

Robert OLENIACZ¹, Mateusz RZESZUTEK¹ and Marek BOGACKI¹

ASSESSMENT OF CHEMICAL TRANSFORMATION MODULES FOR SECONDARY INORGANIC AEROSOL FORMATION IN CALPUFF MODEL

OCENA MODUŁÓW PRZEMIAN CHEMICZNYCH TWORZENIA SIĘ WTÓRNYCH AEROZOLI NIEORGANICZNYCH W MODELU CALPUFF

Abstract: Air quality impact assessment is usually carried out with the application of simplified stationary dispersion models, which omit the chemical transformation process of air pollutants. Omission of this effect in the calculation process increases the uncertainty of the obtained results, and hinders the decision making process, related to air quality management. The paper presents a comparison of atmospheric dispersion modeling related to pollutants emitted from high industrial emitters, performed with and without consideration of various chemical transformation modules pertaining to the formation of inorganic aerosols, available in the CALMET/CALPUFF modeling system. A mechanism of inorganic aerosol formation in a liquid phase, considered in the ISORROPIA/RIVAD+AQUA module was observed to exert strong influence on calculation results referring to concentration levels of some air contaminants. The following was found out: more than a double decrease of the annual average concentration of SO₂, and even more significant increase (from 7 to 10 times) of the annual average concentration of PM₁₀ (as a sum of primary and secondary particles) in comparison to other considered chemical transformation modules (MESOPUFF, RIVAD/ARM3, ISORROPIA/RIVAD), and a variant with a chemical transformation module switched off (without taking into account the secondary inorganic aerosol formation).

Keywords: air pollution, chemical transformations, secondary inorganic aerosols, atmospheric dispersion modeling, CALPUFF, ISORROPIA, RIVAD, MESOPUFF

Introduction

A significant role in the system of air quality management is played by methods of mathematic modeling of air pollutant dispersion. There are plenty of atmospheric dispersion models applied around the world, with various characteristics, and each country usually possesses its own model for regulatory purposes. Here, some stationary models, characterized by simplicity of spatial data preparation, which encompass, among others: AERMOD, ISC3, CTDMPPLUS, OCD, ADMS, OML or AUSTAL [1, 2], as well as non-stationary models, capable of simulating meteorological conditions, variable in space and time, out of which the most popular are: WRF/Chem, CAMX, CMAQ, UAM-V and MCCM [3, 4]. The first group is usually applied in the system of air quality impact assessment, and it treats the chemical transformations, which apply mainly to NO_x chemistry, with simplicity, and omits reactions taking place on the boundary of the gas - liquid - solid states. The second group is characterized by a high level of requirements related to preparation of input data and high level of calculation costs. There are usually applied in the performance of complex air pollutant dispersion simulation in a mesoscale [2].

¹ AGH University of Science and Technology, Department of Environmental Management and Protection, al. A. Mickiewicza 30, 30-059 Krakow, Poland, email: oleniacz@agh.edu.pl

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Particular attention is deserved by the CALMET/CALPUFF modeling system [5, 6], which may be successfully applied in the two cases mentioned above, and it is additionally provided with a relatively comprehensive module of chemical transformations, when compared to stationary models. As suggested by works [7, 8], the application of this module in a current version 6.42, should reflect the processes of chemical transformations taking place in the atmosphere in a more favorable manner. The CALMET/CALPUFF modeling system itself is recommended by the US EPA, for calculations carried out in the area not exceeding 50 km. In a specific situation, when a research field is characterized by a complicated landscape and meteorological conditions changing in time, this model may be applied in areas smaller than 50 km [9].

This paper includes an initial analysis of the importance for air quality impact assessment of chemical transformation modules of the secondary inorganic aerosol formation, available in the CALPUFF model. The simulations were carried out for a real object (a heat and power plant in Krakow, Poland), in 6 variants, to compare the effects of various modules of chemical transformation applications, and to determine the uncertainty level pertaining to the omission of this effect in evaluation of air quality influence. Previous works were mainly focused on validation and adjustment of the input settings of the model [10-13], and they did not pay any attention to consequences pertaining to evaluation of the influence exerted by the analyzed object on the air quality.

