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A REVIEW OF CHEMICALLY REACTIVE PLUME MODELS. PART I. MODELS INCORPORATING MACRO-MIXING PROCESSES

Chemically reactive plume models describing the formation of secondary pollutants in plumes emitted from tall stacks are presented. The models are grouped together in classes according to the way in which turbulent mixing processes are described. The term *turbulent mixing* involves here both macro-mixing and micro-mixing. Macro-mixing processes account for the variation of mean concentrations, while micro-mixing processes affect the deviations from the mean values. The review is divided into two parts: part I presents the models, in which only macro-mixing processes are taken into account, while part II is devoted to the models, which either represent micro-mixing processes or account for both macro- and micro-mixing processes.

1. INTRODUCTION

Chemically reactive plume models are used to simulate transport, dispersion and non-linear chemistry of plumes emitted from high-level point sources such as tall stacks of large industrial boilers and fossil-fuel burning power plants. These models allow us to calculate the concentrations of primary pollutants, i.e. those emitted directly from chimneys to the atmospheric air, as well as the concentrations of secondary pollutants, i.e. those which are formed in the atmosphere due to chemical reactions between stack effluents and ambient air species.

Nitrogen oxides and sulphur dioxide are the main primary species emitted from stacks. Ozone, PAN, sulphuric and nitric acids are the main secondary species formed in the atmosphere. The production of secondary species is strongly influenced by hydrocarbons present in the ambient air. It is especially intensive under sunshine and warm weather conditions. Secondary pollutants are now thought to be more harmful to environment and people health then primary pollutants.

There is a great variety of chemically reactive plume models. They differ in the way of the description of mixing of plume with the ambient air and in the complexity of chemical

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reaction systems applied. In this review, chemically reactive plume models are grouped together in classes according to the way in which mixing processes are described. This criterion was introduced by Georgopoulos and Seinfeld [23], [26], [27].

The term *mixing processes* involves here both macro-mixing and micro-mixing [5], [13], [14], [15]. Macro-mixing is defined as the process of turbulent mixing at a level of mean concentrations. It is related to the expansion of plume as a whole and mixing of the ambient air with stack effluents inside a plume at a level of mean concentrations. Micro-mixing is defined as the process of turbulent mixing on such a scale that chemical reactions take place, i.e. at a molecular level. It is related to fine fluctuations of concentrations, i.e. fluctuations in excess of or below average values. For the models relevant to time-averaged realisations the mean values of concentrations refer to time-averaged concentrations. For the models relevant to instantaneous realisations the mean concentrations refer to ensemble averages.

The review of chemically reactive plume models is presented in two parts:

1. Models in which only macro-mixing processes are taken into account.

2. Models which either focus on micro-mixing processes only or account for both macro- and micro-mixing processes.

In this paper, models of reactive plumes incorporating only macro-mixing processes are presented. There are four classes of these models:

class 1: uniformly mixed expanding volume models,

class 2: partially-perfectly mixed expanding volume models,

class 3: sectionally homogeneous expanding multi-volume models,

class 4: extended Gaussian-type models.

All the models incorporating the macro-mixing processes account for the expansion of plume. They differ in the way of describing mean concentration fields. In the models of class 1, uniform mixing is assumed in a control plume volume. In the models of class 2, we assume partial perfect mixing of stack effluents in a plume. Class 3 comprises the models in which sectionally homogeneous mean concentration fields are considered, while class 4 includes such models in which a continuous mean concentration distribution in plume boundaries is taken into account. For each class general assumptions and main mathematical equations are presented. Examples of specific models, their characteristic as well as the tests performed are discussed.

The authoress hopes that this two-part review of chemically reactive plume models will be of use to a beginner as a text to study and to an expert in the field of air pollution dispersion modelling as a material systematising and summarising the current state of knowledge in this area.

2. CLASS 1. UNIFORMLY MIXED EXPANDING VOLUME MODELS

Models included in this class describe the mixing processes in the most simplified way. They account only for the expansion of plume formed by stack emissions. Uni-

form mixing is assumed in a control plume volume. These models can be considered as the development of the Lagrangian trajectory constant-volume box models in which a box follows a trajectory of the wind [36]. An expanding control volume of plume "takes place" of the moving constant-volume box.

In the models, which fall into this class, plume cross sections are assumed to be circular [9], [10], [21], elliptical [11], [12], or rectangular [37], [38], [42] in shape. In most cases, plume boundaries are defined by time-averaged envelopes. A width and depth of plume are determined by means of time-averaged dispersion coefficients or vertex angles in the horizontal and vertical directions. However, McRAE et al. [38] introduced instantaneous realisations of plume to his model and suggested that dispersion coefficients accounting only for the relative diffusion should be applied.

In the models of class 1, meteorological conditions are assumed to be constant. They are characterised by the mean wind and atmospheric stability class. In most cases, there is no consideration of plume interactions with the ground or inversion layer. Usually many types of species are considered and complex chemistry schemes including about 100 gas-phase chemical reactions are applied [18], [8]. A composition of the ambient air is assumed constant.

