

APPLICATION OF THE MONTE-CARLO METHOD TO THE DESCRIPTION OF THE DYNAMICS OF THE SPREAD OF SALVO POLLUTION COMPLICATED BY ADSORPTION

Serghei Travin 

*Semenov Federal Research Centre for Chemical Physics of the Russian Academy of Sciences,
4, Kosygina str., Moscow 119991, Russian Federation
e-mail: TravinSO@yandex.ru*

Abstract. The possibilities of application of the Monte-Carlo method for simulating the consequences of pollutants emissions with specific adsorption on the underlying surface were considered. The basic techniques for the implementation of the model in the VBA-Excel environment are shown. The possibilities of the developed software toolkit for the application of the Monte-Carlo method to solving problems of the spatio-temporal dynamics of a pollution spot in natural conditions are demonstrated. Effective methods of obtaining kinetic curves for the concentration of a pollutant for a selected square on the field and constructing contamination profiles for a specified time are analysed. The estimation of the necessary parameters of the model for obtaining high-quality kinetic curves was performed and recommendations for their optimization are given. Specific fronts for the spot propagation were obtained and visualised.

Keywords: Monte-Carlo method, mass transfer, adsorption, spatial-time dynamics, computational efficiency.

Received: 7 November 2021/ Revised final: 21 December 2021/ Accepted: 21 December 2021

Introduction

The possibility of using the Monte-Carlo method for modelling of various eco-chemical tasks is a relevant topic of research although difficult to achieve because of different schemes for the numerical integration of systems in partial derivative equations which can offer different solution [1]. It was demonstrated that even with the use of relatively low-power personal computers in a short time, it is possible to obtain sufficiently detailed information on the spread of a pollution spot during an explosive release and to visualize space-time sections for the concentration of the pollutant [1-4]. At the same time, it should be noted that the simplest model of chemical degradation and distribution of matter in a homogeneous medium was used [2]. It was of considerable interest to expand the possibilities of modelling to the cases where the spot spreading occurs at the interface between media with significantly different physicochemical properties [2].

The adsorption of pollutants on the soil can be modeled by the Monte-Carlo simulation approach. A characteristic feature of multimedia (*i.e.*, containing several media) models is the distribution of substance over different components of the natural environment, which

differ in the nature of their behaviour. So far, previously was modeled only the interaction of two media: the surface of soil and the nearest tropospheric layer, which provides active transport [2]. It is equally important to consider the characteristics that arise when a pollutant “clings” to the soil. Without going into explanations, it can be confirmed that using the well-known Langmuir adsorption Eq.(1), it is possible to describe almost all conceivable variants of the interaction of a substance with the soil: from weak interaction in the Henry’s law regime to complete binding, limited by the ultimate soil capacity.

$$N = N_0 \cdot \frac{KA}{1+KA} \quad (1)$$

All variations can be performed using two control parameters, the binding sites N_0 and the adsorption equilibrium constant K . In this case, an unexpected situation arises: the Langmuir isotherm (a curve with saturation), which gives the dependence of the amount of a bound substance on the concentration of an unbound one. But there was no answer to deal with the question of the dependence of the amount of the remaining free substance on its total amount.

© Chemistry Journal of Moldova
CC-BY 4.0 License

Although the answer to it is not difficult at all, surprisingly it remained in the shadows. The balance in terms of the concentration of the adsorbate is reduced to the fact that it can be either in the free (A) or in the bound (N) states:

$$A_0 = A + N \quad (2)$$

Substituting into Eq.(2) the expression for N from Eq.(1), it was obtained Eq.(3).

$$A_0 = A + N_0 \cdot \frac{KA}{1 + KA} = A \left(\frac{1 + KA + KN_0}{1 + KA} \right) \quad (3)$$

And after simple calculations (solving the quadratic Eq.(4) or Eq.(5)), it was obtained Eq.(6) [1] linking the amount of unbound (free) pollutant with its initial amount A_0 , the limiting capacity of the binding sites N_0 and the adsorption equilibrium constant K , this result can be presented graphically (Figure 1).