Purposeful and correct application of advanced atmospheric dispersion modeling systems, which consider chemical transformation modules, may bear special significance for areas, where standards for air quality are not followed, as it happens *eg* in the Krakow urban area [14]. In such a case, it greatly improves reliability of evaluation of influence on air quality, carried out for a given object, especially when it may pose the cause for excessive air pollution.

Methods

In calculations of atmospheric dispersion of pollutants performed within the scope of this work, the real data related to air emissions from two high point emitters that belong to the heat and power plant EDF Poland S.A. Branch No. 1 in Krakow, located near the city center of Krakow (South Poland), were applied. Regarding the character of the combusted fuels (mainly hard coal) and the installed power (460 MWe and 1118 MWt), this combined heat and power station constitutes one of the largest dust and gaseous emission sources, located in the vicinity of Krakow. Thus it has an important role in shaping the air quality in Krakow, especially in situations of abnormal boiler operating conditions (boiler startups) [15]. For the needs of this work, the data coming from the continuous emission monitoring system (pertaining to emissions of particulate matters, SO₂ and NO_x, and parameters of flue gases) from 2012 were applied, with a one-hour step. The results of manual measurements posed a basis for the assumption of air emissions for installations (boilers) startup phases. The basic data of the considered emitters are presented in Table 1.

The calculations were carried out in the CALMET/CALPUFF modeling system [5, 6], with and without consideration of various chemical transformation modules for the formation of secondary inorganic aerosols, including the ISORROPIA/RIVAD+AQUA module, available in the latest version of the CALPUFF program (ver. 6.42) [7, 8]. The

basic calculation domain was the 38 km × 26 km area, with grid resolution of 200 m. The topography and land cover data were obtained respectively from SRTM3 and CLC2006 databases. The spatial data were processed initially in the ArcGIS software, and in so called preprocessors of geophysical data, according to the procedure described in papers [16, 17]. Results of meteorological parameters observations were obtained from numerous sources for 2012. In total, 18 surface stations located within Krakow and its boundaries, together with 3 upper stations (Poprud, Legionowo, Wroclaw) were employed.

Table 1
Dimensions of the analyzed emitters, average parameters of flue gases and total air emissions in 2012

Emitter number	Stack dimensions		Average parameters of flue gases		Total annual emissions to air [Mg y ⁻¹]		
	high [m]	diameter [m]	stack gas velocity [m s ⁻¹]	temperature [K]	dust (PM)	SO ₂	NO _x
E1	225	6.5	7.57	415	700	6505	4178
E2	260	7.0	7.77	406			

Afterwards, the three-dimensional fields of wind and temperature, together with a two-dimensional field of micro-climate parameters (PG stability class, mixing height, Monin-Obukhov length, friction velocity, convective velocity scale) were generated through the CALMET diagnostic model. CALMET model output data were then used as input for the CALPUFF model.

Table 2
A comparison of calculation variants, and their corresponding settings, input data, name of models and source materials

Variant	Settings		Background concentrations			NO _x emission	Model	Reference
	MCHEM	MAQCHEM	NH ₃	O ₃	H ₂ O ₂			
V1	0	0	-	-	-	NO _x	-	-
V2	1	0	month	1-hour	-	NO _x	MESOPUFF	[21-23]
V3	3	0	month	1-hour	-	NO/NO ₂	RIVAD/ARM3	[24]
V4	6	0	month	1-hour	-	NO/NO ₂	ISORROPIA/ RIVAD	[7, 8, 25-27]
V5	6	1	month	1-hour	season	NO/NO ₂	ISORROPIA/ RIVAD+AQUA	
V6	6	1	month	month	season	NO/NO ₂	RIVAD+AQUA	

Calculations of atmospheric dispersion of air pollutants were carried out in 6 variants, including the variant without application of the chemical transformations module. The remaining variants differed among each other with application of MCHEM (chemical transformation module selection) and MAQCHEM (not including or including liquid state for the conversion of SO₂), and the introduced input data (Table 2). Variants 3-5 required determination of separate emission of NO and NO₂. Emission of these substances was estimated on the basis of results of NO_x emission measurements, assuming percentage shares of NO and NO₂ on the level of 95 and 5% respectively [18]. Particulate matter grain size fractions were determined on the basis of literature data [19]. Monthly average background concentrations of NH₃, indispensable during the process of calculations, were

determined on the basis of data coming from continuous monitoring carried out in stations of urban background in various European cities, and the H₂O₂ concentrations were assumed on the basis of a measurement campaign performed in Wroclaw [20]. Concentrations of ozone were introduced with 1-hour (variants V2-V5) or 1-month (variant V6) temporal resolution, on the basis of data coming from the urban background station situated in Krakow, at Bujaka street.