The change of a pollutant concentration in a control volume is based on mass conservation equation. Terms which account for the expansion of plume volume, entrainment of the ambient air and chemical reactions are present in this equation. There is one equation for each species considered in the system. It has the following form:

$$\frac{d\overline{C}_{i,p}}{dt} = \frac{dV}{dt}\frac{1}{V}(-\overline{C}_{i,p} + \overline{C}_{i,a}) + \overline{R}_i\,(\overline{C}_i, \overline{C}_{i+1}, ...),\qquad (1)$$

where: $\overline{C}_{i,p}, \overline{C}_{i,a}$ are the mean concentrations of species i in a control volume of plume and in the ambient air, respectively; dV/dt is the increase in the control volume in time; $\overline{R}_i$ is the change of the concentration of species i due to chemical processes.

Most of the models of class 1 were developed to examine the influence of various environmental parameters on the formation of secondary pollutants in the atmosphere. This includes: the atmospheric stability, wind speed, compositions of plume and ambient air and intensity of solar radiation. In the tests performed, "typical" data were applied, i.e. the data representative of the most common situations. The models were constructed for a travel distance up to 50 km.

The computer simulations confirmed the dependence of plume chemistry on the parameters studied. However, it has been suggested that it is unlikely that these models can account for the plume chemistry, particularly during early stages of the plume expansion in real situations [9].

Table 1

Examples of the uniformly mixed expanding volume models

1. References 2. Institution 3. Performed tests/ Validation	4. Model concept a) Shape of plume cross sections b) Determination of plume boundaries c) Plume interactions with the ground or inversion layer d) Types of primary species considered (plume and ambient air) e) Chemical kinetic scheme applied f) Other physical processes
1. COCKS and FLETCHER [9] 2. Central Electricity Research Laboratories, UK 3. Examination of the influence of ambient air composition and atmospheric stability conditions on the formation of secondary pollutants (particularly acidic products) in power-plant plumes	4. a) Circular b) Cone of a planar vertex angle $2\check{r}$; $\check{r} = f$ (atm. stab.) c) Not considered d) NO, NO_2, SO_2, CO, HCs e) Gas-phase chemistry; ~93 reactions; constant photolytic rates f) Not considered
1. MEAGHER and LURIA [42] 2. Tennessee Valley Authority, AL, USA 3. Examination of various environmental parameters (wind speed, atmospheric stability, solar intensity, stack emissions and ambient-air compositions) affecting production of secondary pollutants (sulphate, ozone, nitrate)	4. a) Elliptical b) Based on dispersion parameters δ, $\delta = f$ (time, atm. stab.) c) Not considered d) NO, NO_2, CO, HCs (olefins, paraffins, aromatics, ethylene, carbonyls), SO_2 e) Carbon bound mechanism (CBM) of WHITTEN et al. [51]; gas-phase chemistry; 65 original reactions + 3 reactions describing conversion of SO_2 to SO_4 added; photolytic rate coefficients calculated based on procedure of SCHERE and DEMERIJAN [17] f) Not considered
1. COCKS, FLETCHER and KALLEND [10], [11], [12] 2. Central Electricity Research Laboratories, UK 3. Examination of the influence of season, time of release and dispersion rate on the chemical behaviour of power plume emitted into an urban/rural ambient atmosphere. Power plume expands into an ambient air after the original oceanic air parcel has travelled ~190 km over land	4. a) Rectangular b) Expanding box with half-angles ϕ and γ in the horizontal and vertical directions, respectively c) Vertical expansion ceases upon simultaneous contact with the ground and top of the mixing layer; plume emissions – injected in a centre of the mixing layer d) NO, NO_2, SO_2, CO, HCs, HCl e) Gas-phase chemistry based on papers of BAULCH et al. [3], ATKINSON and LLOYD [1]; lumped HCs scheme; photolytic rate coefficients modified for diurnal effects using a simple zenith angle correction f) Deposition

1. FORNEY and GIZ [20]	4.
2. Georgia Institute of Technology, GA, USA	a) Circular
3. Prediction of NO, NO_2, O_3 concentrations in a power-plant plume	b) Growth of a plume describes a dilution parameter, which is a function of radius and local plume velocity
	c) Not considered
	d) NO, NO_2;
	e) Single reversible bi-molecular reaction; assumption that reactions are very fast in comparison to mixing times and that chemical equilibrium exists; method adapted to $NO/NO_2/O_3$ system
	f) Not considered

The tests showed that in most cases OH radical is the most important species in the conversion of stack effluents into secondary pollutants and that plume reactivity is determined by the ratio of NO_x concentration in a plume to hydrocarbons' concentration in the ambient air. They confirmed the presence of an "ozone bulge", i.e. an excess of O_3 concentration in a plume in comparison to O_3 concentration in the ambient air [42].

Some of the models of class 1 were used in combination with urban air photochemical models [30], [31], [38]. It was concluded that the introduction of the point source sub-models of this type to the numerical regional models did not change significantly the overall results [13]–[15].

The examples of the specific models of class 1 are given in table 1. For each model its formulation and the tests carried out are given.

3. CLASS 2. PARTIALLY-PERFECTLY MIXED EXPANDING VOLUME MODELS

Models belonging to this class, in addition to the expansion of plume considered in the models of class 1, take into account the gradual mixing of source effluents with the ambient air. In the formulation of these models, it is assumed that source effluents are present in a plume in two phases: undiluted phase and perfectly mixed with the ambient air phase.

