ENVIRONMENTAL PHYSICS

MODELS FOR POLLUTANTS' CORRELATION IN THE ROMANIAN LITTORAL

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Abstract. In this article we present the results of the monitoring of CO, SO_2- H_2S, NO_x and PM_{10} concentration at six sites on the Romanian Black Sea Littoral. The correlation between the imissions' concentrations at their production place and their concentration at the reception points were analyzed and linear models (single and multiple) for the pollutants dispersion have been built. The models quality has been checked by statistical tests on coefficients and residuals. All the proposed modes have the determination coefficients higher than 0.87.

Key words: inorganic pollutants, multiple linear model, validation.

1. INTRODUCTION

The presence and persistence of some inorganic pollutants, like CO, SO_2 - H_2S, NO_x and other particulate matter (PM_{10} or $PM_{2.5}$) poses severe risks for the human health [1]. The earliest and most basic air quality management actions to control the health risks include measures such as the continuous monitoring of criteria pollutants as well as studies to characterize atmospheric emissions or imissions, physical and chemical processes and meteorology. The pollution directly affects the human health and causes environmental modification [2–4]. The main pollution sources are divided into two categories: (1) natural, such as NO and NO_2 from the bacterial activities and (2) artificial, from CO of methane (CH_4) incomplete oxidation, unburned hydrocarbons, H_2S and CH_4 from anaerobic decomposition of organic compounds. The second one the result of human activities: industrial, transportation, domestic combustion that causes the increase of pollution level in the air [3].

The effect of air pollution on animals, plants and human being have been extensively studied [5–7] in the context of future climate change. Different models of air quality have been proposed; some Web resources are emphasized in [8]. The actual international evaluations of air pollution, using extended global fotochemical

models, as CAMx [9] presents a realistic evaluation of atmospheric air quality and of the spatial variability of the climatic parameters in severe condition of medium, at a high salinity and wind [10]. Other authors proposed artificial neural networks or hybrid models for the evolution of poluttants' concentration at a local scale [11–12] or made a statistical analysis of their dispersion [13–17].

In this article we present the results of monitoring the concentrations of imissions (CO, H_2S-SO_2, NO_x, and PM_{10}) in three industrial sites and three tourist zones and to model their concentrations' evolution, using a linear (simple and multiple) approach.

2. MATERIAL AND METHODS

The imissions (CO, SO_2-H_2S, NO_x, and PM_{10}) from six places, situated on the Romanian Black Sea Littoral (Fig.1) were monitored, in compliance with the European air quality legislation [18] for a period of 18 months (January 2008–June 2009). The distances between the pollutants production point – a refinery (Poarta 1 – **I**, Poarta 3 – **II** and Statia de Epurare – **III**) and the reception zones (Intrare Navodari – **IV**, Tabara Navodari – **V**, Intrare Corbu – **VI**) supposed to be affected by the pollution effect are: a. from **I** to **IV**, **V**, **VI** respectively 3.15, 3.8, 3.61 Km; b. from **II** to **IV**, **V**, **VI** respectively 2.31, 3, 3.8 km and c. from **III** to **IV**, **V**, **VI** respectively 4.7, 5, 2.55 Km.

	Latitude	Longitude
Poarta 1	44°20'44.17"	28°37'37.38"
Poarta 3	44°20'21.88	28°38'16.05
Statia de Epurare	44°21 13.71	28°39 34.33"
Intrare Navodari	44°19 18.4	28°37 5.73
Tabara Navodari	44°19 18.4	28°39 53.83
Intrare Corbu	44°22 36.44"	28°37 5.73"

Fig. 1 – The studied sites.

The climate of the monitored zone (Navodari city and the coastal adjacent zone) is temperate continental, with the medium annual temperature of 13.2^0C for 2008–2009. A distinct climatic particularity is the drought (4–6 months/year). The annual precipitation registered in 2008 was of 368.1 mm and in 2009 of 423.9 mm, the last year being considered rainier than that the average annual precipitation registered the last 20 years. In 2008, the winds with the highest speed had the direction directions from North to South (4.6 m/s – in March, 2008) and from West to East (2.5 m/s). For the study period, the maximum mean monthly speed of the wind was of 2.9 m/s. The smallest speed of wind in 2008 was of 1.4 m/s, from South. In this zone, the predominant types of soil are the brown chernozem, carbonaceous and phreatic – humid with sands weak – incondensable, being characterized by a humus content of 2.5–6%, the saturation degree in bases of 85–95%, the pH of 6.5–83, the apparent density of 1.25–1.45 g/cm^3 [19].

