSimon 2006, Pisoni et al. 2010).

The air quality analysis presented below deals with the primary and secondary polluting compounds, which are characteristic for the urban atmospheric environment, including transboundary pollution inflow from distant sources. The main polluting compounds, discussed in this study, are shown in Table 1.

Table 1. Air pollutants considered (primary and secondary).

Emission / primary pollutants	**Secondary pollutants / particulate matter**
SO_2 – sulfur dioxide	$SO_4^{=}$ – sulfate aerosol
NO_X – nitrogen oxides	NO_3^{-} – nitrate aerosol
	HNO_3 – nitric acid
PPM_{10} – primary PM, $\Phi \leq 10\ \mu m$	
PPM_{10_R} – re-suspended PPM10	$PM_{10} = PPM_{10} + PPM_{10\_R} + SO_4^{=} + NO_3^{-}$
$PPM_{2.5}$ – primary PM, $\Phi \leq 2.5\ \mu m$	
$PPM_{2.5\_R}$ – re-suspended PPM2.5	$PM_{2.5} = PPM_{2.5} + PPM_{2.5\_R} + SO_4^{=} + NO_3^{-}$
CO – carbon monoxide	
C_6H_6 – benzene	
NH_3 – ammonia	
BaP – benzo(a)pyrene	
Ni – nickel	
Cd – cadmium	
Pb – lead	
As – arsenic	
Hg – mercury	

The numerical simulation is based on the emission and meteorological dataset for the year 2012. The annual mean concentrations of the pollutants listed in Table 1 were evaluated and compared with the EU and national limits (CAFE 2008, ME 2012). Accuracy of calculation was assessed. The Warsaw metropolitan area (about 520 km2 within the administrative borders), shown in Fig. 1, is discretized for the computational reasons using the homogeneous grid 0.5 km x 0.5 km.

CALLPUFF is a new generation Gaussian puff model (Scire et al. 2000, Trapp 2010), which operates in the Lagrangian system of coordinates and considers the geophysical data, the temporal and spatial variability of meteorological conditions in three dimensions. It is a multilayer, non-stationary model designed for calculating concentrations of many substances, emitted by different types of sources. Chemical and physical transformations of pollutants are considered.

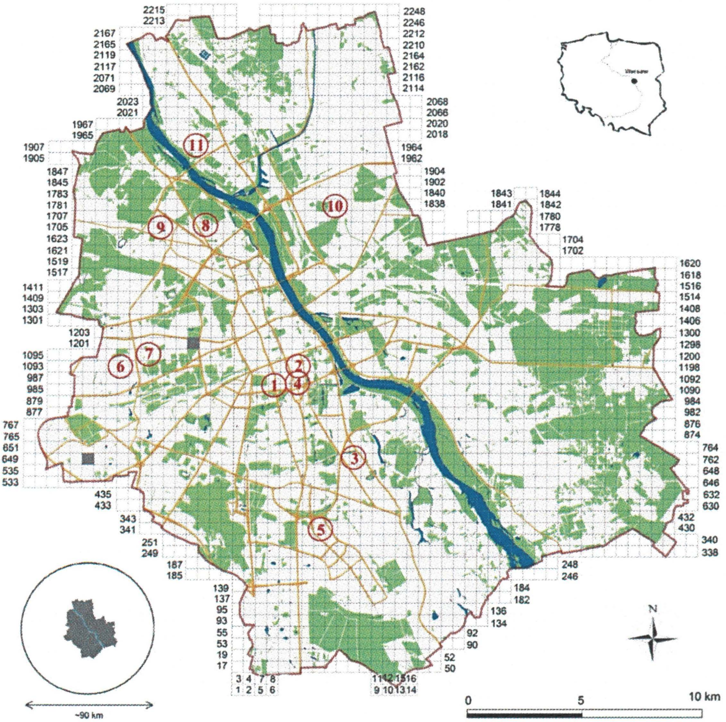


Fig. 1. The Warsaw area – locations of the fictitious receptor points and the monitoring stations

CALPUFF/CALMET modelling system has been used in a number of studies to investigate gaseous (Elbir 2003, Holnicki and Nahorski 2013) and particulate matter (Villasenor et al. 2003, Huber et al. 2004, Trapp 2010, Tartakovsky et al. 2013, ETC/ACM

2013) pollutants dispersions, both in the regional and urban scale. Validation studies (Oshan et al. 2006, Dresser and Huizer 2011) also showed a satisfactory correlation with the observations, especially for annual mean concentrations. This fact is also confirmed in this study by the model performance estimates presented in Section 4. On the other hand, Holmes and Morawska (2006) and Brode (2012) state that the model is not recommended to analyze the near field and short-term episodes.

The concentrations are computed at 2248 fictitious receptor points, which are located in the centers of the basic grid elements shown in Fig.1. The same spatial resolution applies to the local, spatial and line emission sources, located inside the administrative borders. The local emission field is wider than the receptor area – the sources located in the outskirt of Warsaw, but inside the circle of the diameter about 90 km (shown as the bottom corner icon in Fig. 1) are also included in the emission field, but the variable spatial resolution is used in this case. Two exemplary receptors marked gray in Fig. 1 – #658 (residential area) and #1217 (crossroad) – are used in Section 3 to illustrate the relation between a source apportionment and a receptor's location. The figure also shows the locations of the monitoring stations, observations of which have been utilized in the assessment of the model performance (see Section 4).

2.2 Emission dataset

The main activities influencing the Warsaw air quality are: road transport, residential heating, energy production, and industry. In addition to the activity rates in the above sectors, technology emission parameters were collected. The aggregated emissions from the basic sectors in Warsaw agglomeration in the year 2012 are presented in Table 2 below (WIOS, 2012). The table shows the emission volumes of the main pollutants and the share of each sector in the total emission.

Table 2. Emission volumes by sector in Warsaw agglomeration in the year 2012

Sector	SO_2		NOx		PM_{10}		$PM_{2.5}$		CO		C_6H_6	
	[Mg]	[%]	[Mg]	[%]	[Mg]	[%]	[Mg]	[%]	[Mg]	[%]	[Mg]	[%]
Energy/industry	12478	87,6	7781	40,0	803	10,5	264	8,8	2504	7,5	-	-
Residential	931	6,5	614	3,2	2105	27,4	1603	53,3	8830	26,5	0,075	0,0
Transport	837	5,9	11051	56,8	4772	62,1	1141	37,9	21955	66,0	317,4	100,0
Total	14246	100	19446	100	7680	100	3008	100	33289	100	317,5	100

Table 2 (continued). Emission volumes by sector in Warsaw agglomeration in the year 2012

Sector	As		Cd		Ni		Pb		BaP	
	[kg]	[%]	[kg]	[%]	[kg]	[%]	[kg]	[%]	[kg]	[%]
Energy/industry	23,7	12,9	13,5	5,4	754,1	40,4	82,6	1,6	61,8	17,2
Residential	160,2	87,1	233,9	93,9	736,9	39,5	1473,7	29,3	204,0	56,7
Transport	-		1,6	0,6	374,2	20,1	3469,6	69,0	94,0	26,1
Total	183,9	100	249,0	100	1865,2	100	5025,9	100	359,8	100

Emission field in an urban area usually means concentration of a large number of sources in the study domain, which vary in technological parameters, emission characteristics, composition of emitted compounds, and also the assigned uncertainty (Holnicki and Nahorski 2015). To take into account specific technological characteristics of the different emission sources, the total emission field was split down into the following categories: point (high/low), area, and line (mobile) sources. A separate class of the high point sources has been defined to reflect specific technological characteristics of the professional energy sources (mainly power or heating plants, e.g. feeding the district heating system operating in Warsaw).

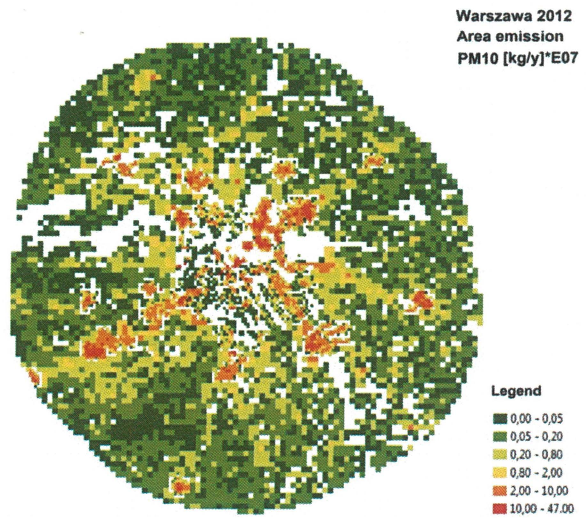
Finally, the aggregate emission field was divided into the six basic categories, mainly based on technological parameters, emission characteristics and the intrinsic data uncertainty. The distinguished emission categories, including the quantity of the individual sources in each category, are:

- High point sources (24) – mainly the energy sector (power or heating plants);
- Low point sources (3880) – other point sources (industry or the local heating installations);
- Area sources 6962) – housing, residential sector;
- Line sources (7285) – urban road transport;
- Agriculture sources (256) – agricultural activity, mainly in peripheral districts and suburban area (also represented as the area sources);
- BC – boundary conditions (the transboundary pollution inflow from sources of the national/regional level).