There are two models reported in the literature which fall into this class. They are described in the papers of CARMICHAEL and PETERS [8] and JANSSEN [3]. In the model of Carmichael and Peters, a time-averaged plume is discussed. Undiluted source effluents form a core surrounded by the ring of a perfectly mixed material. This ring, in turn, is surrounded by the ambient air.

In the model of Janssen, an instantaneous plume is analysed. In this model, source effluents form nuclei of parcels into which stack gases are broken up after their emission from a stack. The outer envelopes of these parcels are formed by the mixed mate-

rial and the individual parcels are separated by the ambient air. Not all the ambient air between the parcels is available for mixing. Part of the ambient air, which stays un-mixed, is determined by an empirical parameter (f_a). Images of a plume in these two models are shown in figure 1a, b.
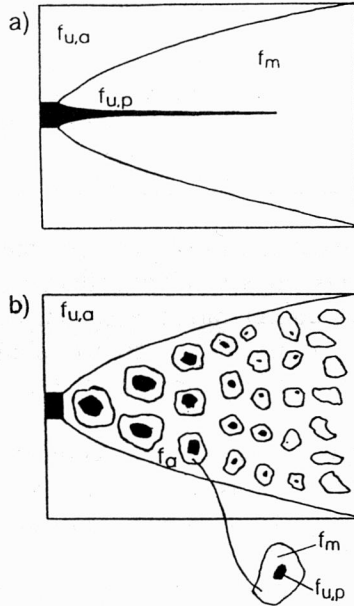

Fig. 1. Schematic representation of plume in partially-perfectly mixed expanding volume models:
a) in the model of CARMICHAEL and PETERS [8], the undiluted source effluent ($f_{u, p}$) forms a core surrounded by a ring of perfectly mixed material (f_m); this ring is surrounded by the ambient air ($f_{u, a}$);
b) in the model of JANSSEN [32], parcels of unmixed flue gas ($f_{u, p}$), mixed plume (f_m) and the ambient air ($f_a, f_{u, a}$) occur next to each other in a plume

In these two models, the mixing process is viewed as a pseudo-kinetic step and is governed by the mixing intensity (an empirical parameter k_m) and concentrations of reactants. As far as mathematical form is concerned, the mixing is expressed by three equations: two derivative equations describing the decrease in the fraction of unmixed stack effluents and the unmixed ambient air and equation describing the growth of mixed fraction. These equations are as follows:

$$\frac{df_{u,p}}{dt} = -k_m f_{u,p}\left(1 - f_{u,p}\right), \tag{2}$$

$$\frac{df_{u,a}}{dt} = -k_m f_{u,a}\left(1 - f_{u,a}\right), \tag{3}$$

$$f_{u,p} + f_{u,a} + f_m + f_a = 1, \tag{4}$$

where: $f_{u,p}$ and $f_{u,a}$ are the fractions of a total volume occupied by unmixed stack effluents and the unmixed ambient air, respectively; f_m and f_a are the fractions of a total volume occupied by mixed material and by the ambient air not available for mixing, respectively; k_m denotes the mixing parameter. In the model of Carmichael and Peters, all the ambient air is available for mixing, i.e. $f_a \equiv 0$.

In these models, meteorological conditions are constant. Deposition processes are neglected. The interactions of plume with the ground or inversion layer are not considered either.

In both models, only basic chemical reactions connected with oxidation of NO and photolysis of NO_2 are taken into account, i.e. only $NO/NO_2/O_3$ system is considered. In the model of Carmichael and Peters, it is assumed that chemical reactions take place only in a mixed phase of plume, while in the model of Janssen, chemistry is allowed to act in both phases of stack effluents: mixed phase and undiluted phase.

The change of pollutant concentration in a mixed volume is calculated based on a set of mass balance equations. There is one equation for one species. Terms representing the entrainment of reactant to the volume, volume expansion and chemical changes are included in this equation. It takes the following form:

$$\frac{d\overline{C}_{i,m}}{dt} = -\frac{\overline{C}_{i,u,p}}{f_m}\frac{df_{u,p}}{dt} \frac{\overline{C}_{i,m}}{f_m}\frac{df_m}{dt} + \overline{R}_{i,m}(\overline{C}_i, \overline{C}_{i+1}, ...) - \frac{\overline{C}_{i,u,a}}{f_m}\frac{df_{u,a}}{dt}, \tag{5}$$

where: $\overline{C}_{i,m}$, $\overline{C}_{i,u,p}$, $\overline{C}_{i,u,a}$ are the mean concentrations of the species i in a mixed phase of plume, undiluted stack effluents and undiluted ambient air, respectively; $\overline{C}_{i,u,p}$ is constant in time or is calculated based on chemical reaction equations; f_m, $f_{u,p}$, $f_{u,a}$ are the fractions of total volume occupied by the mixed material, undiluted stack effluents and undiluted ambient air, respectively; $\overline{R}_{i,m}$ is the change in the concentration of the species i due to chemical processes.

The models of class 2 apply only to the near-field simulation of the behaviour of reactive plumes. The distance of 50 km seems the maximum one.

The model of Carmichael and Peters was used to study NO oxidation in a plume from the Potomac Electric Company power plant at Morgantown, Maryland, the U.S.A. The plume was traced up to a distance of 15 km from the stack. An empirical parameter k_m was estimated based on the paper by SHU et al. [47] and the data generated by Deardoff's numerical turbulence model [16]. Predicted temporal profiles of key pollutants and large deviation from the photostationary state in a plume were consistent with the observations.