There were calculations of maximum 1-hour, 24-hour and annual average concentrations in the air at the land surface, carried out for NO, NO₂ (and/or NO_x), SO₂, primary particulate matter (PPM), secondary inorganic aerosol (NO₃, and SO₄), and the sum of secondary particulate matter (SPM), as well as total primary and secondary particulate matter (PPM+SPM) with consideration of fractions below 10 µm (PM10). The calculations results obtained for particular variants underwent a comparative analysis.

Results and discussion

Results of calculations of the highest values for maximum 1-hour and 24-hour concentrations and maximum and average annual concentrations of the analyzed substances, for a given area, obtained in the assumed computational field for particular variants, are presented in Tables 3 and 4.

Table 3

The highest values of maximum 1-hour and 24-hour concentrations in the air, obtained within the assumed computational area for particular variants

Air pollutant	The highest 1-hour average concentration in the variant [$\mu\text{g m}^{-3}$]						The highest 24-hour average concentration in the variant [$\mu\text{g m}^{-3}$]					
	V1	V2	V3	V4	V5	V6	V1	V2	V3	V4	V5	V6
NO	-	-	53.6	62.4	62.4	66.5	-	-	3.27	3.28	3.28	3.91
NO ₂	-	-	165.8	162.7	162.6	138.6	-	-	20.51	20.50	20.50	20.30
NO _x (NO ₂)	241.3	230.1	240.3	240.1	240.1	240.4	21.62	21.57	21.60	21.60	21.60	21.61
SO ₂	582.1	576.8	581.1	581.2	491.3	492.4	34.09	33.72	34.01	34.03	33.22	33.22
PPM (PM10)	449.1	449.1	449.1	449.1	449.1	449.1	29.09	29.09	29.09	29.09	29.09	29.09
SPM (NO ₃)	-	7.0	4.6	5.3	5.3	4.9	-	0.47	0.25	0.28	0.28	0.33
SPM (SO ₄)	-	13.3	3.2	2.5	264.6	263.4	-	0.78	0.21	0.16	23.66	24.00
SPM (total)	-	20.3	5.6	5.7	264.6	263.4	-	1.18	0.36	0.33	23.66	24.01
PPM+SPM	449.1	449.3	449.1	449.1	466.4	466.0	29.09	29.11	29.10	29.10	31.87	31.78

It should be noticed that the highest values of maximum 1-hour and 24-hour concentrations, listed in Table 3, could exist in various spots of the computational area, and at a various time. Nevertheless, in case of all primary pollutants, maximum values of those concentrations for variants V1-V4 were obtained on the similar level, and in case of PPM and NO_x - the same or similar concentration values were also obtained for V5 and V6 variants.

As suggested by the presented data, application of various chemical transformation modules usually does not influence significantly the obtained results of calculations of the maximum 1-hour and 24-hour concentrations of NO and NO₂ in the air. However, it is possible to obtain an understated value for the highest of maximum 1-hour concentrations of NO₂ during application of the latest version of the CALPUFF model with the

ISORROPIA/RIVAD+AQUA module in ozone background, in a form of monthly average concentrations (variant V6), instead of 1-hour average concentrations (variant V5).

Table 4

The highest and mean values of annual average concentrations in the air, obtained within the assumed computational area for particular variants