As mentioned before, the total emission field encompasses the Warsaw area in the administrative borders and the surrounding belt of approximately 30 km width (compare Fig. 1). Location of the point sources are given in the geographical coordinates. The area and line sources are represented as basic grid emission squares, 0.5 km x 0.5 km, inside Warsaw administrative borders, and more aggregated, 1 km x 1 km, in the surroundings. The local city areas in the suburban belt are also represented by the nested 0.5 km x 0.5 km grid (compare Fig. 2 below).

Air pollutants originated from the agriculture sector have a minor impact on the urban atmospheric environment, especially when compared with the activity of the transportation system, the industry or residential sector. The sources which represent the emissions from farming, soil cultivation and cultivating machinery, are mainly located in the suburban districts and are represented by the area grid cells with aggregated spatial resolution, 5 km x 5 km.

The shape and the structure of the emission fields considered below are illustrated by two exemplary PM_{10} emission maps shown in Fig. 2, which represent the area (top) and line (bottom) sources, respectively. The maps take into account the variability of the spatial resolution in the urban area and the surroundings.



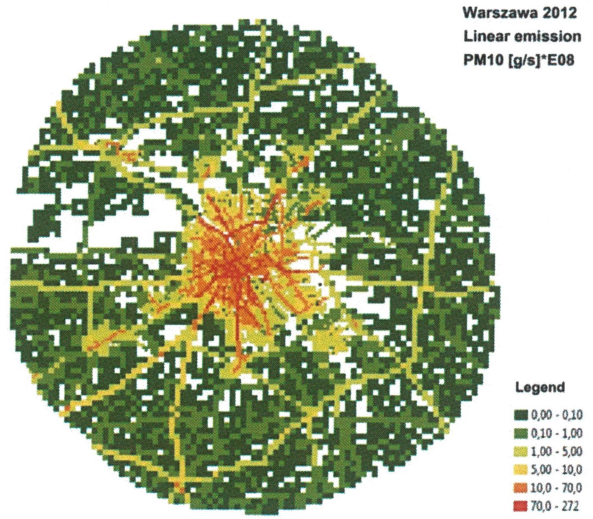


Fig. 2. The PM_{10} emission fields for the area sources (top) and the line sources (bottom).

2.3 Meteorological data

Meteorological data for the year 2012, used in computations, cover the main fields, such as wind, pressure, temperature, humidity, cloudiness, precipitation intensity. The original data sequence (wind rose shown in Fig. 3) was re-analyzed by the mesoscale numerical meteorological WRF model (NCAR 2008) and then used by the CALMET preprocessor to prepare the input data required by CALPUFF in the proper format. Within this step, additional parameters are also generated, e.g. inversion height, atmospheric stability class, etc. The topography, orology and land coverage are used to assess the aerodynamic roughness parameter and generate the final wind field which is interpolated to the grid 0,5 km x 0,5 km, used by the main model. The data (similarly as for the emissions) are finally prepared as a sequence of one hour episodes (8785 time steps) which cover the full year.

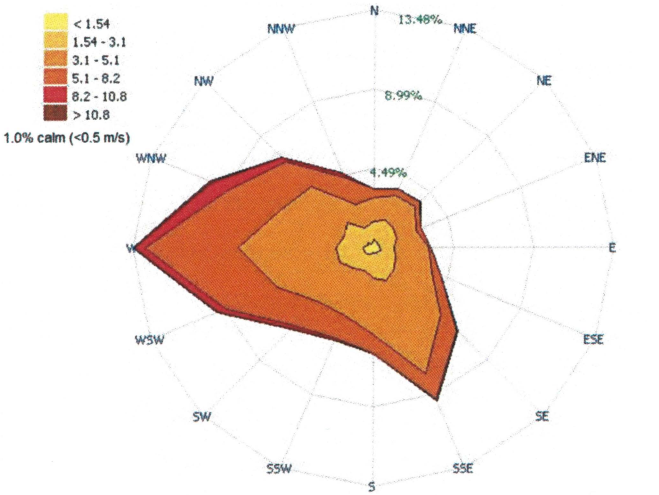


Fig. 3. Wind rose for the Warsaw agglomeration in the year 2012 (WIOŚ 2012)

3. Modeling results

The main objective of numerical simulation was to assess the annual mean concentrations of the considered polluting species at the receptor sites. The recorded concentration values of the main polluting components that characterize Warsaw atmospheric environment, are interpolated to the pollution maps shown in the figures below (ArcMap software is used). Due to the space limits, the resulting concentration maps presented below relate to the most characteristic pollutants of those listed in Table 1, namely: particulate matter, nitrogen and sulfur oxides, lead, and benzo(a)pyrene.

Figure 4 shows concentration maps of the particulate matter, PM_{10} and $PM_{2.5}$, which strongly affect air quality in most of urban agglomerations. As seen in Table 2, in the Warsaw domain, these pollutants get into the atmosphere mainly from the road transport system (PM_{10} – 62% and PM2.5 – 27%) and from the residential sector (PM_{10} – 38% and $PM_{2.5}$ – 53%) (Table 2). The transboundary inflow from distant sources is also significant and mainly contains the fine fraction of $PM_{2.5}$, which is confirmed below in Fig. 4. As seen in Fig. 4, the annual mean concentrations, both for PM_{10} and $PM_{2.5}$, exceed the limits (CAFE 2008) adopted by the Polish Ministry of Environment (ME 2012): 40 µg/m3 for PM_{10} and 25 µg/m3 for $PM_{2.5}$. Violation of these standards occurs mainly in the central (PM_{10}) and S-W districts ($PM_{2.5}$), but the composition depends on the dominating emission category and on receptor location, and is different for both PM fractions (see below).

PM_{10} concentrations are correlated with the topology of the arterial streets (mobile sources) – see Fig. 4, while those of $PM_{2.5}$ more depend on emissions from residential sources and trans-boundary inflow. Figure A1 shows the contribution of emission classes to the PM_{10} or $PM_{2.5}$ pollution depending on the receptor's location. The traffic sources dominate in the central districts and in the vicinity of the main streets, but in the peripheral districts there is a strong impact of the area sources of the local heating installations.

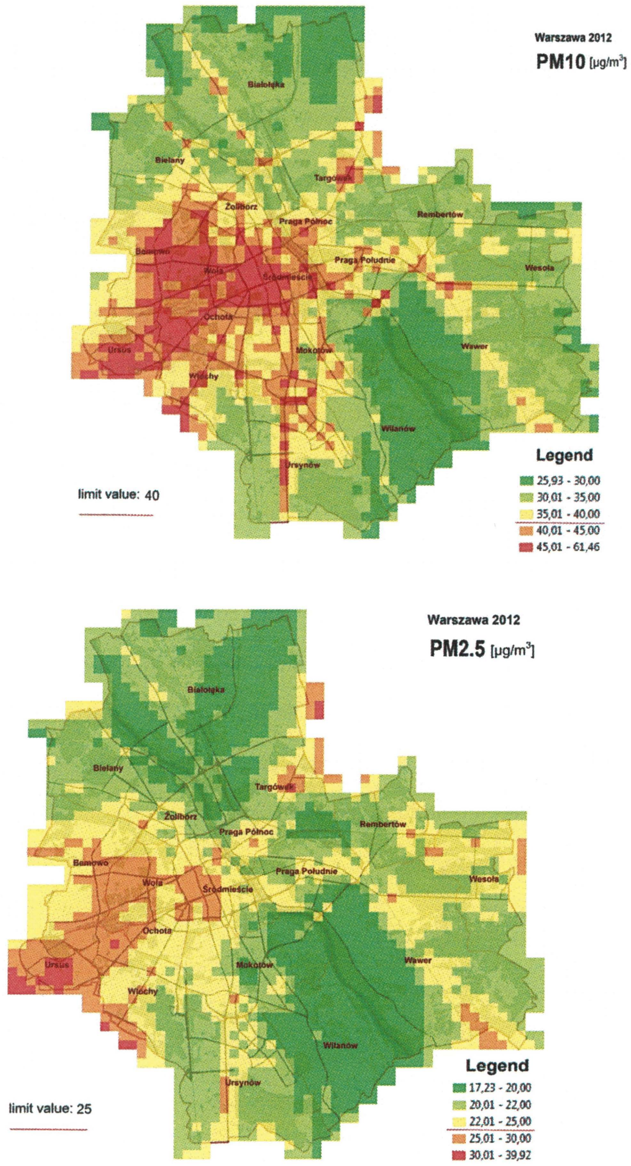


Fig. 4. The computed annual mean concentrations of PM_{10} (top) and $PM_{2.5}$ (bottom)