The model of Janssen was used to study NO oxidation rates in plumes of some Dutch power plants of KNMI database [35] and in one German power plant [24].

Plumes were traced up to a distance of 50 km. The empirical parameters required were chosen in such a way that calculated NO_2/NO ratios agreed with measured values. Results showed the following characteristics. A plume, at some distance from a stack, consists largely of unmixed air. At a height of plume axis oxidation reactions of NO_2 with O_2 must also be taken into account. When a plume is reaching the ground it can be considered to be diluted, well mixed and homogeneous. In such a situation, O_2 oxidation does not need to be considered any longer.

The advantage of the models of class 2 over the models of class 1 seems to be only relative as in the models of class 2 we employ empirical parameters whose values are estimated based on data fitting. These parameters not necessarily are independent of a source height or meteorological conditions [8].

4. CLASS 3. SECTIONALLY HOMOGENEOUS EXPANDING MULTI-VOLUME MODELS

Models belonging to this class account for both expansion of plume and sectionally homogeneous mean concentration fields. Fluctuations of concentrations are not considered here. These models can be regarded as the development of the uniformly mixed expanding volume models of class 1. An expanding plume is divided either into an array of boxes of rectangular cross sections ("multi-box models") or concentric elliptical rings ("multi-ring models"). In each sub-volume, species are perfectly mixed.

In most of "multi-box models", it is assumed that a plume occupies a whole mixing layer. Usually the exchange of material with the air aloft, i.e. above the mixing layer, is taken into account. The horizontal extension of plume is determined based on a time-averaged dispersion coefficient. The boxes have either equal volumes [18], [19], [29] or their volumes are defined by the requirement that the total mass of each pollutant is initially equally divided between the boxes [48]. To evaluate the mass in the boxes or box volumes it is assumed that at a specific distance, close to a stack, there is the Gaussian distribution of concentrations in the horizontal direction inside plume boundaries. Beyond this specific distance chemical reactions do not proceed in a plume. The schematic representation of plume in the multi-box models is given in figure 2a.

The change of pollutant concentration inside each box is calculated based on a set of mass conservation equations. There is one equation for one species. This equation includes terms representing: the expansion of box volume, change of concentration due to chemical reactions and deposition, exchange of material with the air above the inversion layer and between the neighbouring boxes. In the case of outermost boxes, an entrainment of the ambient air is taken into account. The governing equation takes the following form:
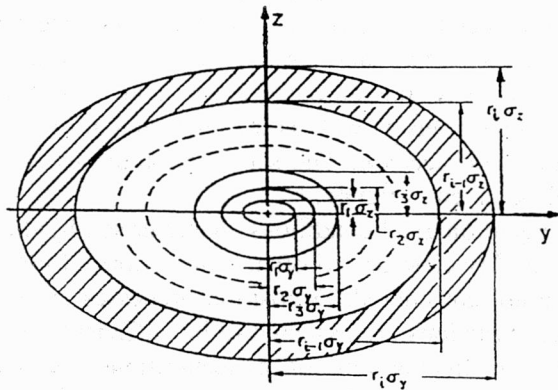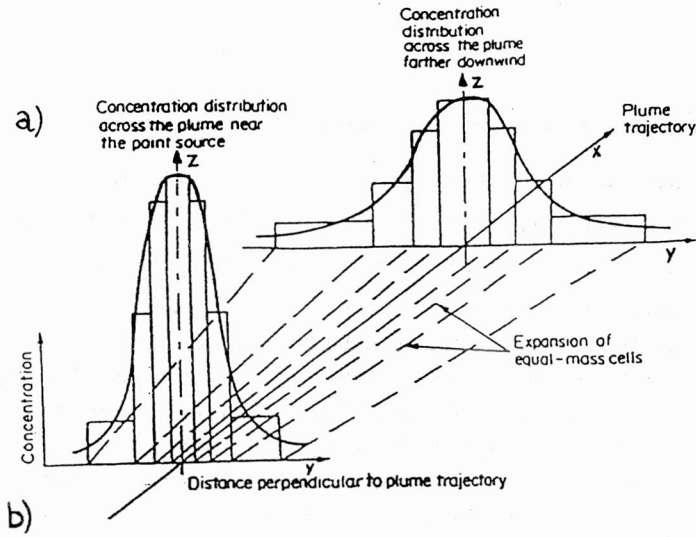
Fig. 2. Schematic representation of plume in sectionally homogeneous expanding multi-volume models:
a) in the muti-box model [48], a cross section of plume is divided into an array of boxes of rectangular
cross sections; plume boundaries in the horizontal direction are described by dispersion coefficient;
initially we have the Gaussian distribution of concentration in the horizontal direction;
b) in the multi-ring model [43], a cross section of plume is divided into concentric rings; plume bounda-
ries are described by dispersion coefficients; initially we have the Gaussian distribution of concentration
in a plume cross section

$$\frac{d\overline{C}_i^j}{dt} = -\left(\frac{1}{w^j}\frac{dw^j}{dt}\right)\overline{C}_i^j - \left(\frac{1}{h^j}\frac{dh^j}{dt}\right)\overline{C}_i^j$$

$$+\left(\frac{1}{h^j}\frac{dh^j}{dt}\right)\overline{C}_{i,a} + F_i^j + \overline{R}_i^j + \frac{v_i}{h_j}\overline{C}_i^j + S_i^j,\tag{6}$$

where: $\overline{C}_i^j$, $\overline{C}_{i,a}$ are the mean concentrations of the species i in the box j and above the inversion layer, respectively; w_j, h_j are the width and height of the box; F_i^j is the mass transfer across the expanding j-th box boundaries; v_d is the deposition velocity of the species i; S_i^j is the flux of the species i from the ground to the box j; $\overline{R}_i^j$ is the change in the concentration of the species i in the j-th box due to chemical processes.