The monitoring instruments used were: a mobile laboratory equipped with a modern analysis system for the air emissions, four modern analyzers and a meteorological station, connected to a PC that offers the possibility for online visualising the registered concentrations values [20].

The Thermo Scientific Model 410i Carbon Dioxide Gas Analyzer was employed to measure the concentration of CO/CO_2 in source emissions. Its functioning is based on Non-Dispersive Infrared technology (NDIR) [21].

Sulphurous Hydrogen Analyzer SO_2 Model 450i (Thermo Environmental Instruments), whose functioning is based on the ultraviolet absorption principle [22], has been used for the determination of Hydrogen Sulphide and Sulphur Dioxide concentrations.

NO_x concentration has been measured by Thermo Environmental 42C Nitrogen Oxides (NO-NO_2-NO_x) analyzer that functions on the principle that nitric oxide and ozone react to produce a characteristic luminescence with intensity linearly proportional to the NO concentration. Nitrogen dioxide (NO_2) is firstly transformed into NO, and then is measured using the chemiluminescent reaction. The NO and NO_x concentrations calculated are stored in memory and the difference between them is used to calculate the NO_2 concentration [23].

The Environmental Particulate Air, monitor Haz - Dust EPAM, 5000, was used for obtaining a complete real-time profile and graphical representation of airborne particulate levels with data read out (mg/m^3) [24].

The mathematical approach followed for data analysis and modeling comprises the analysis of linear correlations between the study variables and building (simple or multiple) linear models of dependence between them. In the following we remember the basic definitions and methods used for this aim.

If (x_t), (y_t), $t = \overline{1, n}$ are two data series the (linear) correlation coefficient between them is defined by:

$$\rho_{x,y} = \left[n\sum_{t=1}^{n} x_t y_t - \left(\sum_{t=1}^{n} x_t\right)\left(\sum_{t=1}^{n} y_t\right) \right]\left[\sqrt{n\sum_{t=1}^{n} x_t^2 - \left(\sum_{t=1}^{n} x_t\right)^2} \sqrt{n\sum_{t=1}^{n} y_t^2 - \left(\sum_{t=1}^{n} y_t\right)^2} \right]^{-1}$$

A correlation coefficient greater than 0.8 indicates a strong correlation and one less than 0.5 indicates a weak correlation.

The form of a (simple or multiple) linear model is:

$$y_t = a_0 + a_1 x_{1t} + a_2 x_{2t} + \ ... \ + a_k x_{kt} + \varepsilon_t, \quad t = \overline{1, \ n},$$

where: n is the number of observations; k is the number of independent variables; y_t is the values of the dependent variable, at the moment t; a_i are the parameters of the model, $i = \overline{1, k}$; x_{it} is the value of the independent variable i, at the moment t, $i = \overline{1, k}, \ t = \overline{1, n}$; ε_t is the specification error, $t = \overline{1, n}$.

The parameters a_i are estimated by the least squared method.

The estimated value of y_t is:

$$\hat{y}_t = \hat{a}_0 + \hat{a}_1 x_{1t} + \hat{a}_2 x_{2t} + \ ... \ + \hat{a}_k x_{kt} + e_t, \quad t = \overline{1, \ n},$$

where $e_t = y_t - \hat{y}_t$ is the residual.

Generally, the statistical hypotheses for the model are:

H1. The errors are normally distributed.

H2. $E(\varepsilon_t) = 0$ (the mathematical expectation of the error is zero).

H3. $E(\varepsilon_t^2) = \sigma_\varepsilon^2$ (the variance of the error is constant, $t = \overline{1, n}$).