The linear structure of the CALPUFF model allows to individually compute the contribution of each source to an overall concentration in any receptor site. The differences in source apportionment between PM_{10} and $PM_{2.5}$ are illustrated in Fig. 5, where two exemplary receptors are considered: # 1217 – the crossroad of two arterial streets, and # 658, representing a residential area (S-W periphery). The vicinity of the main crossroad (1217) shows the strong domination of the line sources in PM_{10} pollution. The major contributor in this case is the re-suspended emission (compare Table 1), with the dominating coarse fractions of PM. The fine components of the re-suspended PM pollution constitute only about 14%. On the other hand, in the case of $PM_{2.5}$ pollution, the impact of the housing sector (area sources) and that of the trans-boundary inflow dominate at both receptor sites. This follows from the very high share of the fine PM fractions in the long distance transport, with relatively high participation of the sulfate and nitrate aerosols in the transported air pollutants, since time is a key factor in the aerosol formation (Oxley et al. 2009, Trapp 2010, ETC/ACM 2013). Due to low deposition velocity, these fractions remain suspended longer in the atmosphere. The diagrams in Fig. 5 shows that the overall $PM_{2.5}$ concentration in the residential area is higher than near the crossroad, opposite than for PM_{10}. Moreover, the total share of $PM_{2.5}$ concentration constitutes about 67% of the total PM pollution at the housing receptor and only 47% at the crossroad.

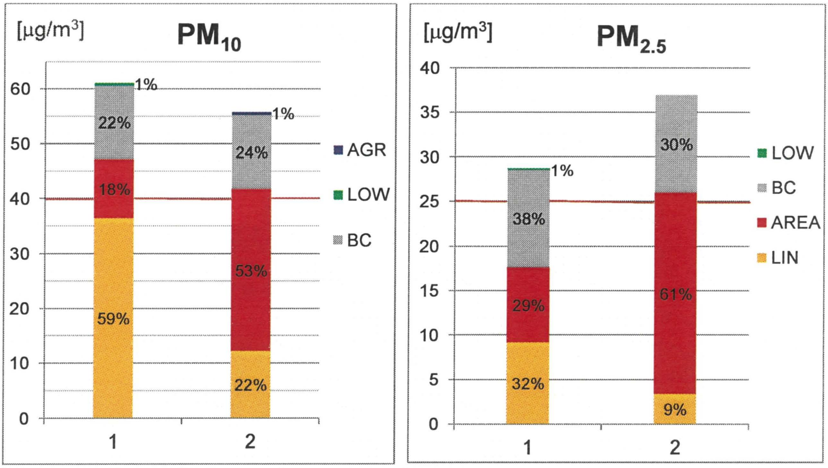


Fig. 5. The share of emission categories depending on receptor's location (PM_{10}, $PM_{2.5}$)
(1) Receptor # 1217 (crossroad), (2) Receptor # 658 (housing).

Abbreviations used in Fig. 5 (and below in Fig. 7 and Fig. 9) mean the emission categories: LIN – line sources, AREA – area sources, HIGH – high point sources, LOW – other point sources, AGR – agriculture sources, BC – boundary conditions (trans-boundary inflow).

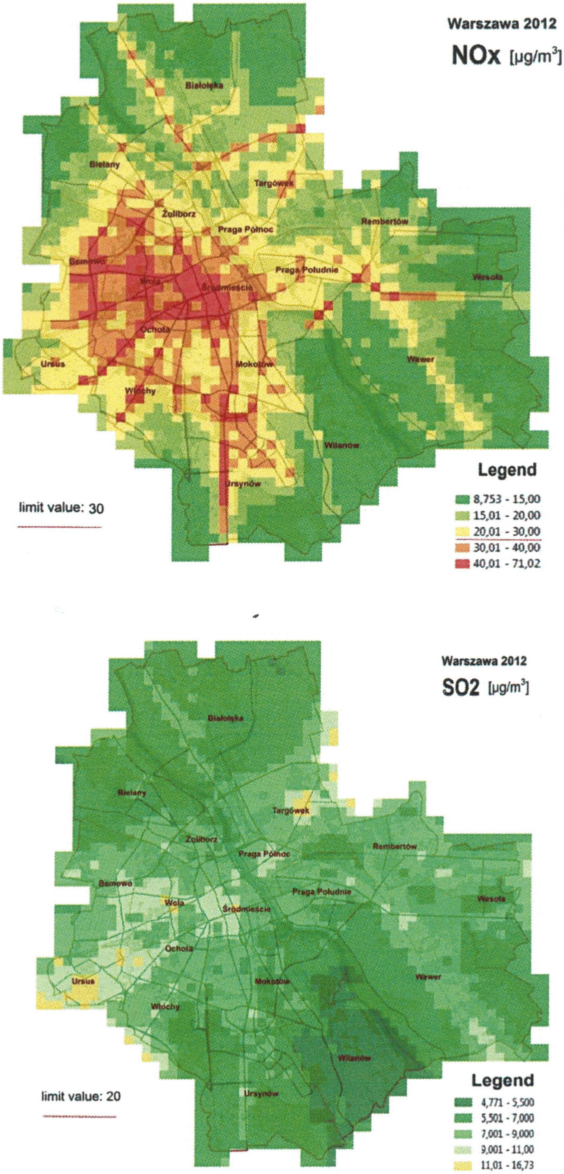


Fig. 6. The computed annual mean concentrations of NO_x (top) and SO_2 (bottom).

Concentration maps for gaseous NO_X and SO_2 pollutions are shown in Figure 6. The spatial distribution of NO_X concentration (Fig. A2, upper panel), which is a typical traffic-originated pollutant, reflects the topology of the road network, where the maximum values coincide with the main arterial streets (compare also Patton et al. 2014). This is additionally confirmed by the source apportionment graph for NO_X pollution at the crossroad receptor site (Fig. 6 left). Concentrations of the nitrogen oxides strongly violate (over twice) the limit value of 30 $\mu g/m^3$. This occurs mainly (see Fig. 6, upper panel) in the city center and in the neighborhoods of the main streets

Concentrations of SO_2 are below the air quality limit of 20 $\mu g/m^3$ (CAFE 2008, ME 2012) on the whole Warsaw territory. The pollution structure (compare Fig. A2) depends on the receptor's location and reflects the neighboring emission sources. Fig. 7 shows the share of emission classes for NO_X and SO_2 at the same receptor points, # 1217 and # 658. In the first case (NO_X), a definite domination of the line sources is seen, especially at the crossroad receptor where 93% of pollution come from the mobile sources. On the other hand, all the emission categories contribute to SO_2 pollution, with the significant domination of the point sources (87%) and a comparable share of the area and line emission (Table 2). Due to the high stacks of the main point sources – power/heating plants – apportion of the first category to the resulting SO_2 concentration over the Warsaw area is minor. As a consequence, the residential and line emission sources decide on the spatial distribution of this type pollution. The area sources (mainly the individual, coal fired installation of the housing area) definitely dominate in pollution of the residential districts (Fig. 7, right panel), while the traffic emission (line sources) contributes remarkably to SO_2 concentration near the arterial streets and crossroads.