Different mixing schemes for parametrisation of the interaction between neighbouring boxes are used. The examination of some schemes can be found in the paper of CLARK and COX [7]. Compositions of the ambient air and air aloft (i.e. above the mixing layer) in most cases are calculated by means of a simple model. Usually many types of species are taken into account and complex chemistry schemes are applied.

The idea of portioning out the plume cross section to boxes in the vertical direction was extended further and in a model of CHANG et al. [6] a plume cross section was divided laterally and vertically into equal rectangular boxes.

In the "multi-ring models" [43], [44], plume boundaries are determined based on horizontal and vertical dispersion coefficients. Surfaces of concentric rings into which plume cross section are divided at each distance from a source are determined by the requirement that each ring contains an equal mass of inert pollutants. The turbulent exchange between adjacent rings as well as the entrainment of the ambient air to the outermost ring is taken into account. The schematic representation of plume in the multi-ring ring models is given in figure 2b.

In these models, meteorological conditions characterised by the mean wind velocity and atmospheric stability class are constant. Interactions of plume with the ground or inversion layer are not considered. Deposition processes are neglected. As far as chemistry is concerned reactions are assumed to be sufficiently slow so they are not influenced by fine-scale fluctuations of concentrations. In some models, only $NO/NO_2/O_3$ system is considered [44]. In other models, a whole range of chemical species is taken into account [4], [19], [29].

The change of concentration in each ring is calculated based on a mass conservation equation. This equation for the ring j for the species i takes the following form [22], [23]:

$$\frac{d\overline{C}_i^j}{dt} = f\left(l_i\overline{C}_i^{j-1} + m\overline{C}_i^j + n\overline{C}_i^{j+1}\right) + \overline{R}_i^j\left(\overline{C}_i,\overline{C}_{i+1},...\right),\tag{7}$$

where: j is the number of the ring; f is the parameter calculated as the function of the product of Gaussian dispersion coefficients δ_y and δ_z; l, m, n are the parameters cal-

culated as the functions of the ring index j and the total number of rings N; $\overline{R}_i^j$ is the change of pollutant concentration due to chemical reactions.

For inert pollutant this method is equivalent to the method of discrete approximation allowing us to arrive at the Gaussian concentration distribution. The goodness of the fit depends on a number of elliptical rings used.

The models of class 3 were applied to simulate the behaviour of reactive plumes emitted from power stacks for distances up to ~150 km. Most of these models were validated based on data collected during intensive field experiments. Good consistence of models results with the measurements was obtained.

Table 2

Examples of the sectionally homogeneous expanding multi-volume models

1. References 2. Institution 3. Tests performed/Validation	4. Model concept a) Shape of plume cross sections b) Determination of plume boundaries c) Plume interactions with the ground or inversion layer d) Parametrisation of the mass transfer between the neighbour boxes/rings in a plume cross section e) Types of primary species considered (plume and ambient air) f) Chemical kinetic scheme applied g) Other physical processes
1. STEWARD and LIU [48] 2. System Applications Incorporated, San Rafael, USA 3. Comparison of model predictions of photochemical oxidants (NO, NO$_2$, O$_3$) in power-plant plumes with field measurements: Widows Creek power plant, Alabama, USA; Oak Greek power plant, Wisconsin, USA	4. a) Rectangular b) Based on dispersion coefficients δ_y, δ_z (Briggs curves). Plume depth/width equals $4\delta_z/4\delta_y$ c) Vertical expansion of the plume limited by the ground and inversion layer d) Array of boxes of different volumes. Initially the Gaussian distribution of concentration inside plume boundaries and total mass of pollutant is equally divided between the boxes; diffusivity coefficients' values are determined in such a way that net mass fluxes across the expanding box boundaries for inert species are equal to zero e) NO, NO$_2$, CO, SO$_2$, HCs (paraffin, olefin, carbonyl, ethylene) f) Carbon bound mechanism (CBM) of WHITTEN et al. [51]; gas-phase chemistry; 65 reactions; NO$_2$ photolysis rates calculated based on algorithm of SCHERE and DEMERIJAN [17] g) Not considered

