MODELLING THE POLLUTANTS DISSIPATION

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ABSTRACT

Nowadays the pollutants affect more and more the human health, especially due to their dissipation in atmosphere. Therefore, maintaining their concentrations into reasonable limits is one of the major directions of the policies of sustainable development of the countries. Modeling the pollutants' dissipation is an important step in taking decisions concerning the limitation of their impact. Considering these reasons, in this article we present different models for the regional dissipation of some pollutants in the Romanian Black Sea Littoral. The data series (concentrations of CO, NO_x, H_2S -SO_2) have been collected in 6 different locations from the Dobrogea region (Romania), in the period January 2008 - June 2009. The proposed approach uses multiple linear regression, for the regional dispersion of pollutants' concentrations, in which the exogenous variables are the atmospheric factors: temperature, air humidity and wind speed. The results prove that the CO dissipation is linear dependent on the temperature, but the NO_x and H_2S -SO_2 dissipations depends on the temperature, the logarithm of humidity and logarithm of wind speed.

Keywords: model, pollutant, concentration, wind speed, humidity, residual analysis.

1. Introduction

The largest vectorial space for the pollutants' propagation is the athmosphere. The pollution effects can be observed in the natural and antropic media. Only a relatively small number of sectorial programs for controlling the main sources of pollution with emission produced by the excesive industrial development in the northern part at the Romanian Black Sea Littoral are sustained.

In general, CO can accumulate to high levels especially during the calm atmosphere from winter and spring when burning fossil fuels reaches a maximum. Carbon monoxide produced from natural sources is rapidly dispersed over a large area without putting human health at risk. At concentrations greater than 10 mg/ m^3, CO is lethal by reducing the transport capacity of oxygen by the blood, with consequences on the respiratory and cardiovascular systems. Nitrogen and sulfur oxides, NO_x and SO_x, form a group of highly reactive gaseous chemical species, resulted from the combustion process of fuels burned at high temperatures, and more often they are the result of road traffic and industrial activities of electricity production from conventional fuels. It is known that SO_2 and NO_2 are especially involved in the process of acid precipitation apparition. These ions, in contact with the sunlight and water vapor form acid compounds that affect the quality of surface water and soil, with major damage on vegetation and fauna and thus on the human health. Prolonged exposure to emissions of nitrogen oxides and sulfur can cause lung disease, reduce the immunity of human organism and favours the accumulation of nitrates and sulfates in the soil, which can cause the alteration of environmental ecological balance. Standardized methods for measuring the concentration of NO_x and SO_2 are respectively the chemiluminescence and ultraviolet fluorescence (Termo Sci.; Termo Environ 1; Termo Environ 2).

Due to the importance of preserving the air and soil quality in the northern part of the Romanian Black Sea Littoral (were the most important resorts are situated), there is a continuous interest in monitoring, analysing and modeling the pollutans' evolution. Some results are reported in (Barbulescu and Barbes, 2013, 2014; Barbes *et al*., 2009, 2013). Different modeling methods could be applied, but only some of them gave good results for this aim, as, for example: linear and nonlinear regression models, generalized additive models (Aldrin and Haff, 2005; Carslaw *et al*. 2007; Pearce *et al*., 2011), GRNN models (Barbulescu and Barbes, 2013), "macroscopic" emission models, such as MOBILE6.2/ CALINE4 (Zhang *et al*. 2010), etc. In this context, our aim was to determine models for *the regional dissipation* of CO, NO_x and SO_2-H_2S, function of the wind speed, the temperature and the humidity of atmospheric air.

2. Data and model description

2.1. Data collection

Data was collected in six places, situated in the Northern part of the Romanian Black Sea Littoral (Fig.1), in the period January 2008 – July 2009. The climate of the study region is temperate - continental, with maritime influences, with warm summers, with poor precipitation and not very cold winters with episodic snows and frequent heating intervals.

In 2008, the average annual temperature was of 11.2º C and the annual rainfall of 347.8 mm. Rainfall were acidic (pH <6.5) in March, June, September, November, December. In June, September, November and December the precipitation had a low ionic content (with conductivity less than 100 m/cm), the acid character being given by the transport of acid gases (SO_2, NO_2) from medium or long distances. The atmospheric general circulation was characterized in the warm semester by slow advections of oceanic air from west, which reached the area strongly transformed (warm and dry), and in the cold semester, by the advection of air masses from north – east (arctic continental air) and south – west (hot and humid Mediterranean air) (Barbulescu and Deguenon, 2014).