H4. $\text{Cov}(\varepsilon_t, \ \varepsilon_{t'}) = 0$, if $t \neq t'$, where $\text{Cov}(\varepsilon_t, \ \varepsilon_{t'})$ is the covariance of ε_t, $\varepsilon_{t'}$.

To check the model quality the following statistical tests will be performed:

– The t test for the parameters' significance [11];

– The F test for the global significance of the model [11];

– The Shapiro – Wilk test, for the errors' normality [25];

– The Levene test for errors' homoscedasticity [26];

– The Durbin-Watson test [27] for the first order autocorrelation and the study of autocorrelation function, for higher orders autocorrelation.

All tests have been performed at the significance level of 0.05.

The empiric autocorrelation function (ACF) of the process X_t, $t \in \mathbb{Z}$ defined by:

$$\hat{\rho}(h) = \left(\sum_{t=1}^{n-|h|} (x_t - \overline{x})(x_{t+|h|} - \overline{x}) \right) \Big/ \sum_{t=1}^{n} (x_t - \overline{x})^2, \quad h \in \mathbb{Z},$$

where $\overline{x}$ is the average of the values of the process (x_t), calculated on n periods.

Together with ACF we shall present the empirical confidence interval at the confidence level of 0.95. If the values of ACF are inside this interval there is no data autocorrelation.

To quantify the proportion of the variance of the dependent variable explained by the independent ones, the determination coefficient was used. It is defined by:

$$R^2 = 1 - \left(\sum_{t=1}^{n} e_t^2 \right) \Big/ \left(\sum_{t=1}^{n} (y_t - \overline{y})^2 \right),$$

where $\overline{y}$ is the average of $y_1, \dots, y_n$.

3. RESULTS AND DISCUSSIONS

The studied series, containing the pollutants' concentrations, are presented in Fig. 2 and the basic statistics' values are given in Table 1.
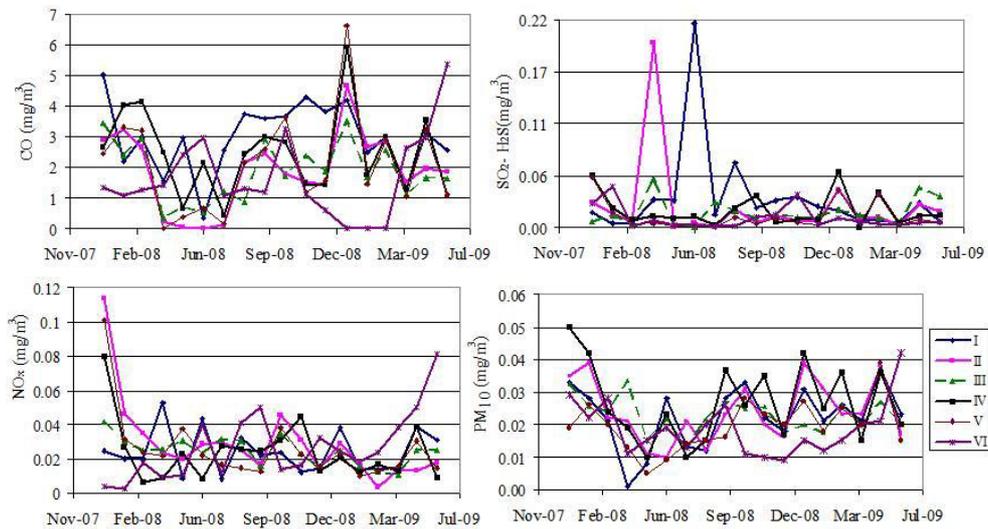

Fig. 2 – Pollutants' series.