1. HOV and ISAKSEN [29] 2. Institute of Geophysics, University of Oslo, Norway 3. Simulation of general characteristics of the secondary pollutants formation in power-plant plumes in a fair weather	4. a) Rectangular b) Vertically plume fills up the whole mixing layer; plume depth equals $4\delta_y$ c) Vertical expansion of the plume limited by the ground and inversion layer; reservoir layer above mixing layer d) Array of boxes of equal volumes. The ambient air enters boxes cross-wind and aloft. In a scheme applied, 2 sequential processes are distinguished: diffusion and grid expansion. Diffusion is calculated on a fixed space grid. After a finite time step the results are interpolated on the expanded grid. Linear transformation is used. Diffusivity coefficients determined assuming the Gaussian distribution for inert species e) SO_2, NO, NO_2, CO, HCs f) Gas-phase chemistry; ~200 reactions, 85 species; scheme developed by DERWENT and HOV [19]. Diurnal variation of solar radiation computed based on the scheme of HOW and ISAKSEN [29]. No chemistry during first 15 minutes of a plume travel g) Deposition
1. DERWENT [18], [19], [20] 2. Harwell Laboratory, UK 3. Examination of major features of secondary pollutants formation in power-plant plumes under typical UK conditions	4. a) Rectangular b) Vertically plume fills up the whole mixing layer, plume depth equals $4\delta_y$ c) See b) d) Array of boxes of equal volumes, the initial mass of pollutant evaluated based on the Gaussian distribution of concentrations. Ambient air enters boxes downwind and aloft. Parametrisation of mass transfer follows that in the model of STEWARD and LIU [48] e) SO_2, NO, NO_2, CO, 28 different groups of HCs f) Gas-phase chemistry, ~100 reactions; scheme developed based on papers of DERWENT and HOV [19]. Photolysis rates vary diurnally with solar zenith angle calculated by the method of DERWENT and HOV [19] g) Deposition, aerosol scavenging

1. MELO and STEVENS [43], [44] 2. Atmospheric Environment Service, Canada 3. Interpretation of field data referring to NO$_2$ formation in a power-plant plume	4. a) Elliptical b) Based on the dispersion parameters δ_y and δ_z c) Not considered d) Concentric rings. Surfaces of rings determined by a requirement that each ring contains equal mass of inert species. Ambient air enters outermost ring. Turbulent exchange of material between adjacent rings e) NO$_2$, NO f) NO/NO$_2$/O$_3$ system, pseudo-steady state for 0 atoms, photolytic rate coefficients vary diurnally g) Not considered
1. BOTTENHEIM and STRAUSZ [4] 2. University of Alberta, Canada 3. Quantitative explanation of field measurements (oxidation rate of SO$_2$ during sunny days within the range of 1–5 h^{-1}. Under certain conditions ozone bulges downwind from a stack: GCOS power plant, Alberta, Canada, and Milwaukee power plant, Wisconsin, Canada	4. a)–d) See above in the model of MELO and STEVENS [43], [44] e) SO$_2$, NO, NO$_2$, HCs f) Scheme developed based on: Carbon Bond Mechanism [51], SCHEME and LIRAQ mechanisms; gas-phase chemistry; ~38 reactions; photochemical rate coefficients estimated based on the procedure of SCHERE and DEMERIJAN [17]. No chemistry during first 2,5 minutes of plume travel g) Not considered
1. MARKIEWICZ [39], [40], [41] 2. Warsaw University of Technology, Poland/AEA Technology, Harwell laboratory, UK 3. Influence of environmental parameters on the behaviour of chemically reactive plumes emitted from a coal-fired power station	4. a)–g) See above in the model of DERWENT

Computer simulations confirmed that secondary pollution formation in power-plant plumes depends on: the intensity of mixing, compositions of stack gases and ambient air, intensity of solar radiation. They showed that the distribution of secondary species in time is a striking demonstration of three stages of plume development. There is an initial stage with depletion and minimum at the centre line, an active fringe region with the centre line chemistry lagged behind, and finally the fully developed stage with maximum at the plume centre line [18], [19], [29], [39], [40], [41].

A multi-box model of STEWARD and LIU [48] in the modified version was used to simulate subgrid processes in a PARIS airshed model [46]. The change of meteorological conditions characterised by the mean wind velocity, atmospheric stability class and height of the mixing layer were included in this model. However, under some conditions the subgrid scale treatment of large point-source emissions is important, for example in determining the impact of specific point source in urban areas, it was

concluded that a detailed treatment of point sources is not critical for conventional urban airshed modelling studies.

The examples of specific models of class 3 with their characteristics and the tests carried out or validation are given in table 2.

5. CLASS 4. EXTENDED GAUSSIAN-TYPE MODELS

In the models included in this class, both the expansion of plume and inhomogeneous continuous concentration fields are taken into account. The fluctuations of concentrations, as in the previous models, are neglected. These models can be considered as equivalent to the Gaussian-type models for inert species as the omission of chemical processes in these models leads to the Gaussian distribution of mean concentrations in plume boundaries.

In the models of class 4, the mathematical description of the behaviour of species is based on a simplified transport/diffusion/chemistry equation. It is assumed that: (i) wind blows along x-axis with mean speed which is constant independently of a height; (ii) the molecular diffusion is neglected; (iii) the turbulent diffusion along the x-direction is neglected; (iv) the concentration field is constant in time; (v) there is no volume sources of considered species from the ground.

The "conventional" first-order closure based on K-theory is used to close the equation with respect to the turbulent fluxes. The "conventional" closure considering only mean concentrations is applied with respect to the chemical term.