$$A_0 + KAA_0 = A + KA^2 + KN_0A \quad (4)$$

$$KA^2 + A(1 + KN_0 - KA_0) - A_0 = 0 \quad (5)$$

$$A = \frac{-1 - K(N_0 - A_0) + \sqrt{(1 + K(N_0 - A_0))^2 - 4KA_0}}{2K} \quad (6)$$

Thus, the main goal of this paper was to demonstrate that the Monte-Carlo approach is suitable for simulation modeling and visualization of the spread of pollution spots. The specific interest of this work was oriented on pollution profile changes due to specific adsorption on the underlying surface (soil, water). Also kinetic behavior of the pollutant concentration in every point became much more complicated (in comparison with „plain” model without adsorptive binding).

Computational details

Production of the “plain model”

For the model, it was assumed that each cell can receive 20 portions of the pollutant. At the same time, the question of what is a “portion” remains open, since this modelling is carried out with an accuracy of up to certain proportionality coefficients, and their determination requires linking model calculations to real situations. Note that at this stage it is considered that chemical (or physical) degradation can occur regardless of whether the pollutant is in a bound or free-state. This approach is undoubtedly appropriate for the analysis of releases of radioactive substances, since the rate of their decay does not depend on the aggregate and chemical state of the radionuclide. Apparently, in most cases associated

with photolysis, oxidation with atmospheric oxygen, *etc.*, this approach remains valid. However, in the presence of appropriate experimental data, it is easy to enter into the model different transformation rate constants for the free and adsorbed forms of the pollutant. In the meantime, the restrictions were introduced only on the mobility of the adsorbed form of the pollutant. Thus, only a fraction of the remaining free pollutant should be introduced. Figure 2 shows how it depends on the total amount of stuffing for different binding constants. As in Figure 1, the limiting cell capacity $N_0 = 20$ was taken for the model. This value was chosen solely for reasons of clarity; in other model calculations, it varied within wide limits.

The calculated fraction of a substance in a free, non-adsorbed state is given by Eq.(7).

$$\alpha = \frac{A}{A_0} \quad (7)$$

Calculation of the relative fraction of unbound matter makes sense, since only unbound matter can migrate as a result of advective (caused by winds and currents) and convective diffusion.

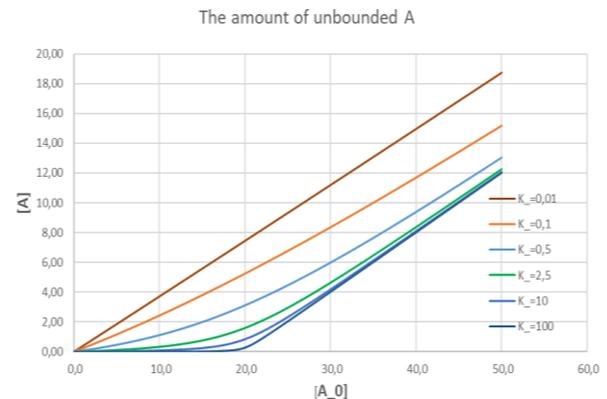


Figure 1. Graphs of the dependence of the amount of free substance on its total amount. (parameter N_0 is set to be equal to 20).

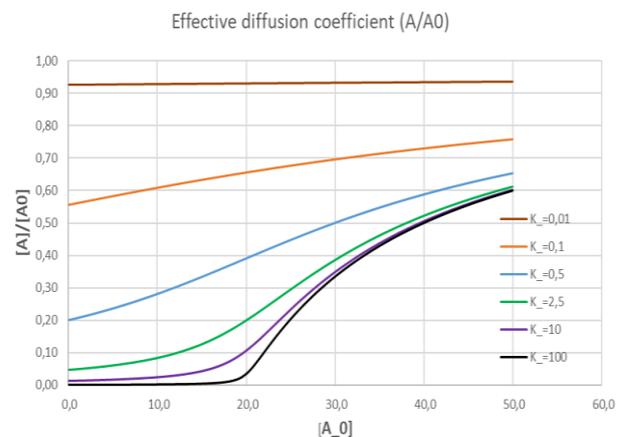


Figure 2. Graphs of the dependence of the fraction of free substance on its total amount.