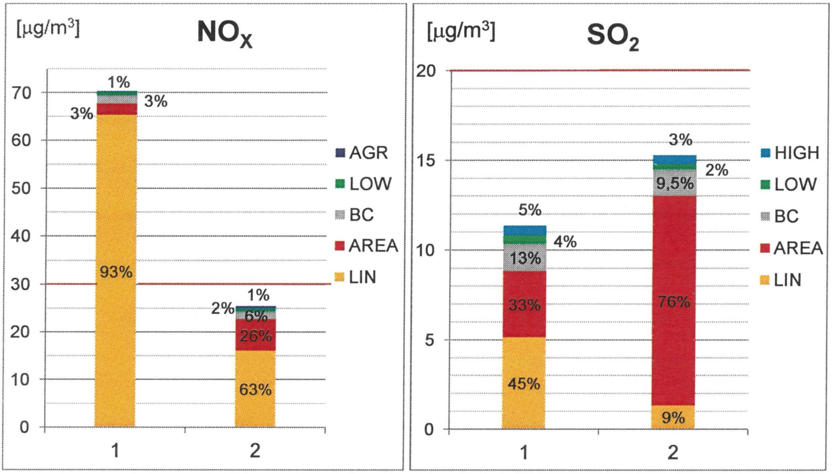


Fig. 7. The share of emission categories depending on receptor's location (NO_X , SO_2)
(1) Receptor # 1217 (crossroad), (2) Receptor # 658 (housing).

Concentration maps for Pb and B(a)P are presented in Figure 8. The lead concentrations in Warsaw are definitely below the limit value (500 ng/m^3), but the spatial distribution apparently coincides with the shape of the street network. Similarly as for NO_X, lead pollution is highly correlated with emission from the line sources, but at very low concentration levels. According to WIOŚ (2012), some trace Pb emission still relates to the traffic, with a small share of old vehicles using leaded gasoline. As seen from Table 2, the line sources are responsible for 69% of the total Pb emission, while the remain part comes from the residential sector. As also shown in Fig. A3, the line sources (which dominate in the center) and the local area emission are the main emission categories responsible for these pollutants.

The severe environmental problem is connected with the B(a)P pollution, responsible for strong adverse health effects (EEA 2012). The concentration limit, adopted by the Polish Ministry of Environment, 1 ng/m^3 (EEA 2012, ME 2012) is surpassed in the whole area of Warsaw agglomeration. The highest standard violations, about 3–4 ng/m^3, occur in the peripheral districts, mainly near the S-W border (Włochy and Ursus districts). The main source of this pollution is the housing sector – the local, coal fired heating installations, to a great extent similar to those which are responsible for high concentrations of $PM_{2.5}$ or SO_2.

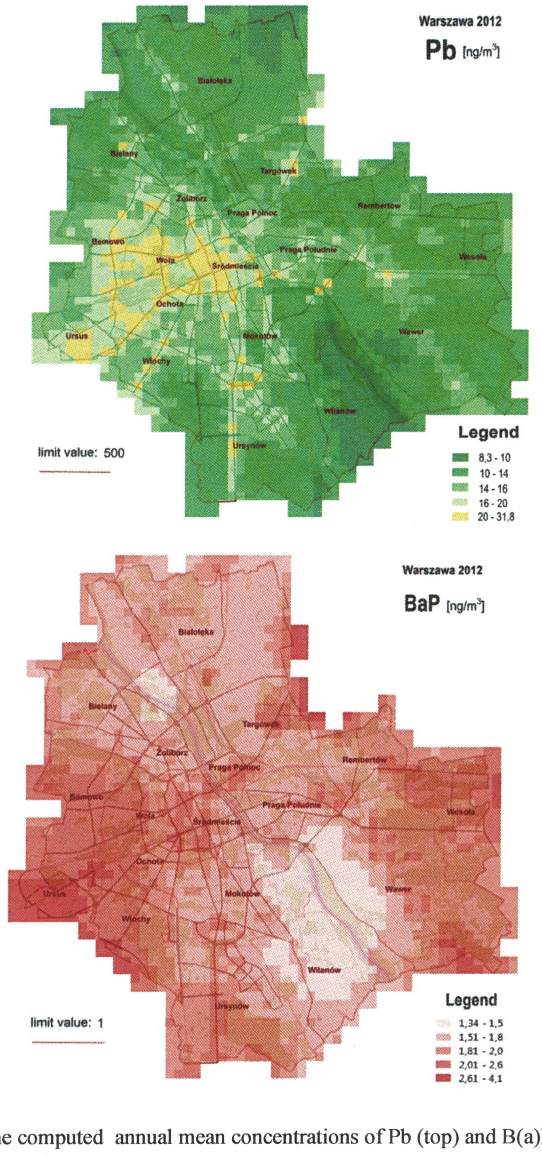


Fig. 8. The computed annual mean concentrations of Pb (top) and B(a)P (bottom).

The above facts are confirmed by the diagrams shown in Fig. 9. Lead concentration at the crossroad site strongly depends on the traffic intensity, but the contribution of the local heating dominates in the residential areas. The local heating activity is also the main source of very harmful B(a)P pollution, which is mainly observed in the peripheral districts of the agglomeration. Local coal combustion can be a source of about 80% of B(a)P pollution in such regions, as shown in Fig. 8 (lower panel). Moreover, about 67% of the B(a)P limit concentration comes from the trans-boundary inflow (compare also Fig. A3), from similar sources located in the outskirt of the study area.

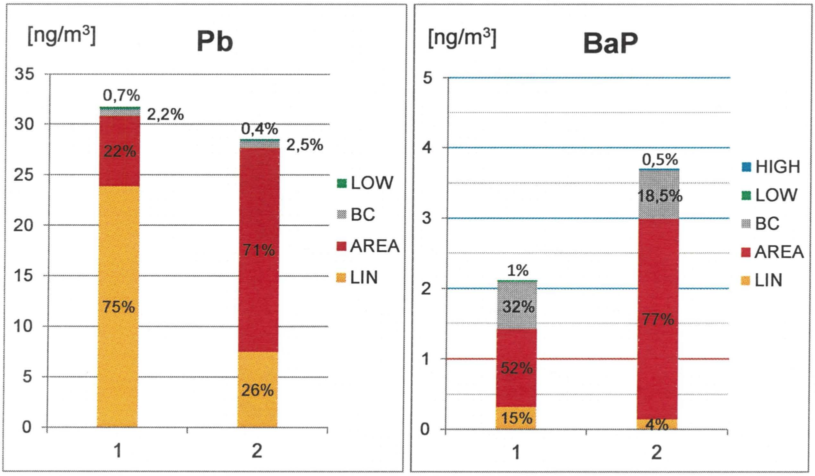


Fig. 9. The share of emission categories depending on receptor's location (Pb , B[a]P)
(1) Receptor # 1217 (crossroad), (2) Receptor # 658 (housing).

4. Assessments of model performance

Comparison with observations allows for evaluation of the overall model accuracy. Fig. 1 shows the locations of 11 stationary air quality monitoring stations, 9 of which were operating in 2012. Short characteristics of each station are presented in Table 3, including the list of the polluting components which are observed in them. The measurements of 1-h concentrations are performed automatically, and some 24-h average observations are gathered manually. In particular, the operation of the station # 7 is based on the manual, 24-h measurements of the components of PM_{10}: heavy metals and polycyclic aromatic hydrocarbons, including B(a)P.

The annual mean concentrations based on the observation data were compared with the computed concentrations at the same receptor sites. As shown in Table 3, each station measures the selected set of compounds. Referring to the main pollutants considered in the study, the following numbers of the measurement results are available: NO_X – 5, SO_2 – 5, PM_{10} – 4, $PM_{2.5}$ – 3, CO – 4, C_6H_6 – 2. Only one measurement point is available for B(a)P and heavy metals (measurement station # 7).

Table 3. Characteristics of the monitoring stations.

No	Site code	Site coordinates [°]	Related receptor	Measurements	Site type
1	MzWarNiepodKom	(21,005;52,219)	1022	NO_X, PM_{10}, $PM_{2.5}$, C_6H_6, CO	Traffic
2	MzWarszKrucza	(21,019; 52,225)	1134	SO_2, NO_X, CO	Urban background
3	MzWarszBernWoda	(21,051; 52,192)	694	SO_2	Industrial
4	MzWarszMarsz	(21,015; 52,225)	1027	CO	Traffic
5	MzWarszUrsynow	(21,034; 52,161)	370	SO_2, NO_X, PM_{10}, $PM_{2.5}$, C_6H_6	Urban background
6	MzWarszPuszSolska	(20,909; 52,226)	1105	SO_2, NO_X	Industrial
7	MzWarszAKrzywon	(20,918; 52,229)	1109	PM_{10}, B[a]P, As, Cd, Ni, Pb	Urban background
8	MzWarPodIMGW	(20,962; 52,281)	1726	inactive	Urban background
9	MzWarszBielan	(20,933; 52,285)	1718	inactive	Urban background
10	MzWarTarKondra	(21,042; 52,291)	1825	SO_2, NO_X, PM_{10}, $PM_{2.5}$, CO	Urban background
11	MzWarszPoraj	(20,959; 52,315)	1932	NO_X	Industrial

