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RECONSTRUCTION OF STOCHASTIC DYNAMICS OF SULPHUR DIOXIDE CONCENTRATION IN LOWER TROPOSPHERE IN SELECTED POLISH MEASUREMENT STATIONS

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In the paper, we propose the algorithm of determination mean level of emission and decay rate of sulphur dioxide (SO_2) in lower troposphere. We applied the stochastic method dedicated to extraction of components affecting the fluctuations of SO_2 concentration. For calculations, we used original time series recorded in two measurement stations in Cracow (Poland) during several years. The deterministic part of the model is represented by linear function, which coefficients can be related directly to first order kinetics of SO_2 chemical reactions. In the analyzed data, we observed large difference between production constants (marker of SO_2 emission to atmosphere) in these two measurement stations. The first value equals 0.67 $[\frac{\mu\mathrm{g}}{h\,\mathrm{m}^3}]$ and was obtained for area in close neighborhood to steelworks. The constant for second station is twice smaller. We estimated total rate of reactions of decay of SO_2, which, in our opinion, can be interpreted as contribution of anthropogenic processes to SO_2 transformation reactions.

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1. Introduction

Air pollution is a global problem [1]. Poland is one of the most polluted countries in the world due to the fossil fuel used in the industry and in heating on a large scale. On the list of the 50 most polluted cities in the European Union selected by the World Health Organization, 33 are in Poland. The situation in December 2016 led municipal authorities (in Cracow, Warsaw) to advise citizens to stay homes during the worst days.

Atmospheric pollutants can be divided into four groups: simple inorganic gases (sulphur dioxide, nitrogen oxides *etc.*), organic substances (such as hydrocarbons or complex multifunctional macromolecules), heavy metals and their compounds. The last subgroup of chemicals is a type of substances, which may affect people health or environment condition (*e.g.* soot particles) [2]. Thus, analysis of their concentration, lifetime, production processes and chemical transformation is essential in planning environmental protection and in healthcare procedures. In this paper, we propose the stochastic analysis of fluctuations of pollutant concentrations. We postulate that such analysis may be directly used to quantitative description of the chemical and physical processes for atmospheric components. The other motivation for undertaking proposed study is a determination of anthropogenic sources and a possibility to construct the model, which could be easily used for prediction the increased concentration of pollutants. There are other models, which are commonly used in the pollution spread studies. Their formalism and assumptions strictly depend on required precision, further application, complexity of computations. The first group of models requires direct numerical solution of diffusion and convection equations for each contaminant component [3]. There are so-called Eulerian models with the dispersion of pollutants in a coordinate system associated with Earth [4]. The computational grid used in their numerical solutions should be dense enough to accommodate the size of the objects in the area under consideration (houses, clusters of trees, single hills *etc.*). For this purpose, the exact numerical model of the terrain is required. Additionally, pollutant spread models must be related to meteorological models. This is caused by the dependence of model parameters (*e.g.* diffusion coefficients of turbulent individual compounds) on the temperature, wind speed and humidity. Thus, practical applicability of such models is limited due to their computational requirements.

There are also simplified models such as Gaussian models and other models jointly called trail models [5]. They allow for fast and precise (from the point of view of practical use) estimation of the concentration of selected pollutants at a certain time and distance from the emitter. Lack of the description of the non-stationarity of the pollution spreading process is a limitation of jointly trail models. These models generally do not take into account changes of wind direction (segment models [6] are exception), temperature profile and other parameters characterizing the local state of the atmosphere.

As a starting point, we propose the analysis of the concentration of simple gases in the air. In this paper, as an example, we used sulphur dioxide, SO_2. We applied the method of reconstruction of stochastic dynamics, which allows for quantification of the chemical transformations of SO_2 in the lower troposphere. We presented the deterministic component of dynamics in two measurement stations in Cracow separately. We supposed that elements of the dynamics should be similar due to neighboring localization of these stations. Finally, we proposed the interpretation of determined components in relation to kinetics of chemical reactions for SO_2.