For obvious reasons, the diffusion rate of the adsorbed part of the pollutant can be considered as negligible. In this case, the effective coefficient of diffusion can be obtained by multiplying the valid coefficient by α . A similar proportion is obtained for the drift velocities in the directions of the axes x and y .

$$D_{eff} = \alpha D \quad (8)$$

Simulation procedure

The calculations were performed according to the previously reported procedure [1]. Briefly, for computer simulation of the “*in silico*” experiments, a simple model was used. An ensemble of N_{dots} pollutant particles was taken as an object for simulation. As a rule, but not necessarily, a number of particles was selected as multiple of powers of 2 and usually in the range from 1024 to 8192. For each of the particles at each step of the simulation, the probabilities of the following events were estimated: random walk on x , random walk on y , drift in the velocity field and the possibility of chemical transformation. Accordingly, the value of the Brownian step (in x and in y) is given by the diffusion coefficient D , the drift by the values of the velocities v_x and v_y . After setting the size of the ensemble, firstly the spatial-temporal boundaries of the model were designated, to determine more precisely the grid division and the time step. As previously shown, dividing the grid into 400 squares (20 horizontally and 20 vertically) $R_x = R_y = 10$, in most cases gives sufficient spatial resolution to obtain an adequate kinetic picture [2]. Then, the magnitude of the time step was determined. When the value of the parameter D , which is responsible for the magnitude of the random walk step, is close to unity, for the spatial grid $R_x = R_y = 10$, the number of time steps $N_{step} \sim 100 \div 400$ was appropriate.

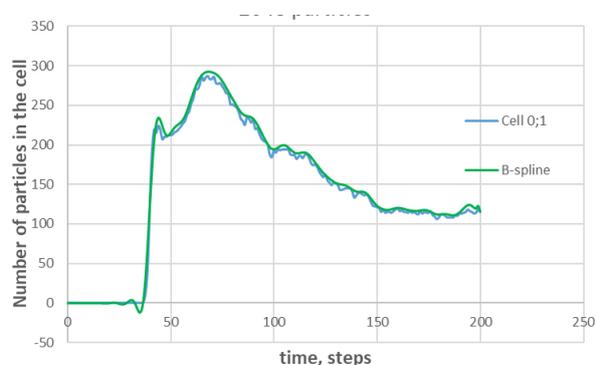
The simulation was achieved with the generation of the spatial distribution of particles after a salvo ejection, following the recommendations of the Guidance Document [3] and taking into account the normal Gaussian distribution of particles at both x and y coordinates. Practically, it was implemented as follows. The regular random number generator built into VBA-Excel is called by the function $RAND()$. In order to avoid completely identical sequences of pseudo-random numbers, before each cyclic access to the generator, the program started a single execution of the Randomize function. The pseudo-random numbers obtained in this way are in the open on both sides interval (0;1) and are distributed evenly over the interval. In order for the coordinate distributions to have a normal Gaussian shape, the built-in Excel function $Norm_Inv()$ should be used, namely: $\xi = WorksheetFunction.Norm_Inv(Rnd(), xx_0, sigma_x)$, where, $xx_0 \in [-R_x; R_x - 1]$ specifies the distribution center, $sigma_x$ – mean-square deviation, which gives the distribution with probability density:

$$f(x) = \frac{1}{\sigma\sqrt{2\pi}} \cdot e^{-\frac{(x-xx_0)^2}{2\sigma^2}} \quad (9)$$