The commonly used metrics to quantify the difference between modelled and observed concentrations are the normalized mean bias, NMB, the fractional bias, FB, and the normalized mean square error, NMSE (Dernwent et al. 2010, Juda-Rezler 2010, ETC/ACM 2013). In the first two metrics the sign of the difference is taken into account, which allows assessing the under- and over-estimations. Another very useful metric is the FAC2 index, based on a scatter plot of points, where the fraction of the measurement to observation should be between 0.5 and 2. The definitions of the above metrics are as follows:

Normalized Mean Bias, $NMB = \sum_{k=1}^{n}(C_{ok} - C_{mk}) / \sum_{k=1}^{n} C_{ok}$

Fractional Bias, $FB = 2(\bar{C}_o - \bar{C}_m)/(\bar{C}_o + \bar{C}_m)$

Normalized Mean Square Error, $NMSE = \sum_{k=1}^{n}(C_{ok} - C_{mk})^2 / n\bar{C}_o\bar{C}_m$

Fraction of two, $0.5 \leq FAC2 = C_{mk}/C_{ok} \leq 2$

where: C_o, C_m – observed and modeled concentrations, $\bar{C}_o$, $\bar{C}_m$ – the mean values, n – the number of the observation points. Table 4 shows the first 3 metrics for six basic pollutants, where at least two measurement points are available. Similar estimates can be found in (Trapp 2010) for PM_{10}, NO_2 and SO_2 in Mazovian Voivodship or in (Elbir 2003) for SO_2 in Izmir.

Table 4. The model accuracy metrics (dimensionless).

	PM_{10}	$PM_{2.5}$	NO_X	SO_2	CO	C_6H_6.
NMB	0,123	-0,088	-0,079	0,034	-0,239	0,252
FB	0,116	-0,092	-0,083	0,034	-0,272	0,224
NMSE	0,004	0,002	0,070	0,073	0,123	0,123

The diagrams shown in Table 5 depict scatter plots for assessments of FAC2 index (see also Holnicki and Nahorski 2015, Juda-Rezler 2010, Trapp 2010) for the above 6 basic compounds. The most of the results satisfy the accuracy standard, $0.5 \leq FAC2 \leq 2$. The only exception relates to the monitoring station #1, where the model (60 $\mu g/m^3$) underestimates the measured NO_X concentration (142 $\mu g/m^3$). This case, however, refers to a traffic observation, where the point-wise, street-canyon measurement is performed, while the model calculates a spatially averaged concentration.

The computed CO concentrations are very low, in the range of 200–700 μg/m^3 (Table 5), as compared with the limit value, 10000 μg/m^3. In this situation, the share of the transboundary inflow, close to 130 μg/m^3, is considerable. The pollution in the center is mainly due to mobile source emission (Table 2), with a higher share of the inflow in the peripheral districts (Fig. A4). On the other hand, the line emission is a dominating contributor to C_6H_6 in the central districts, while the high point sources (major power plants) or the low point sources (local industry) have a substantial share locally, e.g. in some peripheral districts (see Fig. A4). The accuracy results (Table 4) show slight underestimation of CO and similar overestimation of C_6H_6 concentrations, however FAC2 criteria are satisfied.

Table 5. Modeled to observed concentrations (in μg/m^3) and FAC2 index at the monitoring stations

Site No	**PM_{10}**		**$PM_{2.5}$**		**NO_X**		**SO_2**		**CO**		**C_6H_6**	
	$\frac{C_m}{C_o}$	FAC2	$\frac{C_m}{C_o}$	FAC2	$\frac{C_m}{C_o}$	FAC2	$\frac{C_m}{C_o}$	FAC2	$\frac{C_m}{C_o}$	FAC2	$\frac{C_m}{C_o}$	FAC2
#1	51.5 / 38.6	1.33	25.6 / 25.1	1.0	59.4 / 144	0.41		–	463 / 671	0.69		–
#2		–		–	46.3 / 41.0	1.13	8.65 / 5.7	1.52	426 / 459	0.93	2.26 / 1.74	1.30
#3		–		–		–	7.03 / 5.4	1.30		–		–
#4		–		–		–		–	441 / 608	0.73		–
#5	39.9 / 37.2	1.07	21.8 / 23.1	0.9	31.4 / 32.1	0.97	6.8 / 7.0	0.97		–	1.42 / 1.20	1.18
#6		–		–	30.1 / 26.6	1.13	8.3 / 11.4	0.72		–		–
#7	44.7 / 33.1	0.80		–				–		–		–
#10	33.5 / 42.1	1.35	25.6 / 19.9	0.8	21.4 / 39.8	0.54	8.04 / 8.0	1.01	271 / 366	0.74		–
#11		–		–	31.0 / 34.2	0.91		–		–		–

The manual monitoring station # 7 is the only one where the measurements of four heavy metals (As, Cd, Pb, Ni) and B(a)P pollutions are performed. As shown in Figs. 8–9, the annual average B(a)P concentration violates in Warsaw the limit value 1 ng/m^3. The measured value of the monitoring station (# 7) is 3.1 ng/m^3 while the respective model prediction value is 2.1 ng/m^3 (FAC2 = 0.68).

Table 6 shows the limit concentration of lead in 2012 and the more restrictive target values for other heavy metals, in force since 1st January 2013 according to EU (2008) and ME (2012). The threshold values are compared with the corresponding ranges (min–max) of the resulting concentrations obtained from the model computation. For all heavy metals considered in this study, the maximum concentrations are below the limits. The last column in Table 6 gives the values of FAC2 index for 4 heavy metals analyzed at station # 7. For Cd and Ni the computed values tend to be overestimated.

Table 6. Heavy metals annual concentrations vs. EU Regulations (ME 2012)

Pollutant	Limit (2012) [ng/m^3]	Target (2013) [ng/m^3]	Computed (2012) [ng/m^3]	FAC2
Arsenic	-	6	0,4 – 2,5	0,8
Cadmium		5	0,6 – 3,7	3,1
Lead	500		8,3 – 32	2
Nickel	-	20	2,5 – 12	3
Mercury	-	-	0,1 – 15	–

5. Discussion

The results indicate some categories of air pollutants which exceed the admissible concentration limits, and have negative environmental impact. High concentration level of particulate matter is one of the main problems related to the air quality in Warsaw. Compared with the earlier results for the year 2005 (Holnicki and Nahorski 2013), the maximum concentrations of PM fractions are higher, and the area of the limit level exceedance is essentially enlarged. As shown in Fig. 4, the PM10 limit (40 μg/m3) is violated in the city center and in peripheral (mainly S-W) districts, while the exceedances of the PM2.5 limit values (25 μg/m3) mainly occur in the S-W peripheries and in the close outskirt of Warsaw. In this case a compact settlement of individual houses along the main railroad line (SW-NE) contributes considerably to Warsaw area pollution. This effect is additionally strengthened due to the S-W wind directions which dominate in Warsaw (Fig. 3).

Source apportionment differs for both PM fractions. As seen in Fig. 5 and Fig. A1, the coarser fractions of PM_{10} mainly come from the line sources (the center), with a higher impact of the area emission in the residential zones, and also with a remarkable share of the transboundary inflow. The dominating category in case of $PM_{2.5}$ is individual housing emission (compare Fig. A1 and Fig. 5), with a high contribution of the transboundary inflow. These are mainly fine PM fractions, transported from distant sources as the sulfate and nitrate aerosols (compare Table 1).

The distribution of the nitrogen oxides is typically closely related to the car traffic intensity, and Fig. 6 shows the correlation between high NO_X concentrations and the topology of the main streets. The city center and vicinity of arterial streets are the regions where the limit concentration level (30 $\mu g/m^3$) is violated. Both the area of this exceedance and the maximum concentrations increased considerably (about 20%) comparing with the year 2005 (Holnicki and Nahorski 2013, 2015). In this case, the source of this standard's worsening lies in the city itself and is mainly caused by the increasing traffic intensity in Warsaw. During the last 7 years, the number of cars has increased about 20–25%. Fig. 6 and Fig. A2 confirm that the mobile sources are the dominating contributor to NO_X pollution, not only near the main arterial streets, but also in residential areas.

The level of SO_2 concentrations in Warsaw is below the admissible limit value 20 μg/m^3 (Fig. 6) and has not changed much since the previous analysis in 2005 (Holnicki and Nahorski 2013), but the structure of the contributing emission categories is different (Fig. 7). Due to the modernization of the energy sector and the lower energy consumption during the last years (energy conservation policy and the economic crisis), the contribution of the professional point sources is much lower, also in the transboundary inflow (WIOŚ 2012). On the other hand, one can see a relative increase of the line source contribution in SO_2 pollution, mainly in roadside receptors (Table 2). The residential site receptors show, similarly as for $PM_{2.5}$, high contribution of the area sources in SO_2 concentration (Fig. 7 and Fig. A2).