Air pollutant	The highest annual average concentration in the variant [$\mu\text{g m}^{-3}$]						The mean of annual average concentrations in the variant [$\mu\text{g m}^{-3}$]					
	V1	V2	V3	V4	V5	V6	V1	V2	V3	V4	V5	V6
NO	-	-	0.369	0.371	0.371	0.429	-	-	0.024	0.025	0.025	0.027
NO ₂	-	-	1.443	1.438	1.439	1.367	-	-	0.198	0.196	0.196	0.192
NO _x (NO ₂)	1.999	1.980	1.993	1.992	1.993	1.993	0.240	0.222	0.235	0.234	0.234	0.233
SO ₂	3.108	3.104	3.106	3.104	2.610	2.625	0.363	0.360	0.361	0.361	0.172	0.174
PPM (PM10)	0.307	0.307	0.307	0.307	0.307	0.307	0.028	0.028	0.028	0.028	0.028	0.028
SPM (NO ₃)	-	0.019	0.010	0.005	0.005	0.006	-	0.006	0.003	0.001	0.001	0.002
SPM (SO ₄)	-	0.013	0.008	0.006	1.955	1.952	-	0.005	0.003	0.002	0.250	0.249
SPM (total)	-	0.031	0.017	0.011	1.956	1.954	-	0.011	0.006	0.003	0.251	0.251
PPM+SPM	0.307	0.320	0.313	0.310	2.130	2.127	0.028	0.039	0.034	0.032	0.279	0.280

Application of chemical transformation modules for the analyzed objects did not exert any greater influence on the maximum 1-hour or 24-hour PM10 (PPM+SPM) concentrations measured in the air. It was caused by a fact that the maximum values were recorded in a situation of abnormal operating conditions of the installation (the boiler startup, with an electrostatic precipitator turned off), which was accompanied by significant dust emission, resulting in extremely high maximum values of PM10 concentration in air (PPM). In such a situation, omission of chemical transformation modules in the evaluation of this object impact on the air quality is not burdened with a high level of error, regarding an insignificant share of the secondary inorganic aerosols in the total level of PPM+SPM concentration in the air in that period. If the periods of boilers startups are not considered in calculations, it is possible to obtain great discrepancies between the calculations results of the maximum 1-hour and 24-hour concentrations of PM10 in the air, obtained with and without consideration of chemical transformation modules.

Great disproportions between the analyzed variants were obtained in case of calculation results for annual average concentration for PM10 and maximum 1-hour and annual average concentrations of SO₂. Omission of the chemical transformation module causes that results of evaluation of influence on air quality, carried out for sources, which emit these substances in significant amounts, will always be burdened with considerable uncertainty, and they may bear great differences when compared to the modeling results obtained with consideration of the inorganic aerosol creation module. In this case, special role is played by a module of chemical transformations in a liquid state, implemented in version 6.42 of the CALPUFF model, which intensifies the conversion process of SO₂ to sulfate forms. Omission of this effect in the process of atmospheric dispersion modeling may contribute to overprediction of SO₂ concentration calculations (to various degrees, depending on the average period), and significant underprediction of annual average PM10 concentrations in the air. For the object in consideration, the maximum 1-hour and annual average concentrations of SO₂ were overpredicted on the level of ca. 15-16%, regarding the reference variants (V5 and V6). More than double overprediction of annual SO₂

concentrations, and underprediction of maximum and average (in the computational area) annual average PM10 concentrations, by *ca* 7-10 times, was also obtained for the variant V1, V2, V3, and V4, in comparison with the variant V5 or V6. In particular variants, there were maximum annual concentrations of those substances in the air recorded also in other places, what is illustrated on the example of annual PM10 concentrations obtained for V1 and V5 variants in Figures 1 and 2.