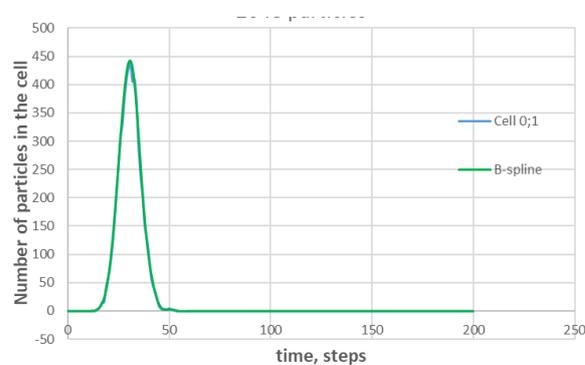
The same was done with the distribution along the y coordinate [1].

Results and discussion

One of the various time profiles (analog of the kinetic curves) is presented in Figure 3(a), the data were obtained taking into account the adsorption. There is no need to remind that at similar parameters of diffusion and mass transfer, but neglecting adsorption, similar curves had an incomparably simpler form, and were even described by equations of reactions of simple orders (from zero to second).



(a)



(b)

Figure 3. The changes in the concentration of a substance in one of the selected cells with (a) and without (b) adsorption.

However, it is appropriate to consider the recommendation to solve a part of the problem analytically, and, using this partial solution to try to build a Monte-Carlo method for solving the entire problem with a variance less than the original one. The obtained kinetic curves cannot be described analytically, therefore, the only acceptable way to deal with noise and natural variance inherent in the Monte-Carlo method is to increase the number of points in the ensemble and the number of accumulations is working, *i.e.*, in this sense, the ergodic hypothesis is confirmed). Although the reduction in noise proportional to $1/\sqrt{N}$ is considered to be relatively slow, as the computational capacity grows as $O(N)$ or even as $O(N^n)$, there is no other way at the moment. Moreover, such a path (brute force) does not actually require so much machine costs. In all experiments “*in silico*”, the operator never had to wait more than two minutes for a response from the desktop computer (without any cloud computing calculations). At the same time, the produced result always possessed acceptable and sometimes even excessive accuracy.

The attention was paid to one more non-trivial fact. Figure 4(a)-(f) shows the successive shapes of a spot, then of contamination

plume of pollution at different points in time. Surprisingly, the trajectory of the spread of pollution narrows as it progresses. It would seem that this fact contradicts both common sense and everyday experience. Note that in this series of computational experiments, the adsorption capacity of the cell was doubled as compared to the usual one (40 instead of 20), which makes it possible to demonstrate more clearly the effect of spot pulling and the concentration of the pollutant at the boundary. Such an unexpected result of a computational experiment even raises questions about the adequacy of the applied model and its performance. In fact, the resulting picture has a completely rational explanation. At the periphery of the plume (more precisely, on the sides), the number of particles is initially less than in the centre. This is a completely natural property of the original Gaussian distribution. And here the adsorption effect begins to play its role. In those cells where $A_0 < N_0$ the fraction of free particles is vanishingly small; they simply do not exist (Figure 1). And the ability of adsorbed particles to move, due to diffusion and due to wind drift is a couple of orders of magnitude lower than for free ones (for this series of models, the adsorption constant $K=100$ was chosen; see also Figure 2).

