# DYNAMIC MODEL OF DAILY OZONE AND NITROGEN DIOXIDE CONCENTRATION FOR THE BACKGROUND CONDITIONS

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Abstract

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In this study, by means of the memory content the dynamic model of the evaluation and prediction of the ground-level ozone variation depending on the nitrogen dioxide concentration in the background conditions was established. The predictive model was developed based on 5-year daily ozone and nitrogen dioxide concentration data. The model was applied to the background stations Preila and Rucava located on the Baltic seashore. The daily ozone concentrations estimated and predicted by the model were found to be in agreement with the measured values of daily ozone concentrations at the monitoring stations.

*Key words*: dynamic model, ground-level ozone, nitrogen dioxide, memory content

## Introduction

The forests and natural vegetation are very important constituents of the landscape, especially in the surroundings of the resorts and unurbanized areas. The conditions of forests, especially their crown, in Europe have deteriorated considerably since 1990. After some recuperation in the mid-1990s the deterioration of the trees is observed. In 2002 more than 20% of the sample trees were rated as damaged (UNECE EC, 2002.) The most important causes of this damage include extreme weather conditions, insect and fungi attacks and air pollution. Statistical analyses have shown that the nitrogen compounds and ozone ($O_3$) are ascribed to main parameters, which influence the tree defoliation. Tree damage by ozone mostly occurs under Mediterranean climate conditions. However, ozone concentrations could also explain some of the observed defoliation in the northern parts of Europe (Krause, Sanz, 1999; Hendriks et al., 1997). Ozone damages the most sensitive plants at concentrations lower than those that are harmful to people. The effects of nitrogen very much depend on the area of concern.

Ozone and nitrogen oxides ($NO_x$ = NO+$NO_2$) are two of the main pollutants in the troposphere. Ozone and its precursor NO2 can be transported from pollution sources into an area found hundreds kilometres upwind. Ozone is not emitted directly into the air but is formed by the reaction of volatile organic chemicals (VOCs) and $NO_x$ in the presence of heat and sunlight (Bronnimann et al., 2000).

Following the so-called *indicator approach*, three chemical regimes can be generally distinguished (Silmann, 1999): *VOC sensitive*, typical of urban areas; *$NO_x$ sentensive*, typical of rural areas and *transitional*, that can be treated as a broad region that divides the previous two regimes. In the $NO_x$ – limited region control of $NO_x$ should reduce ozone concentrations (Derwent, Davies, 1994).

The fundamental theory of stochastic control is aimed at studying the control of physical, biological and engineering systems, which are subject to modelling-measurement errors or external disturbances that have evident random and uncertain characteristics. Atmospheric simulation models are the typical tools that can be employed to quantitatively estimate the relationship between ambient $O_3$ and precursors estimations. Prediction of ground-level atmospheric pollutant concentration is an important issue and much attention has already been given to this problem. The time series from ground-level concentration of ozone and nitrogen dioxide data are often modelled in terms of regression models or state space models corresponding to trend, seasonal effects and irregular noise components (Graf-Jaccottet, Jaunin, 1998; Bloomfield et al., 1996; Zvyagintsev, 2003). Sometimes, the observed series have almost identical seasonal components, but it is more often the case that the seasonal factors vary from time to time, year after year, in some relatively smooth features.

The aim of this study was to develop the dynamic model of the evaluation and prediction of the ground-level ozone variation depending on the nitrogen dioxide concentration in the background conditions by means of the memory content.

## Materials and methods

### *Site description and material*

The ground–level ozone and nitrogen dioxide concentration data from two background stations were used in the investigations. The Preila monitoring station (55°55' N and 21°00' E, Lithuania), which is located on the Curonian Spit, a narrow sandy strip separating the Baltic Sea and the Curonian Lagoon, was established in 1980 (Fig. 1). There are no powerful sources of anthropogenic pollution of the atmosphere, soil or water close to the observation site. The nearest anthropogenic sources are Klaipeda located 40 km to the north and Kaliningrad 90 km to the south.