The transport/dispersion/chemistry equation for the species i under these conditions takes the following form:

$$\overline{u}\frac{\partial \overline{C}_i}{\partial x} = \frac{\partial}{\partial y}\left(K_y\frac{\partial \overline{C}_i}{\partial y}\right) + \frac{\partial}{\partial z}\left(K_z\frac{\partial \overline{C}_i}{\partial z}\right) + R_i\left(\overline{C}_i, \overline{C}_{i+1}, ...\right), \qquad (8)$$

where: $\overline{u}$ is mean wind speed; $\overline{C}_i(x, y, z)$ is the mean concentration of the species i at a point (x, y, z) of the Cartesian co-ordinate system; K_y, K_z are the eddy diffusivity coefficients in the horizontal and vertical directions, respectively; $\overline{R}_i$ is the change in concentration of the species i due to chemical processes.

Two types of models can be distinguished in this class. The first group involves the models in which a set of governing equations (there is one equation for one species) is solved directly with respect to mean concentrations (numerical extended Gaussian-type models). The second group comprises the models in which a set of governing equations is rearranged by introducing auxiliary variables to a set of equations which do not involve any chemical terms and which can be solved analytically with respect to the auxiliary variables (analytical extended Gaussian-type models).

In the numerical extended Gaussian-type models, a set of transport/dispersion/chemistry equation is considered in the Lagrangian co-ordinate system [43], [34]. In addition to the listed assumptions (i)–(iv), the turbulent diffusion is considered to be isotropic. In this condition, the governing equation for the mean concentration of the species *i* takes the following form:

$$\frac{\partial \overline{C}_i}{\partial t} = K_r(t)\left(\frac{\partial^2 \overline{C}_i}{\partial r^2} + \frac{1}{r}\frac{\partial \overline{C}_i}{\partial r}\right) + \overline{R}_i\left(\overline{C}_i, \overline{C}_{i+1}, ...\right), \qquad (9)$$

where: $\overline{C}_i$ is mean concentration of the species *i* at the receptor point in the Lagrangian co-ordinate system; K_r is the eddy diffusivity; *r* is the distance from a plume centre; $\overline{R}_i$ is the average reaction rate of the species *i*.

The eddy diffusivity coefficient has a constant value [43] or it varies with travel time [34]. The change of the eddy diffusivity coefficient $K_r(t)$ is described by the following equation:

$$\delta_r = \left(\delta_y \cdot \delta_z\right)^{0.5} = 2K_r(t)x/\overline{u}, \qquad (10)$$

where: δ_y, δ_z are horizontal and vertical dispersion coefficients, respectively; δ_r is an effective dispersion coefficient; $K_r(t)$ is eddy diffusivity coefficient; *x* is the distance from a stack; $x = \overline{u} \cdot t$; $\overline{u}$ denotes mean wind speed.

In the numerical extended Gaussian-type models, meteorological conditions do not change. They are characterised by mean wind speed and atmospheric stability class. We do not consider the plume interactions with the ground or inversion layer. Deposition processes are neglected. Only $NO/NO_2/O_3$ system is considered.

In the analytical Gaussian-type models, the transport and dispersion are studied separately from chemical reactions in terms of auxiliary variables [45], [50]. These auxiliary variables are linear functions of concentrations. A set of *n* differential equations with respect to *n* species is transformed to a set of $n-1$ differential equations with respect to $n-1$ auxiliary variables.

The transport/diffusion/chemistry equation with respect to the auxiliary variable $\overline{\phi}_{i,k} = f\left(\overline{C}_i, \overline{C}_k\right)$ has the following form:

$$\frac{\partial \overline{\phi}_{i,k}}{\partial t} = \frac{\partial}{\partial y}\left(K_y\frac{\partial \overline{\phi}_{i,k}}{\partial y}\right) + \frac{\partial}{\partial z}\left(K_z\frac{\partial \overline{\phi}_{i,k}}{\partial z}\right), \qquad (11)$$

where: $\overline{u}$ is mean wind velocity; $\overline{\phi}_{i,k}$ is mean auxiliary variable; K_y, K_z are horizontal and vertical eddy diffusivity coefficients, respectively.

The equation has the same form as the transport/diffusion/chemistry equation for an inert species, if variable $\overline{C}_i$ takes place of variable $\overline{\phi}_{i,k}$. Standard methods of solving this equation for an inert species can be applied. Introducing assumptions and initial boundary conditions, which lead to a Gaussian plume model [45], we arrive at the following formula with respect to $\overline{\phi}_{i,k}$

$$\overline{\phi}_{i,k}(x, y, z) = \overline{\phi}_{i,k} + \frac{Q_{i,k}}{(2\pi\overline{u}\,\delta_y\delta_z)} \exp\left[-\frac{y^2}{(2\delta_y^2)}\right]$$

$$\times\left\{\exp\left[-\frac{(z-H)^2}{(2\delta_2^2)}\right] + \exp\left[-\frac{(z+H)^2}{(2\delta_2^2)}\right]\right\}, \tag{12}$$

where: $Q_{i,k} = v_k Q_i + v_i Q_k$; Q_i, Q_k are intensities of the emission of respective species i, k from the stack; v_i, v_k are stoichiometric coefficients of the species i, k, respectively; $\overline{u}$ is mean wind speed; H is the height of effective emission; δ_y, δ_z are horizontal and vertical dispersion coefficients, respectively.

The concentrations $\overline{C}_i$, $\overline{C}_k$ of the species i, k are obtained by solving a set of algebraic equations combined with an equilibrium equation. Algebraic equations are those which relate concentrations to auxiliary variables.