Figure 1: Monitoring sites

For monitoring the athmospheric pollutants (NO_x, SO_x, CO) we used a mobile laboratory equipped with a modern system for the immissions' analysis, consisting of three modern analyzers for the detection of gaseous compounds and a weather station connected to a PC that enables online monitoring. Thermo Environmental 42C Nitrogen Oxides (NO-NO_2-NO_x) analyzer, Thermo Scientific Hydrogen Sulfide and Sulfur Dioxide Analyzer, Model 450i and Thermo Environmental 48C Carbon Monoxide (CO) analyzer were used for measuring respectively the nitrogen oxides, H_2S-SO_2 and CO concentrations (Barbulescu and Barbes, 2013, 2014, 2015). The average concentrations of NO_2 and CO exceeded the hourly limit values (VL) in July and October, especially in urban areas.

2.2. Model specification

The aim of our study was to determine models for the regional dissipation of CO, NO_x and SO_2 – H_2S, function of the wind speed, temperature and humidity of atmospheric air. Therefore, we looked for a model of the type:

$$Y_i = \alpha_i + \beta_1 v_i + \beta_2 H_i + \beta_3 T_i + \varepsilon_i, \tag{1}$$

where the variables Y_i, v_i, T_i represent respectively the pollutant concentration, the wind speed and the temperature, registered at the site *i* and ε_i is the random variable.

Eq. (1) is equivalent with:

$$y_{ij} = \alpha_i + \beta_1 v_{ij} + \beta_2 h_{ij} + \beta_3 t_{ij} + e_{ij}, \tag{2}$$

where: $y_{ij}, v_{ij}, h_{ij}, e_{ij}$ are respectively the pollutants' concentration, the wind speed and the temperature, registered at the site *i*, at the moment *j*, and the corresponding residual.

Eq. (2) can be written in matrix form as:

$$\boldsymbol{Y} = \alpha + \beta_1 \boldsymbol{v} + \beta_2 \boldsymbol{H} + \beta_3 \boldsymbol{T} + \boldsymbol{e}, \tag{3}$$

where:

$$\alpha = (\alpha_1 \ \cdots \ \alpha_6),\ \boldsymbol{Y} = \begin{pmatrix} y_{1,1} & \cdots & y_{6,1} \\ \vdots & \cdots & \vdots \\ y_{1,18} & \cdots & y_{6,18} \end{pmatrix}, \boldsymbol{v} = \begin{pmatrix} v_{1,1} & \cdots & v_{6,1} \\ \vdots & \cdots & \vdots \\ v_{1,18} & \cdots & v_{6,18} \end{pmatrix}, \boldsymbol{H} = \begin{pmatrix} h_{1,1} & \cdots & h_{6,1} \\ \vdots & \cdots & \vdots \\ h_{1,18} & \cdots & h_{6,18} \end{pmatrix},$$

$$\boldsymbol{T} = \begin{pmatrix} t_{1,1} & \cdots & t_{6,1} \\ \vdots & \cdots & \vdots \\ t_{1,18} & \cdots & t_{6,18} \end{pmatrix}, \mathrm{e} = \begin{pmatrix} e_{1,1} & \cdots & e_{6,1} \\ \vdots & \cdots & \vdots \\ e_{1,18} & \cdots & e_{6,18} \end{pmatrix}.$$

$e_{i,j}$ being the values of the random variable ε_i, at the place *i* at the moment *j*.

For modelling the dissipation of CO concentration, Eq.(2) was used at the beginning. After the analysis of the significance of estimated coefficients, it resulted that the model was over-parameterized, so the reduction of the non-significant variables was done. In the models for NO_x, H_2S - SO_2, the exogenous variables were the temperature, the logarithms of wind speed and the humidity of atmospheric air. The models' significance was checked using the t tests for the coefficients, the F test for the significance of the entire models. The residual analysis was performed by the Shapiro – Wilk test (for normality) (Shapiro, 1980), Levene test (for homoscedasticity) (Levene, 1960) and the computation of autocorrelation function and the comparison of its values with the upper and lower limits of the confidence interval at the confidence level of 95% (Bourbonais, 2000).

3. Results

3.1. Model for CO

We tried to find a model of the form (3) for the dispersion of CO concentration (Fig.2). After the parameters' estimation, and performing the t tests on the parameters, it resulted that the parameters corresponding to the variables wind speed and humidity are not significant. Therefore, these variables were removed from the model and a new estimation has been done. The results are:

$$\hat{\alpha}_1 = -0.0684, \hat{\alpha}_2 = 2.9938, \hat{\alpha}_3 = 3.3706, \hat{\alpha}_4 = 2.8359, \hat{\alpha}_5 = 3.9441,\ \hat{\alpha}_6 = 2.8442,\ \hat{\beta}_3 = 2.4904.$$

The p-values computed in the t tests for the significance of each parameter were respectively 2.66E-06, 1.2E-14, 4.35E-17, 2.23E-20, 3.57E-13, 8.54E-12, so less than 0.05, therefore the hypothesis that the parameters are zero could be rejected. The value of the statistic of the F test on the model significance was 57.65, and the p-value, 2.66 E-32, so the model is significant.