2. SO_2 concentration in atmosphere

Global emission of SO_2 is estimated to 64.2 Tg of sulphur per year [1], which makes SO_2 the main sulphur-containing compound of pollutant gases. Mainly, the emission is caused by fossil fuel combustions and industry sources (56.3 Tg of sulphur per year). Another anthropogenic source of SO_2 is biomass burning (*ca.* 1.3 Tg of sulphur per year). SO_2 is also present in volcanic gases. In summary, the highest concentration of SO_2 and its highest emission is observed in big cities and industrial regions. SO_2 is emitted and then it undergoes a few physical or chemical transformations, which are responsible for decrease of its concentration in the air. Sulphur dioxide reacts under tropospheric conditions via both gas- and aqueous-phase processes [2]. In gas-phase processes, the most important is the reaction with hydroxyl radical, which is a common product of various atmospheric reactions and is a very reactive oxidant

$$\mathrm{SO_2} + \mathrm{OH}\cdot \rightarrow \mathrm{HOSO_2}\cdot\ . \tag{1}$$

Hydroxysulfonyl radical $HOSO_2\cdot$ transforms further to sulphur trioxide (SO_3) and sulphuric acid (H_2SO_4). The first stage of aqueous-phase processes is usually a dissolution of SO_2 in water and its dissociation. Dissolved SO_2, sulfite (SO_2^{2-}) and bisulfite (HSO^{3-}) ions may react in liquid phase with ozone, hydrogen peroxide and organic peroxides [7, 8]. Finally, the oxidation of SO_2 catalyzed by ferrum or manganium ions is also possible.

2.1. Dynamics of SO_2 concentration

The first order reactions dominate in chemical transformations of SO_2. The first order reaction proceeds at a rate that depends linearly only on one reactant concentration, therefore the time evolution of its concentration is given by

$$x(t+\Delta t) = x(t) - k\,x(t)\,\Delta t + E\Delta t + g(x(t))\mathit{\Gamma}\,, \tag{2}$$

where $x(t)$ denotes the concentration of SO_2 in time t, E is its mean emission at area of measurement station and k denotes the total rate of reactions of decay of SO_2. Δt is the period between two successive measurements. Last term represents the stochastic part related to atmospheric circulation or other natural phenomena, short-period changes of emission level. Stochastic term is a product of a function g (which may depend on SO_2 concentration) and random variable Γ. Γ is white noise with zero mean and unit variance. This simple model can quantify the emission and transformations of SO_2. Note that the influence of anthropogenic sources [1] of pollutants is also considered.

3. Data

In this study, we analyzed time series of SO_2 concentrations, measurements of which were carried automatically and continuously. However, the recorded data were averaged hourly. The measurements are available in the open-source database of Chief Inspectorate of Environmental Protection in Poland [9]. From the database we selected two stations in Cracow: MpKrakBujaka (height placement: 195 meters above sea level) and MpKrakBulwar (height: 225 m respectively). We performed an analysis of fluctuations of SO_2 concentration on successive five datasets (in years: 2011–2015). Studied signals were recorded with precision of 1 [μg/m^3] and have low number of missing values (less than 7%) beside one recording in 2011. For MpKrakBulwar, the number of missing recorded measurements varies from 149 to 601 (total number of points in year is 8760), while for MpKrakBujaka, varies from 117 to 587, with exception for 2011 year, where this number is equal to 1504. In Fig. 1, we present variability of SO_2 concentration in MpKrakBulwar in the year 2015.