Table 1

Pollutant extreme and average values and standard deviations (mg/m^3±SD)

Pollu-tant	Stat.	Series					
		I	II	II	IV	V	VI
CO	max	5.022±2.03	4.651±1.82	3.503±1.71	5.916±2.67	6.612±3.01	5.336±2.34
	min	0.371±0.12	0.000±0.00	0.348±0.24	0.448±0.52	0.001±0.01	0.000±0.01
	mean	2.968±1.07	1.892±0.93	1.859±0.97	2.454±1.60	2.086±1.62	1.665±1.20
SO$_2$-H$_2$S	max	0.217±0.14	0.196±0.12	0.051±0.15	0.059±0.23	0.052±0.27	0.043±0.25
	min	0.004±0.03	0.001±0.00	0.001±0.01	0.000±0.01	0.000±0.02	0.001±0.01
	mean	0.031±0.08	0.022±0.07	0.016±0.06	0.018±0.13	0.012±0.14	0.010±0.16
NO$_x$	max	0.053±0.03	0.114±0.12	0.042±0.28	0.080±0.34	0.101±0.21	0.081±0.29
	min	0.008±0.01	0.004±0.01	0.011±0.01	0.006±0.02	0.010±0.07	0.002±0.03
	mean	0.024±0.05	0.029±0.06	0.025±0.17	0.024±0.22	0.026±0.19	0.027±0.24
PM$_{10}$	max	0.037±0.02	0.039±0.04	0.034±0.18	0.050±0.20	0.039±0.25	0.042±0.31
	min	0.001±0.01	0.010±0.00	0.013±0.07	0.010±0.02	0.005±0.07	0.009±0.05
	mean	0.022±0.01	0.024±0.02	0.023±0.15	0.027±0.16	0.020±0.14	0.019±0.18

The mean monthly concentrations registered for the air pollutants were, generally higher in the urban zones (**IV–VI**) than in the industrial ones (**I–III**), but they didn't surpass the limits admitted by legislation. For example, the values registered for CO in **IV–VI** were in the range from 5.336 ± 2.34 mg/m^3 to 6.612 ± 3.01 mg/m^3, smaller than the maximal mean value of pollutant for 8h. The highest value of SO$_2$ – H$_2$S concentration were of 0.217 ± 0.14 mg/m^3 for **I,** respectively of 0.196 ± 0.12 mg/m^3 in **II**, with the mean of 0.031 ± 0.08 mg/m^3 respectively 0.022 ± 0.07 mg/m^3, situated under the value accepted by the European legislation for a 24h interval (0.125 mg/m^3). The maximum mean monthly value of NO$_x$ was registered at site **II** (0.114 ± 0.12 mg/m^3), with a annual mean of 0.035 ± 0.14 mg/m^3, that less than 0.040 mg/m^3, established in the legislation. PM$_{10}$ had a maximum of the mean monthly values of 0.050 ± 0.20 mg/m^3 and a mean annual average of 0.027 ± 0.16 mg/m^3 for the urban site **IV,** that doesn't surpass the annual value of 0.040 mg/m^3, established by law [28–29].

The correlation coefficients between the immision points (I, II, III) and the reception ones (**IV**, **V**, **VI**) are given in Table 2, where the significant linear correlations are marked in grey. The correlation coefficients of pollutants' concentration registered in the urban areas sites **IV** (and **V)** and the industrial zones **II** (and **III**) are respectively 0.758 and 0.609 (0.864 and 0.728) for CO, 0.770 and 0.601 (0.916, 0.705) for NO$_x$, 0.737 0.729, 0.626 (0.680, 0.762) for PM$_{10}$.

Table 2

Correlation coefficients

Pollutant	Sites	IV	V	VI
CO	I	0.237	0.485	-0.309
	II	0.758	0.864	-0.401
	III	0.609	0.728	-0.440
SO$_2$-H$_2$S	I	-0.089	-0.181	-0.171
	II	0.084	0.042	-0.003
	III	-0.105	-0.129	0.117
NO$_x$	I	-0.170	0.046	0.271
	II	0.770	0.916	-0.467
	III	0.601	0.705	-0.379
PM$_{10}$	I	0.737	0.680	0.288
	II	0.729	0.762	0.024
	III	0.626	0.326	0.173

Significant correlations were not detected between the H$_2$S-SO$_2$ concentration at the production and the reception points. The same situations appear in the cases of CO produced at site **I** and NO$_x$ produced at the site **III.** The pollutants concentrations registered at site **VI** is not linearly correlated with those produced at **I, II** and **III**. Therefore, we could accept the idea that the imissions registered in the urban monitored zones (**IV–VI),** situated at a distance of about 5 km from the industrial sites (**I–III)** are derived, in proportion of 60–80%, from the antropic emissions generated by the industrial activities cumulated with those from the heavy traffic on the roads in the study zones.