The value of the determination coefficient is: R^2=0.89, proving a good linear correlation between the concentration' dissipation and the wind speed. The residual analysis confirmed the model quality, since the hypothesis of normality, homoskedasticity and of the autocorrelation's absence couldn't be rejected.

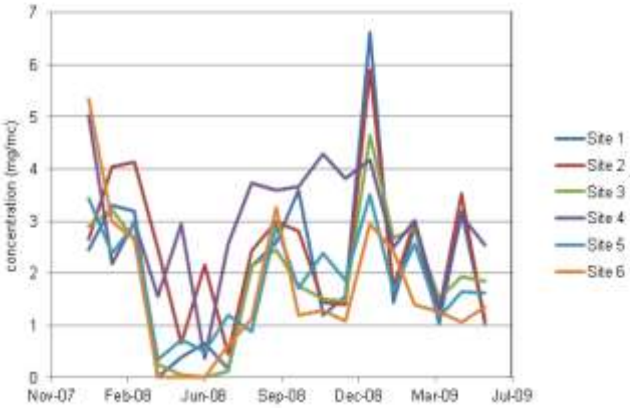

Figure 2: CO concentrations registered at the monitoring sites

3.2. Model for NO_x

After analysing the dependence between the NO_x concentration and each of the variables the wind speed, temperature and humidity, a version of model (3) has been proposed:

$$\boldsymbol{Y} = \alpha + \beta_1 \ln \boldsymbol{v} + \beta_2 \ln \boldsymbol{H} + \beta_3 \boldsymbol{T} + \boldsymbol{e}, \quad (4)$$

where $\ln \boldsymbol{v}$ and $\ln \boldsymbol{H}$ are the matrices containing respectively the logarithms of wind speed and of the humidity.

The parameters resulted in the model for $\mathbf{NO_x}$ are:

$$\hat{\alpha}_1 = -4.944,\ \hat{\alpha}_2 = -5.062,\hat{\alpha}_3 = -4.888,\ \hat{\alpha}_4 = -4.998,\ \hat{\alpha}_5 = -4.918,\ \hat{\alpha}_6 = -5.062,$$
$$\hat{\beta}_1 = 0.064,\ \hat{\beta}_2 = 0.026,\hat{\beta}_3 = 0.255\ .$$

The p-values calculated in the t-tests for the coefficients' significance were respectively 3.75E-05, 2.56E-05, 4.63E-05, 4.66E-05, 5.85E-05, 3.2E-05, 4.922E-03, 8.49E-03, 3.37E-3, so less than 0.05; therefore the models' coefficients are significant. The value of F statistics was of 422.355 and the corresponding p-value, 3.11 E-74, so the model is significant. R^2 = 0.976, so correlation between the exogenous variable and the endogenous one is significant.The value of the statistics of Levene test for residual was of 0.16 and the p-value = 0.976. The value of Shapiro-Wilk statistics was of 0.539, with a p-value = 0.168. So, at the significance level at 0.05, the residuals' homoskedasticity and normality couldn't be rejected. The autocorrelogram analysis didn't reveal residuals' autocorrelation. Therefore, the model proposed by us is good from statistics viewpoint.

A model of the same type has been built for H_2S - SO_2 dissipation with good results. From luck of space, we mention only the value of the determination coefficient: R^2=0.942.

4. Conclusions

In this article we presented two types of models for the dispersion of some pollutants at the regional scale in Dobrogea, Romania. The first one, for the CO dissipation is linear simple, with the temperature as exogenous variable. The second one for NO_x and H_2S - SO_2 is linear multiple, in which the exogenous variables were the temperature, the wind speed logarithm and the humidity.The study emphasized that the air temperature influences the dissipation of all studied pollutants at regional scale. Also, the pollutants' concentration in air reached the maxima in the winter month, due to the low temperature at the soil level, the more frequent and persistent thermal inversions and the predominant anticyclonic system that prevent the characteristic downward movement, the ascending transportation and spreading the pollutants in the atmosphere. The absence of the humidity influence on CO dissipation could be explained by the fact that CO is less soluble in water in comparison with NO_2 and SO_2 (that quickly react with the water and under the influence of ultraviolet radiation generate acids that contribute to the apparition of acid rain). Our results are in concordance with (Hamdy and Elmir, 2005).

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