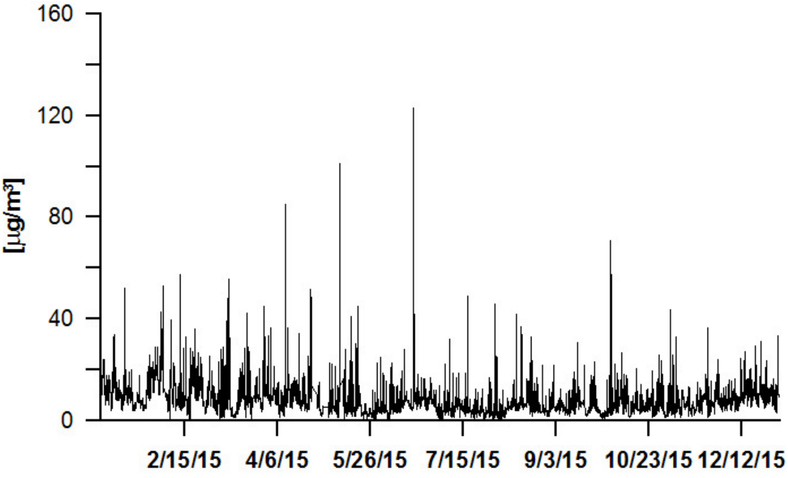

Fig. 1. Fluctuations of SO_2 concentration in MpKrakBulwar in the year 2015. Time series were recorded every hour.

None preprocessing procedures such as interpolation techniques or filtering procedures were applied to recorded data. We did not smooth the experimental time series, because natural variations and outliers occurrence are related to temporal changes of SO_2 concentrations due to activity of local pollutant sources. Such smoothing algorithms are especially useful, when the computations used in the study do not depend on the histogram binning. Here, the construction of discretized bins is necessary, thus smoothing the curves would incorporate quantitative change in resultant probability densities.

4. Method description

We introduced the dedicated stochastic approach for construction of stochastic model of time evolution of SO_2 concentration in the air. In the proposed method, the studied process is separated into deterministic part and noisy component. Deterministic part represents an internal mechanism, which governs the observed process. It can be related to the emission process and kinetics of chemical reactions which SO_2 undergoes during its decay. The noise component is responsible for external, natural perturbations such as weather conditions. These two parts were reconstructed directly from time series as elements of discrete model of time evolution of the SO_2 concentration fluctuations. The method of the extraction of the stochastic dynamics has been presented in papers of Petelczyc *et al.* [10, 11]. The basic equation of the one-dimensional discrete system with noise is given by

$$x_{n+1} = f\left(x_n\right) + g\left(x_n\right) \xi_n \,, \tag{3}$$

where $f(x_n)$ is a deterministic part and $g(x_n)$ is a stochastic component of the dynamics. The ξ_n denotes the noise term. The noise is uncorrelated with the mean equal to zero and standard deviation equal to one, respectively (compare to Eq. (2)). Note that we do not assume its Gaussian form but only statistics of first two moments. For simplification of analytical and numerical procedure of the method, we replace (3) by

$$x' = f\left(x\right) + g\left(x\right) \xi \,. \tag{4}$$

From comparison of the elements of Eq. (4) and Eq. (2), the expected form for $f(x)$ can be found as

$$f(x) = x(t)[1 - k\Delta t] + E\Delta t \,. \tag{5}$$

Referring to [10], the $f(x)$ and $g(x)$ are determined analytically from

$$f\left(x\right) = \int\limits_{-\infty}^{+\infty} x' q\left(x' \mid x\right) \mathrm{d}x' \tag{6}$$

and

$$g\left(x\right)=\sqrt{\int\limits_{-\infty}^{+\infty}x'^{2}q\left(x'\mid x\right)\mathrm{d}x'-f^{2}\left(x\right)}\,,\tag{7}$$

where $q(x'|x)$ is the conditional probability density. $q(x'|x)$ is determined from time series and for this purpose, the adequate construction of histograms is performed. The width of bin is constant and depends on precision of measurement of concentration of the $\mathrm{SO_2}$. Construction of histograms requires searching pairs x_k, x_{k+1} with $x_k = x$ and $x_{k+1} = x'$. The number of such pairs is denoted by N, and M is the number of the points $x_k = x$ in the data. Thus, the conditional probability density is given by formula

$$q(x'|x)=\frac{N}{M\cdot\varDelta}\tag{8}$$

with $\varDelta = 1$(unit: [μg/m^3]), which is exactly the accuracy of measurement concentration. After calculation of conditional probability density from experimental time series, the integrals in (6) and (7) may be discretized and numerically determined. In the study, the trapeze rule was used for discrete summarization.