We also remark the existence of major influences of the coastal climate, favoured by the marine currents, the seasonal winds and the high precipitation quantity in the analyzed period. Moreover, there are large variations between the imissions' accumulations in the urban zones in the warm and cold periods, when the pollutants dispersion is influenced by the temperature variation and the pressure of the atmospheric air.

Taking into account the results from Table 2, we built multiple linear models for the dependence between the pollutants concentration at the production point and their concentration at the reception ones. We present them in the following.

Let us denote by: x_{2t}, x_{3t}, y_{4t}, y_{5t}, $t = 1, ..., 18$, the CO concentrations registered respectively at the sites **II**, **III**, **IV**, **V**. Then, multiple linear model can be written respectively:

$$\hat{y}_{4t} = \hat{a}_0 + \hat{a}_2 x_{2t} + \hat{a}_3 x_{3t} + e_t, \qquad t = 1, ..., 18, \tag{1}$$

for the dependence of CO concentrations at **IV** on those at **II** and **III**, and

$$\hat{y}_{5t} = \hat{b}_0 + \hat{b}_2 x_{2t} + \hat{b}_3 x_{3t} + e'_t, \quad t = 1, ..., 18, \tag{2}$$

for the dependence of CO at **V** on those at **II** and **III,** where $e_t, e_t^{'}$ are the residuals.

The estimated coefficients in (1) are: $\hat{a}_0 = 0.90$, $\hat{a}_2 = 0.91$, $\hat{a}_3 = -0.09$, but applying the t – test, we remark that the first and the third one are not significant. Also, the determination coefficient R^2 is only 0.57. So, we remove the first variable and we built the linear model:

$$\hat{y}_{4t} = 0.167x_{2t} + e_t, \quad t = 1, \ ..., \ 18, \tag{3}$$

for which the t and F tests confirm that the coefficient 0.167 and the model are significant. The residual is normally distributed (the p-value associated to the normality test is greater than $0.10 > 0.05$), is not correlated, with null expectation and the same variance (the p-value associated to the Levene test is $0.762 > 0.05$). In this case, $R^2 = 0.891$.

The estimated coefficients in (2) are: $\hat{a}_0 = -0.08$, $\hat{a}_2 = 1.08$, $\hat{a}_3 = 0.07$, but the t-test rejected the hypothesis that the first and the third are significant different from zero, so an alternative model is built:

$$\hat{y}_{5t} = 1.108x_{2t} + e_t^{'}, \quad t = 1, \ ..., \ 18, \tag{4}$$

where the errors satisfies the hypotheses H1 – H4 and $R^2 = 0.908$ (Table 3).

Let us denote by: $u_{2t}, u_{3t}, z_{4t}, z_{5t}, t = 1, ..., 18$, the NO_x concentrations registered respectively at the sites **II**, **III**, **IV**, **V**. Then, multiple linear model can be written respectively:

$$\hat{z}_{4t} = \hat{c}_0 + \hat{c}_2 u_{2t} + \hat{c}_3 u_{3t} + \eta_t, \quad t = 1, \ ..., \ 18, \tag{5}$$

for the dependence of NO_x concentrations at **IV** on those at **II** and **III**, and

$$\hat{z}_{5t} = \hat{d}_0 + \hat{d}_2 u_{2t} + \hat{d}_3 u_{3t} + \eta_t^{'}, \quad t = 1, \ ..., \ 18, \tag{6}$$

for the dependence of NO_x concentrations at **V** on those at **II** and **III,** where $\eta_t, \eta_t^{'}$ are the residuals.