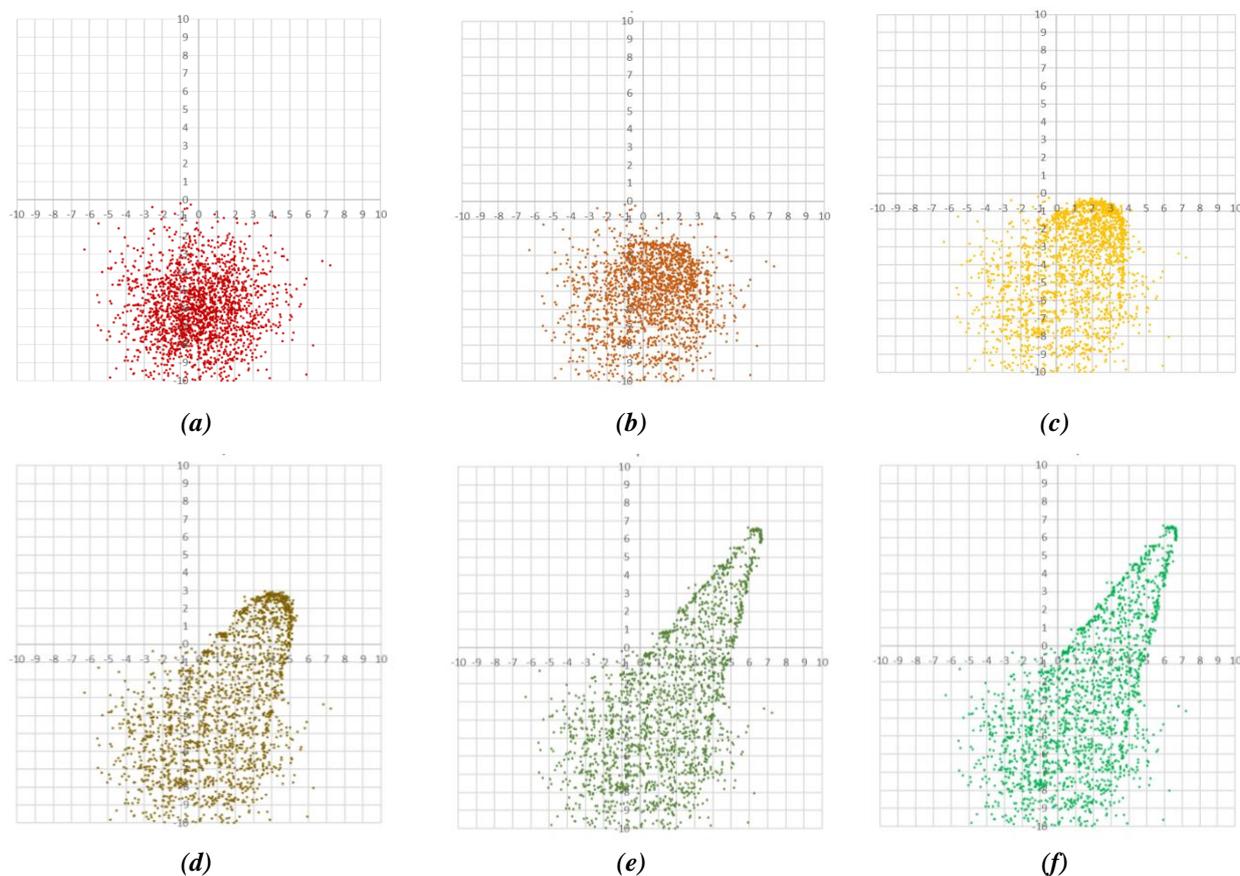


Figure 4. Time evolution of the contamination plume: initial distribution (a); after 10 steps (b); after 25 steps (c); after 50 steps (d); after 100 steps (e); after 200 steps (f).

Therefore, only that part of the spot in which $A_0 > N_0$ is capable of moving, *i.e.* central. Thus, the strange, at first glance, behaviour of the model only confirms its adequacy and compliance with physical principles. It can be also added that the model with adsorption demonstrates a higher concentration of particles at the leading edge of the dispensing front. Anyone who has done thin layer chromatography, or just spilled tea (coffee, wine, any coloured liquid) on a tablecloth, will attest that the edges of the stain are always darker.

Figures 5-8 present non-trivial information about the passage of a pollution spot through an adsorbed medium, which allows determining if the model is adequate. According to the obtained results (Figure 7), until the 40th step, the pollution is unable to reach the cell. This is followed by a rapid increase in the number of particles and a subsequent decline - the center of the spot has passed the cell. The residual number of particles in the cell for a long time is about 20. This is the adsorption capacity of the cell, which is included in the model.