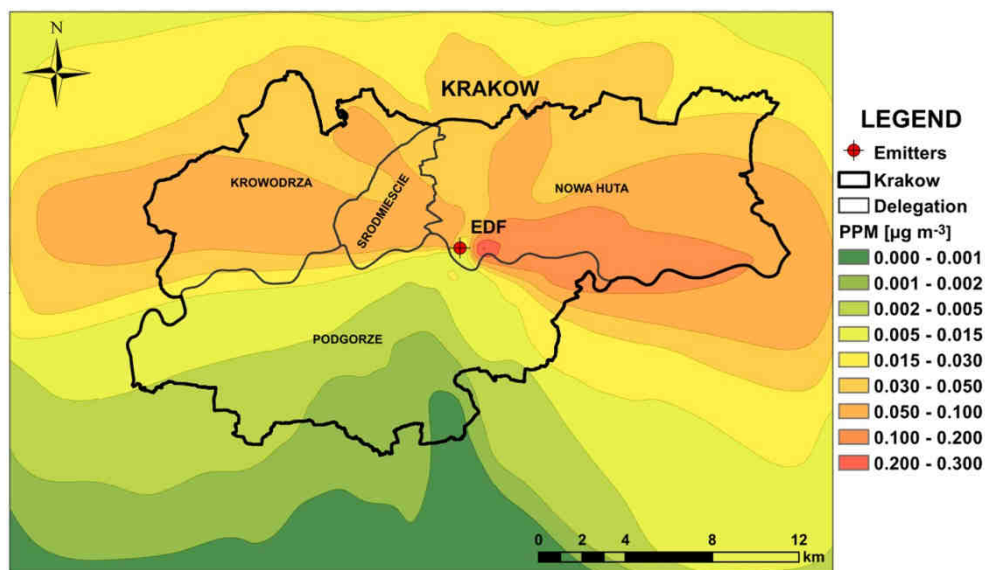


Fig. 1. Spatial distribution of annual average PM10 (PPM) concentrations in the air, obtained for the variant V1

SPM share in the total annual concentration of PM10 (PPM+SPM) is elevated along with an increase of distance from the emission source, what is especially observable in areas located along dominating wind directions, which are exposed to the influence of the analyzed object to the highest extent. Within the whole computational area, average SPM share in relation to the sum of annual average PPM+SPM concentrations for variants V2, V3, V4, V5 and V6 was as follows: 38.45; 25.70; 17.77; 90.08 and 90.10% respectively. Even greater shares of SPM in relation to PPM+SPM were present in case of the maximum values of annual concentrations, which were as follows for the variants mentioned above: 72.26; 53.28; 48.15; 95.96 and 95.95%. It proves large influence of SO_2 and NO_x emission of the analyzed object on the caused total level of annual concentrations of PM10 (PPM+SPM) in the air. In case of V5 and V6 variants, a surge of this influence was caused first of all by secondary inorganic aerosols, formed as a result of chemical transformations of SO_2 in the air, in a liquid state. What is more, in variants V4-V6, in comparison to variants V2 and V3, annual concentrations of secondary nitrate aerosols were significantly reduced. It results from the reduction or elimination of the phenomenon of overpredicting their concentrations, characteristic for MESOPUFF and RIVAD/ARM3 modules, presented among others in the paper [28].

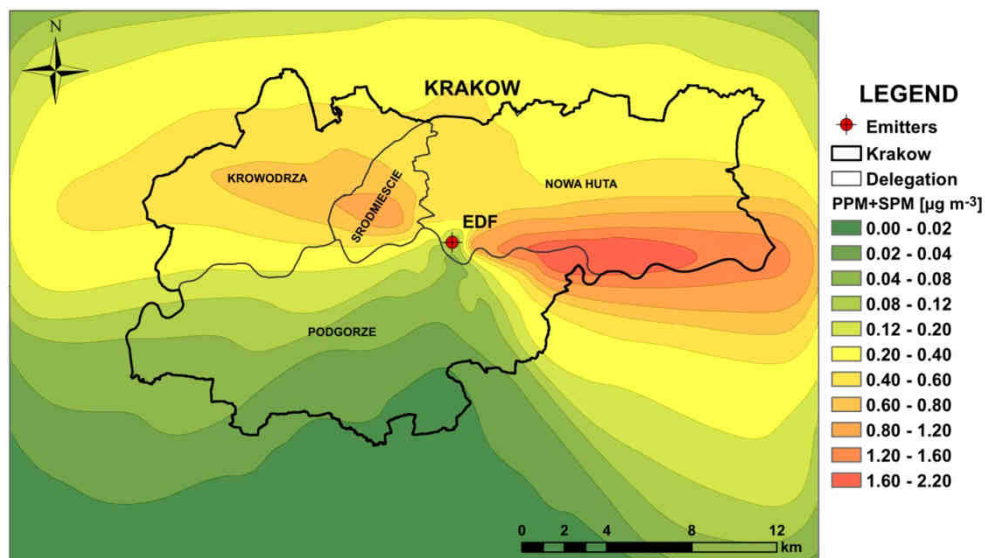


Fig. 2 Spatial distribution of annual average PM₁₀ (PPM+SPM) concentrations in the air, obtained for the variant V5

Conclusions

Application of advanced atmospheric dispersion models for air quality impact assessment, allows to consider chemical transformation modules available in the model for air pollutants emitted from the analyzed emission source, including reactions that lead to formation of secondary inorganic aerosols. In the CALMET/CALPUFF modeling system, several features of chemical transformation modules may be applied for this purpose, including the following modules: MESOPUFF, RIVAD/ARM3, ISORROPIA/RIVAD and ISORROPIA/RIVAD+AQUA.