Similarly to the numerical models described in this section meteorological conditions in these analytical models are constant. There are no interactions of plume with the ground or inversion layer. Deposition processes are neglected. In the analytical extended Gaussian-type models, it is assumed that chemical reactions are fast enough so the local chemical equilibrium is achieved at a receptor side. However, an equilibrium equation is valid only for instantaneous concentrations and it is assumed that it applies to average concentrations as well. In these models, only NO/NO$_2$/O$_3$ system is considered and photostationary state is assumed. As the auxiliary variables conserved scalars of this system are applied, i.e. total oxidants: $\overline{\phi}_1 = $ NO$_2$ + O$_3$ and total nitrogen oxides: $\overline{\phi}_2 = $ NO + NO$_2$. The photostationary-state equation is used in this case instead of an equilibrium equation.

The models of class 4 were used to study the behaviour of reactive plumes from power stacks for the distances up to 50 km. Some models were verifed. The importance of specific chemical reactions in the oxidation of NO to NO$_2$ was examined. Other models were validated based on a large number of experiments carried out under different emission and meteorological conditions[2], [32], [33], [34], [45], [50]. The comparisons confirmed that much better results are obtained when we use instantaneous values of dispersion coefficients instead of time averaged ones [2].

Table 3

Examples of the extended Gaussian-type models

1. References 2. Institution 3. Tests performed/validation	4. Model concept a) Shape of plume cross sections b) Determination of plume boundaries c) Plume interactions with the ground or inversion layer d) Types of primary species considered (plume and ambient air) e) Chemical kinetic scheme applied f) Other physical processes
1. PETERS and RICHARDS [45] model verification: BANGE et al. [2] 2. University of Kentucky, USA/Environmental Research Department, NV KEMA, Arnheim, the Netherlands 3. Influence of introduction of instantaneous dispersion parameters on modelling the oxidation of NO emitted into O_3 containing atmosphere: 10 year KEMA field experiments carried out on many Dutch power plants and one German plant	4. a) Circular b) Based on the dispersion coefficients δ_y, δ_z c) Not considered d) NO, NO_2 e) $NO/NO_2/O_3$ system. Photostationary state f) Not considered
1. VAREY, SUTTON and MARSH [49] 2. – 3. Examination of the roles of specific reactions in oxidising NO to NO_2 in a plume $NO + O_3 \rightarrow NO_2 + O_2$ (1) $2NO + O_2 \rightarrow 2NO_2$ (2)	4. a) Circular b) Based on turbulent diffusivity coefficient c) Not considered d) NO, NO_2 e) $NO/NO_2/O_2$ system. Photostationary state not assumed f) Not considered
1. WHITE [50] 2. Meteorology Research Inc, California, USA 3. Analysis of field measurements of power-plant plumes.(Plume O_3 concentrations below background levels, O_3 deficit and HO–NO to NO_x decrease with distance from a stack): Labadie coal-fired power plant, Mo, USA	4. a)–f) See above in the model of Peters and Richards
1. JANSSEN, van HAFEN, BANGE and van DUUREN [32], [33], [34] 2. Environmental Research Department, NV KEMA, Arnheim, the Netherlands 3. Comparison of the formation of secondary species in power-plant plumes during the day and night time. (Model prediction and measurements: power plant, Amer., the Netherlands	4. a)–f) See above in the model of VAREY [49]. Diffusion equation for each species with chemistry term added

The examples of the specific models of class 4 with their characteristics and the tests conducted or validation are given in table 3.

6. CONCLUSIONS

Based on the first part of the review of chemically reactive plume models the following conclusions can be drawn:

1. Chemically reactive plume models incorporating turbulent mixing processes related to mean concentrations (i.e. macro-mixing processes) differ in the treatment of plume dispersion and the complexity of the chemical schemes applied.

2. Chemically reactive plume models incorporating macro-mixing processes are an important aid in learning how environmental parameters influence the plume dispersion and in exploring processes occurring in chemically reactive stack plumes.

3. Chemically reactive plume models incorporating macro-mixing processes are a useful tool in engineering studies.

4. Investigating the turbulent reactive flows in the atmosphere we have to account of mixing processes related to both mean concentrations and concentration fluctuations (i.e. macro-mixing and micro-mixing processes). The models incorporating macro-mixing and micro-mixing processes will be discussed in the second part of this review.

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PRZEGLĄD MODELI SMUG REAKTYWNYCH CHEMICZNIE
CZEŚĆ I. MODELE UWZGLĘDNIAJĄCE PROCESY MAKROMIESZANIA

Przedstawiono modele smug reaktywnych chemicznie. Opisują one proces powstawania zanieczyszczeń wtórnych w smugach emitowanych z wysokich punktowych źródeł emisji. Modele zostały podzielo-

ne na klasy zależnie od sposobu opisu procesów mieszania turbulencyjnego. Termin *mieszanie turbulencyjne* obejmuje makromieszanie i mikromieszanie. Procesy makromieszania odnoszą się do zmian stężeń średnich, podczas gdy procesy mikromieszania są związane z fluktuacjami stężeń, tj. odchyleniami stężeń od wartości średnich. Przegląd modeli obejmuje dwie części. W pierwszej z nich pokazano modele, w których uwzględniono tylko procesy makromieszania, w części drugiej natomiast modele dotyczące procesów mikromieszania, jak też modele opisujące oba te procesy, tj. mikro- i makromieszanie.