The spatial distribution of Pb concentrations (Fig. 8) is similar to that of NO_X and also coincide with the main street network. During the last decade concentrations of Pb has not increased (compare the results in Holnicki and Nahorski (2013)) in spite of the substantial increased number of cars in Warsaw. The concentration values of Pb, similarly as for the other heavy metals, are definitely below the admissible thresholds shown in Table 6. As seen from Fig. A3, the line sources dominate in Pb pollution in the center, but the area sources (housing) are the main contributors in the border areas. The area sources are also dominating in As and Cd pollution and highly contribute to Ni concentrations. The share of the mobile sources is quite important for the latter metal. The mercury pollution is mainly due to the transboundary inflow.

Poland is among the European countries with the highest B(a)P concentrations (EEA 2012, EMEP/EEA 2013, EEA 2014), and very high concentrations of this compound are also observed in Warsaw. As shown in Fig. 8, the threshold value (1 ng/m^3) is exceeded in the whole receptor area. The basic source of B(a)P emission in Poland is the individual housing sector, where simple coal-based, often obsolete, heating and cooking installations are used (see Fig. 9). The same sector is mainly responsible for $PM_{2.5}$ pollution (EEA 2012, Chafe et al. 2014), so the spatial distributions of concentration maps are very similar in both cases (Fig. A3). Commonly used cheap but low quality coal and poor buildings insulation, cause high emissions of both B(a)P and $PM_{2.5}$. In Warsaw the highest concentrations of B(a)P occur in the border residential districts, mainly S-W and N-E, where majority of the individual houses is concentrated. In Warsaw, as compared to some other Polish regions, the problem is relatively less severe and mainly refers to the border districts, because most of the town area has the city district heating system. A big share, about 0,7 ng/m^3 of B(a)P concentration in Warsaw comes from the transboundary inflow.

6. Conclusions

In this study the results of computer analysis of air quality in the Warsaw metropolitan area are shown and discussed. The analysis deals with the main types of urban air pollutants and relies on the real meteorological data and emission field inventory for the year 2012. For computational purposes, the overall emission field has been split down into four categories: (a) high point sources (power and heating plants), (b) other point sources (industry), (c) area sources (residential sector, housing), (d) line sources (urban transport). The impact of the agricultural activity, mainly in the outskirt of Warsaw, is also represented as the area emission field. The regional/national scale transboundary inflow of the main pollutants is taken into account as the boundary conditions for the dispersion model. The main forecasting tool used in the air pollution transport simulations is the regional scale transport modeling system CALMET/CALPUFF (Scire et al. 2000).

The air quality results show the polluting compounds and the regions where some remedial actions are required to eliminate violations of air quality limits and reduce the population exposure. Implementation of such a policy often involves a cost-effective approach or optimization methods (ApSimon et al. 2002, Carnevale et al. 2012). The uncertainty of the model predictions, which is mainly related to the input data, such as emission inventory or meteorological forecast (Sax and Isakov 2003, Park et al. 2006, Maxim and van der Sluijs 2011) is also an important factor in decision taking. Quantifications of emission related uncertainty discussed in Holnicki and Nahorski (2015) show that high uncertainty values relate to the cases of strongly dominating contribution of one individual source or one category of emission sources. Within this study such domination occurs in the central zone for NO_X (domination of line sources), or in peripheral districts for B(a)P and $PM_{2.5}$ (domination of area sources). When dealing with the high uncertainty, the control actions should be more conservative, i.e. the abatement activity should be greater than that obtained for the dominating emission values obtained from the inventory (see e.g. Hryniewicz et al. 2014) to have higher probability of obtaining the required concentration reductions.

The results presented in Section 3 show that the violations of the air quality standards refer mainly to both fractions of particulate matters, nitrogen oxides, and benzo(a)pyrene. The main source of high NO_X and PM_{10} concentrations, and the related adverse environmental impact, is emission of the mobile sources. The contribution of the traffic intensity to PM_{10} pollution takes place via re-suspended particulates and mainly relates to the central district and arterial streets. The problem has intensified due to the steadily increasing number of cars (including transit traffic) observed in Warsaw during the last years. Several actions are implemented or being discussed to improve the air quality in this scope, including new ring roads, which are now under construction, modernization of the public transport, with the introduction of the hybrid and electric buses, or the network of Park&Ride places, connected to the public transport network. Moreover, discussion lasts about creating the exclusion zone for the motor traffic in the city center.

Air Quality Plan is much more complicated in case of B(a)P and fine particulates $PM_{2.5}$, because the problem has not only local but rather a regional character, and any local action cannot be fully effective in this case. To improve the situation, complex modernization strategy of the individual housing sector in Poland, and particularly in the surrounding belt of Warsaw is necessary and must be implemented. The projects proposed by the Polish Ministry of Environment include: (i) the subsidized modernization of the heating boiler installations in the individual housing sector, (ii) stopping up distribution of the worst quality coal, commonly used for heating purpose, (iii) activating low-emission fuels where economically efficient (e.g. gas instead of coal). These actions first of all refer to B(a)P pollution, as violations of the limit values are very high in this case. The above actions will also be effective in reduction of PM_{10} and, first of all, $PM_{2.5}$ concentrations, where exceedances of the quality limits are less drastic. The share of these compounds in urban air pollution is increasing and the fine dust fractions have strong adverse health effects. When taking into account also the cost of emission abatement, the multicriterial character of the air quality plans is clearly visible. It requires application of computer multicriteria optimization for achieving effective abatement scenarios.

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References

ApSimon, H.M., Warren, R.F. & Kayin S. (2002). Addressing uncertainty in environmental modeling: a case study of integrated assessment of strategies to combat long-range transboundary air pollution, *Atmospheric Environment*, 36, 5417–5426.

Berkowicz, R., Winther, M. & Ketzel, M. (2006). Traffic pollution modelling and emission data, *Environmental Modelling & Software*, 21, 454–460.

Brode, W.R. (2012). CALPUFF Near-field validation. 10th Conference on Air Quality Modeling. Research Triangle Park, NC, March 13, 012 (//epa.gov/scram001/10thmodconfpres.htm).

Buchholz, S., Krein, A., Junk, J., Heinemann, G. & Hoffmann, L., (2006). Simulation of Urban-Scale Air Pollution Patterns in Luxembourg. *Environmental Modelling & Assessment,* DOI 10.1007/s10666-012-9351-1

CAFE (2008). Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe.

Calori, G., Clemente, M., De Maria, R., Finardi, S., Lollobrigida, F. & Tinarelli, G. (2006). Air quality integrated modelling in Turin urban area, *Environmental Modelling & Software*, 21, 468–476.

Carnevale, C., Finzi, G., Pisoni, E., Volta, M., Guariso, G., Gianfreda, R., Maffeis, G., Thunis, P. White, L. & Triacchini, G. (2012). An integrated assessment tool to define effective air quality policies at regional scale, *Environmental Modelling & Software*, 38, 306–315.

Chafe, Z.A., Braue,r M., Klimont, Z., van Dingenen, R., Mehta, S., Rao, S., Riahi K., Dentener, F. & Smith, K.R. (2014). Household Cooking with Solid Fuels Contributes to Ambient $PM_{2.5}$ Air Pollution and the Burden of Disease, *Environmental Health Perspectives & Software*, 122, 1–30.

Dernwent, D., Fraser, A., Abott, J., Jenkin, M., Willis, P. & Murrells, T. (2010). Evaluating the Performance of Air Quality Models, No 3, June 2010. (http://naei.defra.gov.uk/reports?
report_id=616)

Dimitriou, K. & Kassomenos, P. (2014). A study on the reconstitution of daily PM_{10} and $PM_{2.5}$ levels in Paris, *Atmospheric Environment*, 98, 648–654.

Dresser, A.L. &Huizer, R.D. (2011). CALPUFF and AERMOD model validation study in the near field: Martins Creek revisited. *Journal of the Air & Waste Management Association*, 61, 641 -657.

EEA (2012). European Environment Agency. Air quality in Europe – Report No 4/ 2012.

EEA (2014). European Union emission inventory report 1990–2012 under the UNECE Convention on Long-range Transboundary Air Pollution (LRTAP). EEA Technical report No 12/2014.