The station Rucava (56°10' N and 21°11' E, 18 m a. s. l., Latvia) is about 100 km to the north from the Preila station. The station is situated in the south-western part of Latvia, about 10 km east from the Baltic Sea, 50 km south from the city of Liepaja and 50 km north from Klaipeda. The station is located in the agricultural area. Within the radius of 300 m, there is an area covered with farmland and small groups of trees. The locality is scarred with drainage channels. These two stations are operated according to the EMEP (Cooperative program for monitoring and evaluation of the long-range transmission of air pollutants in Europe) requirements.

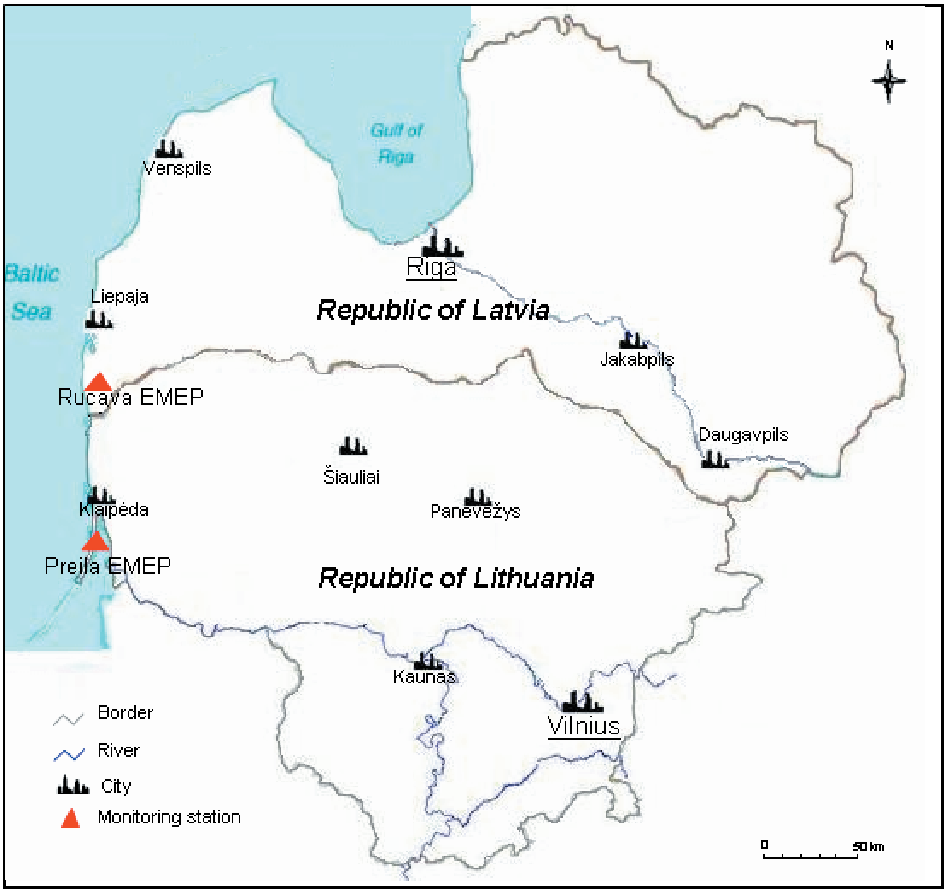


Fig. 1. Location of the Preila and Rucava monitoring stations.

Data obtained at these stations well reflect the air pollution level determined by the transported air masses. These data are important especially taking into account the fact that 75% of air masses entering Lithuania are from the southwest–northwest. Predominant air masses transport from the west–northwest was established for the Latvian station Rucava (Lyulko et al., 2003). Continuous ozone and nitrogen dioxide measurements were started in Preila in 1981 (Girgzdiene et al., 2002) and in Rucava in 1994.

The ozone concentration at both stations was measured with the commercial ozone UV absorption analysers O341M, which were calibrated against the reference standard UV photometer SRP11 at the Stockholm University, Sweden. The lower detection limit of these instruments was 2 μg $m^{-3}$. The ozone measurement cycles were several seconds. The obtained data were averaged over the 1-hour period.