In Fig. 2, we presented a form of deterministic component of the model, computed for data given in Fig. 1. We proposed the linear function for $f(x)$ in the limited range of arguments (in Fig. 2, this range is from zero to argument marked by vertical line). Our previous studies indicate that there is a necessity for limitation of the range of arguments to bins of histogram,

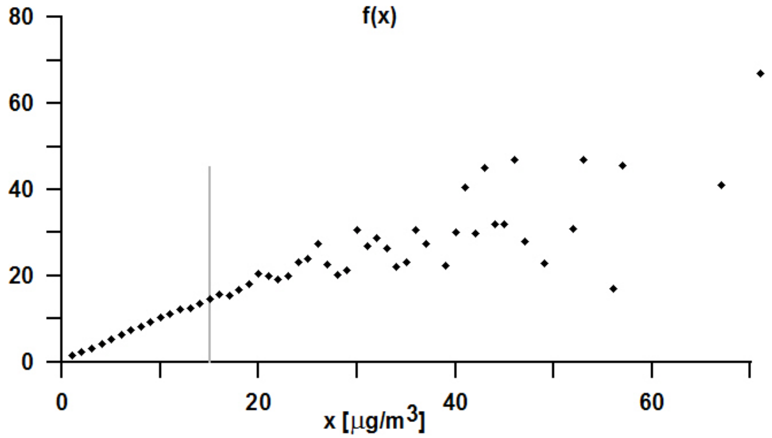

Fig. 2. $f(x)$ function determined for time series presented in Fig. 1. Vertical line limits the range of linear fit. Details are given in the text.

in which number of points exceeds 100. It is caused by large fluctuations of deterministic (and also stochastic) function outside selected range of x. In the presented case, fitting procedure was limited to data given to the left of vertical line in Fig. 2. In result, 7.8% of measurement points were excluded from analysis (it is percentage sum of measurement points to the left of vertical line). Note that in our calculus, the coefficient of determination for linear fit exceeds 0.99 in each case.

5. Results

In the study, we focused on comparison of SO_2 concentration in two stations, which are in the same city. For such comparison, we determined a linear fit for deterministic function $f(x)$. Coefficients of the linear fit for MpKrakBulwar and for MpKrakBujaka station are presented in Table I. Note the repeatability of determined linear coefficients in successive years in both stations. The intercept differs from year to year. It is caused by large number of factors influencing on SO_2 concentration such as changes of pollution emission intensity from industry. In this situation, we decided to discuss the average values of parameters determined from linear fit.

TABLE I

Coefficients of the linear fit for MpKrakBulwar and MpKrakBujaka. Note the repeatability of linear slope. The slope of the linear fit is smaller than 1.0 and the total rate of reactions of decay can be calculated.

	MpKrakBulwar		MpKrakBujaka	
Year	Slope $\left[\frac{\mathrm{m}^3}{\mu\mathrm{g}}\right]$	Intercept $\left[\frac{\mu\mathrm{g}}{\mathrm{m}^3}\right]$	Slope $\left[\frac{\mathrm{m}^3}{\mu\mathrm{g}}\right]$	Intercept $\left[\frac{\mu\mathrm{g}}{\mathrm{m}^3}\right]$
2011	0.92	0.83	0.96	0.22
2012	0.96	0.47	0.99	0.23
2013	0.93	0.73	0.99	0.24
2014	0.93	0.72	0.96	0.38
2015	0.94	0.58	0.94	0.47

The mean of slope is $0.94(+/-0.02)$ $[\mathrm{m}^3/\mu\mathrm{g}]$ for MpKrakBulwar and $0.97(+/-0.02)$ $[\mathrm{m}^3/\mu\mathrm{g}]$ for MpKrakBujaka station. The linear coefficient measures the kinetics of first order chemical reaction. The linear slope of function $f(x)$ from Eq. (5) is equal to $1-k\Delta t$, thus it was possible to estimate k value. We obtained $0.064(+/-0.015)$ for MpKrakBulwar and $0.032(+/-0.022)$ $[1/h]$ for MpKrakBujaka, respectively. Total rate of reactions of SO_2 decay has large standard deviation in both stations.