Elbir, T. (2003). Comparison of model predictions with the data of an urban air quality monitoring network in Izmir, Turkey, *Atmospheric Environment*, 37, 2149–2157.

EMEP/EEA (2013). Air pollutant emission inventory guidebook 2013.

ETC/ACM (2013). Technical Paper 2013/11 (R. Rouil, B. Bessagnet, eds). How to start with PM modelling for air quality assessment and planning relevant to AQD.

Holmes, N.S. & Morawska, L. (2006). A review of dispersion modelling and its application to the dispersion of particles: An overview of different dispersion models available, *Atmospheric Environment*, 40, 5902–5928.

Holnicki, P. & Nahorski, Z. (2013). Air quality modeling in Warsaw Metropolitan Area. *Journal of Theoretical and Applied Computer Science*, 7, 56–69.

Holnicki, P. & Nahorski Z. (2015). Emission Data Uncertainty in Urban Air Quality Modeling – Case Study, *Environmental Modeling and Assessment,* DOI 10.1007/s10666-015-9445-7.

Hryniewicz, O., Nahorski, Z., Verstraete, J., Horabik, J. & Jonas, M. (2014). Compliance for uncertain inventories via probabilistic/fuzzy comparison of alternatives, *Climatic Change*, 124, 519–534.

Huber, A., Georgopulos, P., Giliam, R., Stenchikov, G., Wang, S., Kelly, B. & Feingersh H. (2004). Modeling Air Pollution from the Collapse of the World Trade Center and Assessing the Potential Impacts on Human Exposures, *EM*, February 2004, 35–40.

Juda-Rezler, K. (2010). New Challenges in Air Quality and Climate Modeling, *Archives of Environmental Protection*, 36, 3–28.

Kiesewetter, G., Borken-Kleefeld, J., Schöpp, W., Heyes, C., Thunis, P., Bessagnet, B., Terrenoire, E. & Amann M. (2014). Modelling street level PM_{10} concentrations across Europe: source apportionment and possible futures, *Atmospheric Chemistry and Physics. Discussions*, 14, 18315–18354.

Lim, L.L., Hughes, S.J. & Hellawell, E.E. (2005). Integrated decision support system for urban air quality assessment, *Environmental Modelling & Software*, 20, 947–954.

Maxim, L., van der Sluijs J. (2011). Quality in environmental science for policy: Assessing uncertainty as a component of policy analysis, *Environmental Science & Policy*, 14, 482–492.

Mediavilla-Sahagún, A., ApSimon, H.M. (2006). Urban scale integrated assessment for London: Which emission reduction strategies are more effective in attaining prescribed PM_{10} air quality standards by 2005? *Environmental Modelling & Software*, 21, 501–513.

ME (2012). Ministry of the Environment. Decree 1031, 24 Aug. 2012, On the admissible levels of some substances in the air (in Polish).

NCAR (2008). A description of the advanced research WRF Version 3. NCAR Technical Note,
TN–475+STR. Boulder, Colorado, USA June 2008.

Oshan, R., Kumar, A. & Anand,M. 2006. Application of the USEPA's CALPUFF model to an urban area. *Environmental Progress & Sustainable Energy*, 25, 12–17.

Oxley, T., Valiantis, M., Elshkaki, A. & ApSimon, H.M. (2009). Background, Road and Urban Transport modeling of Air quality Limit values (The BRUTAL model), *Environmental Modelling & Software*, 24, 1036–1050.

Park, S.-K., Cobb, C.E., Wade, K., Mulholland, J., Hu Y. & Russel, A.G. (2006). Uncertainty in air quality model evaluation for particulate matter due to spatial variations in pollutant concentrations, *Atmospheric Environment*, 40, S563–S573.

Patton, A.P., Perkins, J., Zamore, W., Levy, J.I., Brugge, D. & Durant, J.L. (2014). Spatial and temporal differences in traffic-related air pollution in three urban neighborhoods near an interstate highway, *Atmospheric Environment*, 99, 309–321.

Pisoni, E., Carnevale, C. & Volta, M. (2010). Sensitivity to spatial resolution of modeling systems designing air quality control policies, *Environmental Modelling & Software*, 25, 66–73.

Sax, T. & Isakov, V. (2003). A case study for assessing uncertainty in local-scale regulatory air quality modeling applications, *Atmospheric Environment*, 37, 3481–3489.

Scire, J.S., Strimaitis, D.G. & Yamartino, R.J. (2000). A User's Guide for the CALPUFF Dispersion Model. Earth Technology Inc.

Tartakovsky, D., Broday, D. M. & Stern E. (2013). Evaluation of AERMOD and CALPUFF for predicting ambient concentrations of total suspended particulate matter (TSP) emissions from a quarry in complex terrain, *Environmental Pollution*, 179, 138–145.

Thunis, P., Rouil, L., Cuvelier, R., Stern, R., Kerschbaumer, A., Bessagnet, B., Schaap, M., Builtjes, P., Tarrason, L., Douros, J., Moussiopoulos, N., Pirovano, G & Bedogni, M. (2007). Analysis of model responses to emission-reduction scenarios within the CityDelta project. *Atmospheric Environment*, 41, 208-220.

Trapp, W. (2010). The application of CALMET/CALPUFF models in air quality assessment system in Poland, *Archives of Environmental Protection*, 36, 63–79.

Villasenor, R., Lopez-Villegas, M. T., Eidels-Dubovoi, S., Quintanar, A. & Gallardo, J.C. (2003). A mesoscale modeling study of wind-blown dust on the Mexico City Basin, *Atmospheric Environment*, 37, 2451–2462.

WIOŚ (2012). Environment Quality in Mazovian Voivodship in the year 2012. Voivodship Inspectorate of Environment Protection (WIOŚ). Report for the year 2012 (in Polish).

Annex

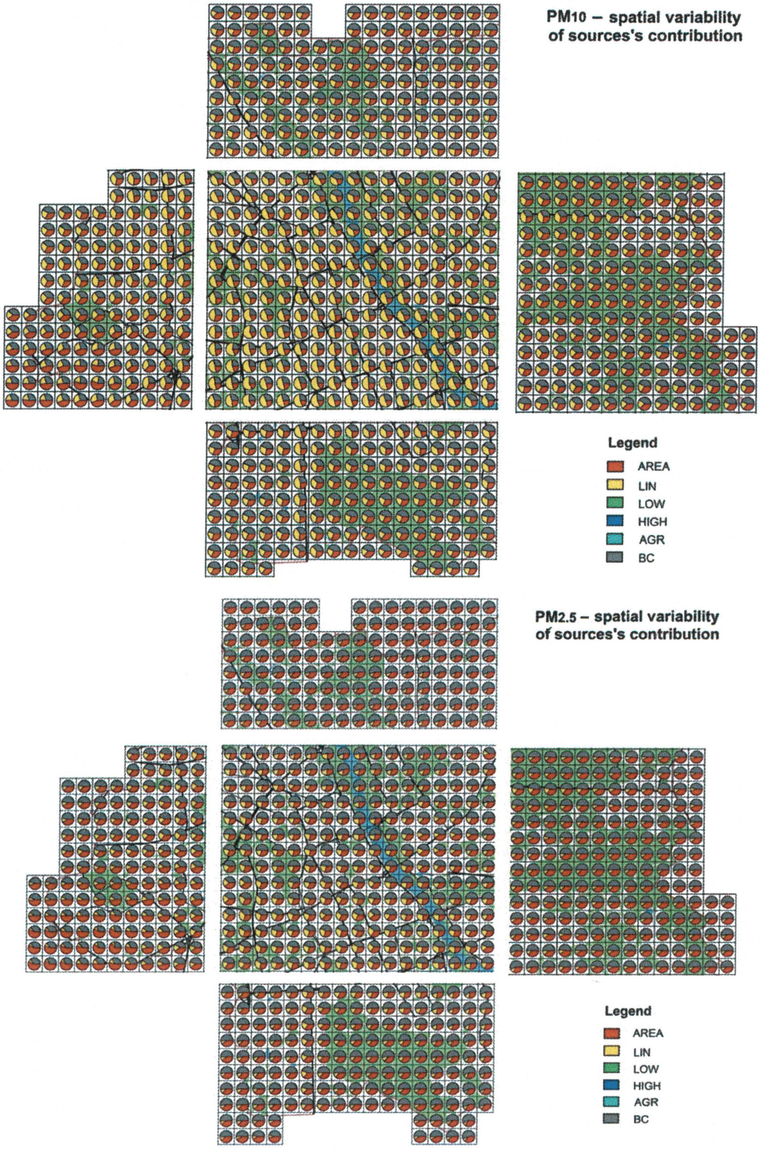
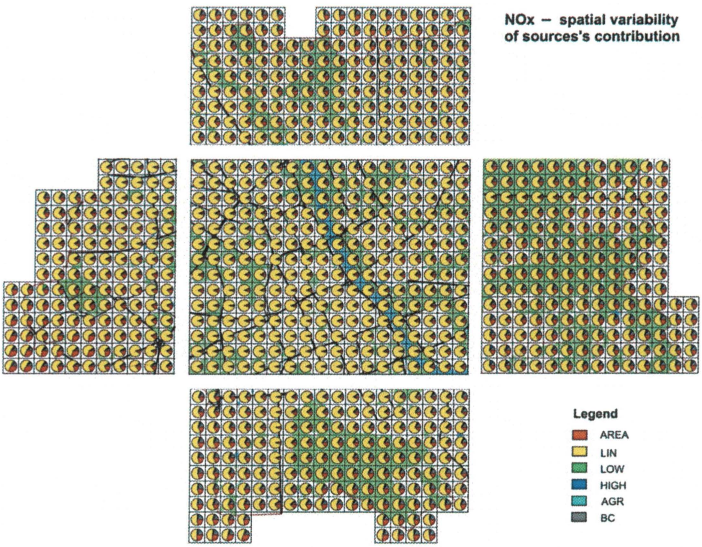