Table 1

The parameters of the model.

R_x	R_y	N_dots	N_step	σ_x	σ_y	xx_0	yy_0	$D_$	V_x	V_y	$k_$
10	10	4 096	200	2.00	2.00	0.00	-6.00	0.10	0.1	0.2	0.0002

$K_$	N_0
100	40

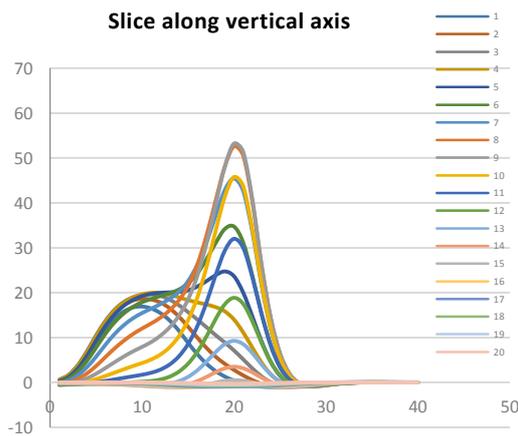


Figure 5. Evolution of slices as a function of time. ($N_0=20$ is the adsorption capacity of the cell).

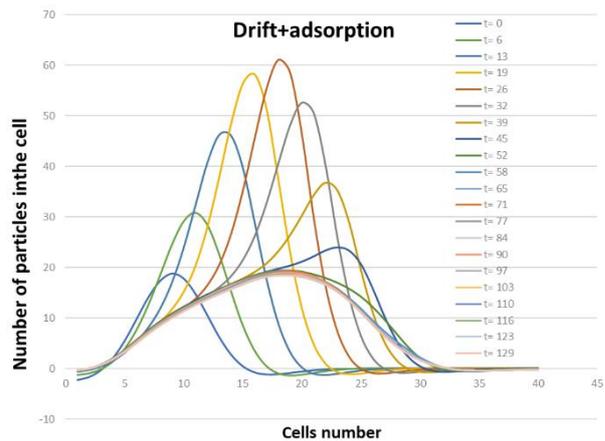


Figure 6. Change of profiles “along” the spot of time. (The attraction of the number of particles to $N_0=20$ is obvious).

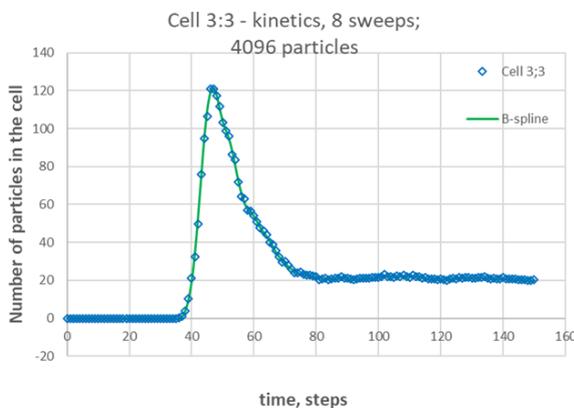


Figure 7. Kinetics of changes in the number of particles in one of the cells.

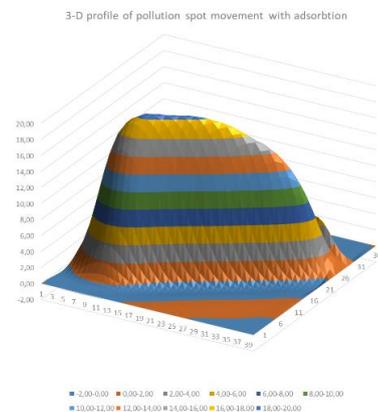


Figure 8. Typical 3D profile of concentrations in a pollution spot during distribution, taking into account adsorption.