The intercept of function $f(x)$ in Eq. (5) is given by $E\Delta t$ and its mean is equal to $0.67(+/-0.14)$ for MpKrakBulwar and $0.31(+/-0.11)$ $[\frac{\mu\mathrm{g}}{h\,\mathrm{m}^3}]$ for MpKrakBujaka station. It leads to a conclusion that SO_2 production differs in measurement stations. It can be explained by neighboring industry. In the close neighborhood (less than 1.5 km) to MpKrakBulwar, there is a large steelwork. Steelworks are ones of greater SO_2 emitters because of relatively high sulphur content in coke which is used as a redactor in blast furnace process.

The second component of the model $g(x)$ is not studied in detail in this paper. However, in general, we observe an increasing function for $g(x)$ with fluctuations around linear trend (see Fig. 3). The proposed linear fit is marked in Fig. 3 for better visualization. The fit was determined for the data to the left of vertical line and then it was marked for wider range. Note that the form of the best fitted function should be verified. Above the range of satisfactory number of counts, the fluctuations increase significantly, and the trend is disturbed or even destroyed. The second observation is the difference between ranges of functions $f(x)$ and $g(x)$. The stochastic component has lower values, which may indicate the domination of anthropogenic processes in chemical transformations of SO_2 rather than natural processes.

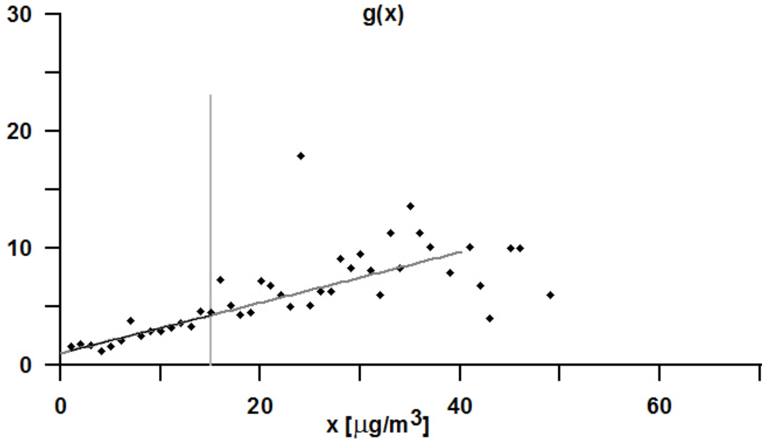

Fig. 3. $g(x)$ function determined for time series presented in Fig. 1. The vertical line limits the range of linear fit (black line). The graphical presentation of the fitted line is extended (gray line) to wider range.

6. Conclusions

In this paper, we presented the stochastic model of fluctuations of sulphur dioxide concentration in lower troposphere and its determination procedure. The model consists of two components, whose physical and chemical interpretation is proposed. We focused on the linear form of deterministic part of the model. As an example, we performed computations on time series recorded during several years in measurement stations located in Cracow (Poland). One of the stations is localized in the neighborhood to steelworks. The emission of different reactants, which can undergo transformations with SO_2, was expected. We obtained larger average value of the total rate of reaction of SO_2 decay for the station closer to steelworks. However, standard deviation values of this parameter do not provide statistical difference between stations. It can be easily explained by the fact that pollutant gases in lower troposphere are transported by the wind on long distances [12]. Thus, the total rate of reactions of SO_2 decay should be rather on a similar level in neighboring stations. On the other hand, the parameter responsible for constant of SO_2 production was twice larger in MpKrakBulwar in comparison to MpKrakBujaka station. The interpretation of such difference is directly related to high emission of SO_2 from the steelwork. The presented results indicate that it is possible to quantify and identify the impact of anthropogenic sources on concentration changes of pollutants. The applied method can work as a model of time evolution of pollutant concentrations. Thus, it can be used for assessing the occurrence of the increased and dangerous concentration levels of pollutants in the troposphere.

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