Analogous to case of modeling CO dependences, the intercept and the second variables' coefficients ($\hat{c}_3, \hat{d}_3$) in (5) and (6) were not found significantly different from zero, so the resulted models have the respectively the equations:

$$\hat{z}_{4t} = 0.726x_{2t} + \eta_t, \quad t = 1, \ ..., \ 18 \ (R^2 = 0.838), \tag{7}$$

$$\hat{z}_{5t} = 0.850x_{2t} + \eta_t^{'}, \quad t = 1, \ ..., \ 18 \ (R^2 = 0.937). \tag{8}$$

In both cases, the errors satisfy the hypotheses H1-H4 (Table 3).

Denoting by: $v_{1t}, v_{2t}, v_{3t}, w_{4t}, w_{5t}, t = 1, ..., 18$, the PM_{10} concentrations registered respectively at the sites **I–V**, the multiple linear model can be written as:

$$\hat{w}_{4t} = \hat{f}_0 + \hat{f}_1 v_{1t} + \hat{f}_2 v_{2t} + \hat{f}_3 v_{3t} + \xi_t, \quad t = 1, \ ..., \ 18, \tag{9}$$

for the dependence of NO_x concentrations at **IV** on those at **II** and **III**, and

$$\hat{w}_{5t} = \hat{g}_0 + \hat{g}_1 v_{1t} + \hat{g}_2 v_{2t} + \xi'_t, \quad t = 1, \ ..., \ 18, \tag{10}$$

for the dependence of PM_{10} concentrations at **V** on those at **II** and **III,** where ξ_t, ξ'_t are the residuals.

After determining the coefficients in (9) and testing their significances, it results that the second variable is doesn't significantly differ from zero. Building the model without this variable, it results that the intercept is not significantly different from zero, so, the final model is:

$$\hat{w}_{4t} = 0.590 v_{1t} + 0.561 v_{2t} + \xi_t, \quad t = 1, \ ..., \ 18 \ (R^2 = 0.946). \tag{11}$$

Analogous, we obtain:

$$\hat{w}_{5t} = 0.317 v_{1t} + 0.508 v_{2t} + \xi'_t, \quad t = 1, \ ..., \ 18 \ (R^2 = 0.952), \tag{12}$$

with the *p*-value corresponding to the t-test for the second coefficient equal to 0.05. Since this value is the limit for which the null hypothesis that the corresponding variable is not significant, we built also a model without considering the influence of the second variable:

$$\hat{w}_{5t} = 0.791 v_{1t} + \xi', \quad t = 1, \ ..., \ 18 \ (R^2 = 0.939). \tag{13}$$

$\xi_t, \xi'_t, t = 1, ..., 18$ are the residuals.

The determination coefficients in the models (11) and (12) are comparable and the residuals satisfy the hypotheses H1 – H4. If we consider the best model the one for which R^2 is greater, we accept (13).

Summarizing, the results of the tests on the models' errors are presented in Table 3.

Table 3

Results of tests on models' errors

Model	R^2	mean	Shapiro - Wilk		Levene		
			statistic	*p*-value	statistic	*p*-value	Cov
(3)	0.874	0.002	0.983	>0.100	0.100	0.762	0
(4)	0.908	-0.012	0.977	>0.100	0.920	0.351	0
(7)	0.838	0.002	0.988	>0.100	0.020	0.882	0
(8)	0.937	0.001	0.933	>0.150	0.060	0.815	0
(11)	0.946	0.000	0.986	>0.100	0.430	0.523	0
(12)	0.952	0.000	0.985	>0.100	0.010	0.923	0
(13)	0.939	0.000	0.983	>0.100	0.560	0.463	0

3. CONCLUSION

Our study proves the existence of linear correlation between the concentrations of some pollutants in different industrial zones and their presence in some neighbour zones. Linear dependences have been modeled by linear simple and multiple models, whose fitting quality was checked by the residual analysis and the calculus of determination coefficients (found in the interval 0.874 – 0.952).

The correlation coefficients of the pollutants' concentrations in the industrial sites and those in the urban ones were influence by the distance between the sites. Also, the highest concentrations of imissions in the last zones with respect to the first ones could be explained by the considerable dependence that exists between the pollutants' dispersion and the marine climate, specific to the monitored area that was characterized by high seasonal variations, wind intensifications and frequent precipitations, in the period January 2008 – July 2009.

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