The performed modelling shows that the expansion of the model obtained according to the methodology for calculating the dispersion of pollutants in the atmosphere [3,4], becomes much more complicated in the case of a multiphase propagation area. The produced model, using CHIMERE 2013 [5,6], consumes approximately 1 hour 30 minutes of computation time on an AMD node of a 64-bit 16 processor computer to simulate 1 month for the case considering the district of Paris *d* with a resolution of 15 km, the domain size is 45×48×8 with an average time step of 360 seconds (7200 steps by time) [4-6]. It should be noted that a simpler model, at least in terms of the grid parameters, has comparable or similar indicators: in this paper was used a 20×20×1 spatial grid (deliberately abandoning the vertical coordinate at this stage) and it can be easily extended to the CHIMERE exponents. As for kinetic calculations, it is usually required from 150 to 250 steps by time and to obtain high-quality kinetic curves it is sometimes necessary to launch up to 128 runs (128*250= 3200). As a reasonable alternative for these models, which require huge computational resources, a simple and effective scheme was proposed that gives visual results on any personal computer and requires a few seconds of computational time.

Conclusions

In conclusion, in a relatively short time, powerful modern means of software support and mathematical processing of data on the dynamics of the distribution and transformation of pollutants in natural conditions, taking into account the specific sorption of the pollutant on the underlying surface, have been developed. The basic model has been substantially supplemented with new scenarios with the adsorption of a pollution spot on the soil.

The developed model is most suitable for so-called “greedy” computer modeling, *i.e.* using the capabilities of a conventional desktop computer without parallel and/or cloud computing. The model allows you to get an understandable visualization of the consequences

of a salvo release of a pollutant in a matter of minutes, including in the presence of specific binding properties of the underlying surface. Time-series (analogues of kinetic curves) for arbitrary chosen coordinates can be obtained as well.

References

1. Travin, S.O.; Roshchin, A.V.; Duca, G.G. Application of Monte-Carlo method in environmental chemistry. *Chemical Safety Science*, 2020, 4(2), pp. 35-54. (in Russian). DOI: <https://doi.org/10.25514/CHS.2020.2.18003>
2. Travin, S.O.; Skurlatov, Yu.I.; Roshchin, A.V. Possibilities and limitations of mathematical models used for ecological safety prediction. *Chemical Physics*, 2020, 39(2), pp. 3-17. (in Russian). <http://j.chph.ru/>
3. Shershakov, V.M.; Klepikova, N.V.; Troyanova, N.I.; Freimundt, G.N.; Stogova, I.V.; Zharova, L.N. RD 52.18.717-2009. Methodology for calculating the dispersion of pollutants in the atmosphere during accidental emissions. State Institution “Research and Production Association” Typhoon, Guidance document, 2009. (in Russian). <https://docs.cntd.ru/document/1200105085>
4. Chen, Z.; Hartmann, A.; Goldscheider, N. A new approach to evaluate spatiotemporal dynamics of controlling parameters in distributed environmental models. *Environmental Modelling & Software*, 2017, 87, pp. 1-16. DOI: <https://doi.org/10.1016/j.envsoft.2016.10.005>
5. Menut, L.; Bessagnet, B.; Khvorostyanov, D.; Beekmann, M.; Blond, N., Colette, A.; Coll, I.; Curci, G.; Foret, G.; Hodzic, A.; Mailler, S.; Meleux, F.; Monge, J.-L.; Pison, I.; Siour, G.; Turquety, S.; Valari, M.; Vautard, R.; Vivanco, M.G. CHIMERE 2013: a model for regional atmospheric composition modelling. *Geoscientific Model Development*, 2013, 6, pp. 981-1028. DOI: <https://doi.org/10.5194/gmd-6-981-2013>
6. Bessagnet, B.; Hodzic, A.; Vautard, R.; Beekmann, M.; Cheinet, S.; Honoré, C.; Liousse, C.; Rouil, L. Aerosol modeling with CHIMERE — preliminary evaluation at the continental scale. *Atmospheric Environment*, 2004, 38(18), pp. 2803-2817. DOI: <https://doi.org/10.1016/j.atmosenv.2004.02.034>