Calculations of pollutant dispersion in the air, carried out for a large combustion plant, with consideration of the CALMET/CALPUFF modeling system, allow to conclude that the chemical transformations modules exert no significant influence on calculations results for concentrations of NO, NO₂, and NO_x in the air. However, they may influence the calculation results for SO₂ and PM₁₀ concentrations significantly, especially in case of applying the version 6.42 of the CALPUFF model with the ISORROPIA/RIVAD+AQUA module, taking conversion of SO₂ in a liquid phase into consideration [7, 8]. In calculations applying the model version mentioned above, maximum 1-hour and annual average SO₂ concentrations were higher by *ca* 15-16%, and the annual average PM₁₀ (primary and secondary particle matter) concentrations were at least 7 times higher, when compared to the remaining analyzed variants, including the one that does not consider the chemical transformations.

Therefore, omission of chemical transformations of the secondary inorganic aerosols in the process of atmospheric dispersion of air pollutants may lead to a wrong conclusion in the scope of evaluation of the emission sources impact on air quality, if SO₂ emission from

those sources is significant. If the CALPUFF model is applied for this evaluation, it is recommended to apply the ISORROPIA/RIVAD+AQUA module, allowing better reflection of the sulfate aerosol formation, hence to obtain more probable air concentrations of SO₂ and secondary particle matter. In this module, it is advisable to consider the ozone background with 1-hour temporal resolution, if such data are available. The use of monthly average concentration values may cause certain underprediction of maximum values of 1-hour and annual concentrations of NO₂ in the air. Moreover, application of the ISORROPIA/RIVAD or ISORROPIA/RIVAD+AQUA modules allows elimination of the phenomenon of overprediction of secondary inorganic nitrate aerosol concentrations, characteristic for MESOPUFF and RIVAD/ARM3 modules.

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OCENA MODUŁÓW PRZEMIAN CHEMICZNYCH TWORZENIA SIĘ WTÓRNYCH AEROZOLI NIEORGANICZNYCH W MODELU CALPUFF

AGH Akademia Górniczo-Hutnicza w Krakowie, Katedra Kształtowania i Ochrony Środowiska

Abstrakt: Ocena wpływu źródeł emisji na jakość powietrza wykonywana jest zwykle przy użyciu uproszczonych stacjonarnych modeli dyspersji, pomijających procesy przemian chemicznych zanieczyszczeń powietrza. Pominięcie tych efektów w procesie obliczeniowym powoduje zwiększenie niepewności uzyskanych wyników oraz utrudnia proces podejmowania prawidłowych decyzji związanych z zarządzaniem jakością powietrza. Praca przedstawia porównanie wyników modelowania dyspersji atmosferycznej zanieczyszczeń emitowanych z wysokich emitorów przemysłowych prowadzonych bez uwzględniania i z uwzględnianiem różnych modułów przemian chemicznych tworzenia się nieorganicznych aerozoli, dostępnych w systemie modelowania

CALMET/CALPUFF. Wykazano istotny wpływ mechanizmu tworzenia się wtórnego aerozolu nieorganicznego w fazie wodnej, uwzględnianego w module ISORROPIA/RIVAD+AQUA, na wyniki obliczeń poziomów stężeń niektórych zanieczyszczeń w powietrzu. Stwierdzono m.in. ponad 2-krotny spadek średniego poziomu stężeń średniorocznych SO_2 i jeszcze większy (od 7 do 10 razy) wzrost średnich wartości stężeń średniorocznych pyłu PM_{10} (suma cząstek pierwotnych i wtórnych) w porównaniu z innymi rozpatrywanymi modułami przemian chemicznych (MESOPUFF, RIVAD/ARM3, ISORROPIA/RIVAD) oraz wariantem z wyłączonym modułem przemian chemicznych (bez uwzględniania tworzenia się wtórnego aerozolu nieorganicznego).

Słowa kluczowe: zanieczyszczenie powietrza, przemiany chemiczne, wtórne aerozole nieorganiczne, modelowanie dyspersji atmosferycznej, CALPUFF, ISORROPIA, RIVAD, MESOPUFF