Fig. A1. Spatial variability of the sources contribution for PM_{10} (top) and for $PM_{2.5}$ (bottom)



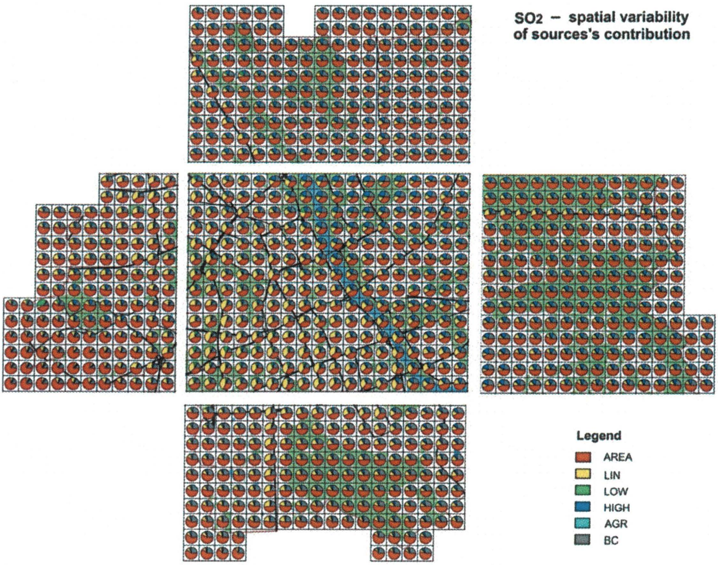


Fig. A2. Spatial variability of the sources contribution for NO_X (top) and for SO_2 (bottom)

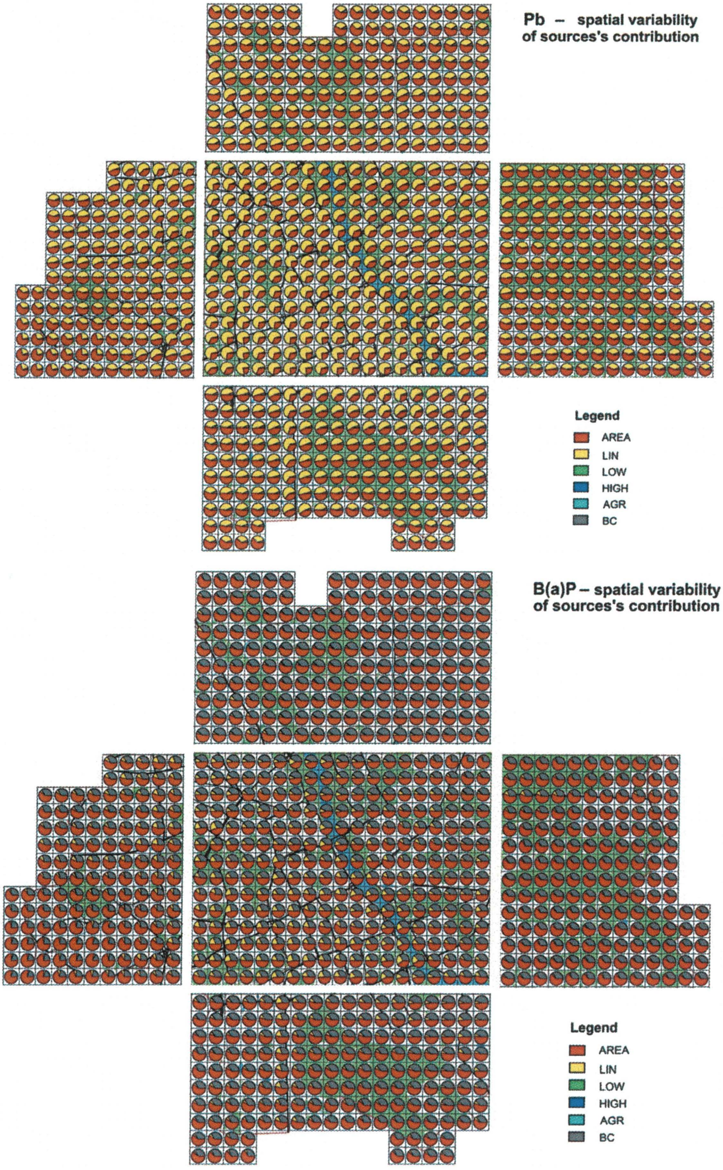


Fig. A3. Spatial variability of the sources contribution for Pb (top) and B(a)P (bottom)

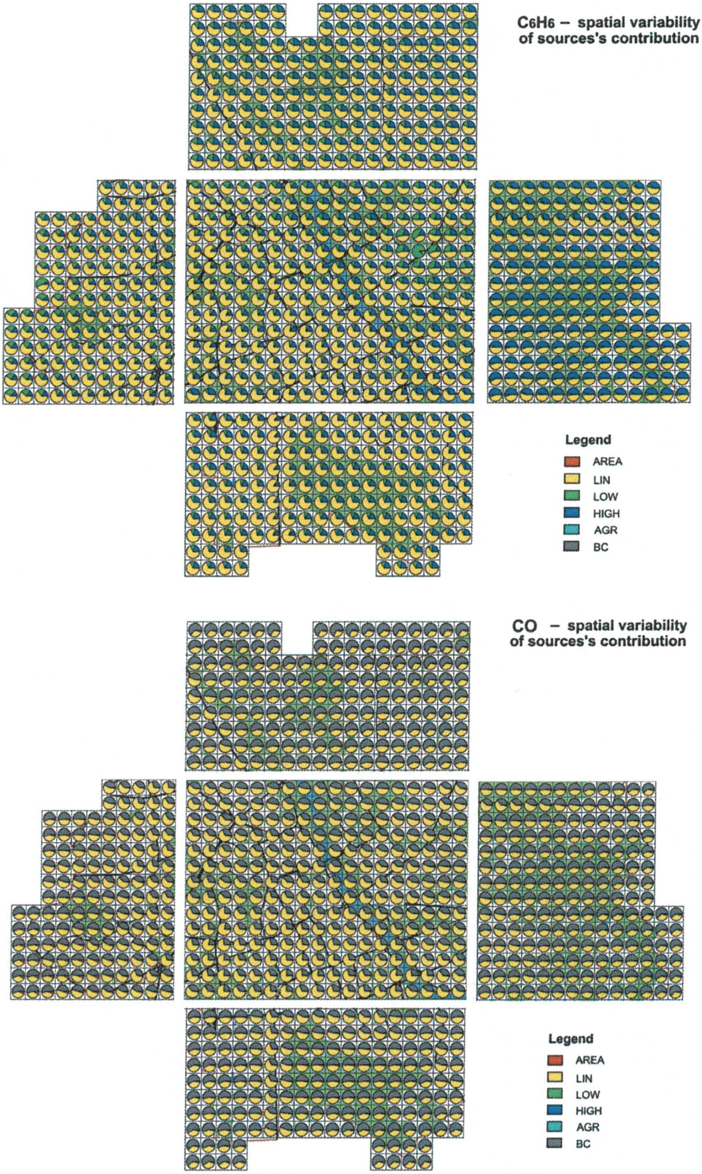


Fig. A4. Spatial variability of the sources contribution for C_6H_6 (top) and CO (bottom)