Nitrogen dioxide was sampled with the sodium iodide (NaI) impregnated glass sinter filter. The sample collection was performed continuously for 24 h with the air flow rate of 0.4–0.7 $m^3$ per day. The analysis of the samples was performed using spectrophotometry by the Griess method. The detection limit is 0.17 μg N $m^{-3}$. The air inlets for all pollutants were at 2 m above the ground.

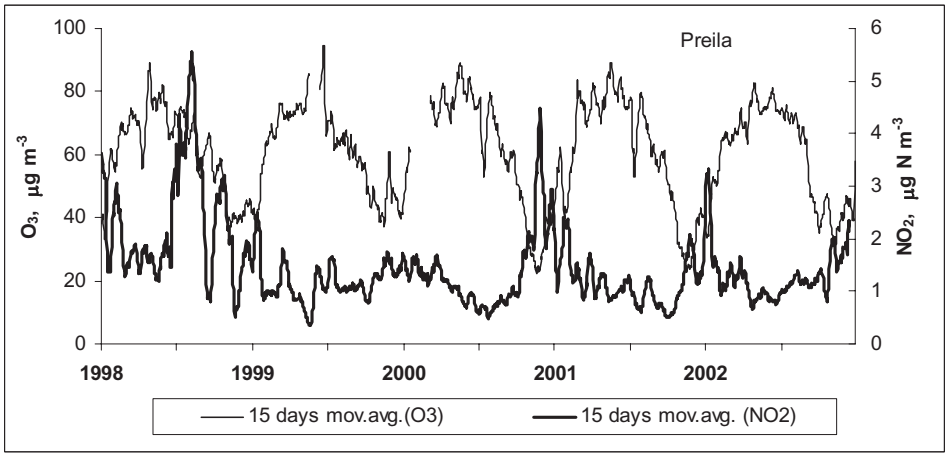


Fig. 2. The 15-day moving average of daily $O_3$ and $NO_2$ concentrations at the Preila station, 1998–2002.

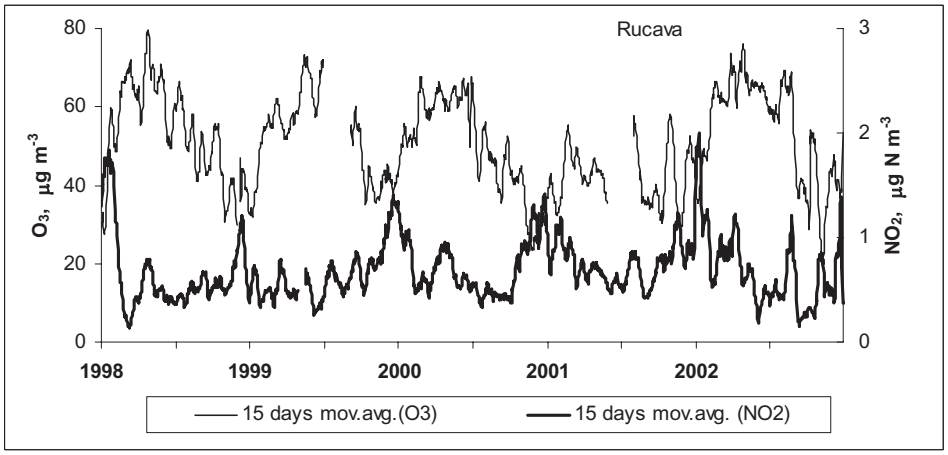


Fig. 3. The 15-day moving average of daily $O_3$ and $NO_2$ concentrations at the Rucava station, 1998–2002.

The daily mean concentrations of ozone and nitrogen dioxide, overall 3393 and 3365 values, respectively, were used in the study. For the simplification of the pictures, the 15-day moving average of these pollutants at Preila and Rucava stations is presented in Figs 2 and 3, respectively. The statistical data of ozone and nitrogen dioxide concentrations of 1998–2002 are displayed in Table 1.

T a b l e 1. Statistics of ozone and nitrogen dioxide data in the Preila and Rucava stations during 1998–2002.

| Percentage of sample that did not exceed indicated concentration | $NO_2$ μg N $m^{-3}$ | $O_3$ μg $m^{-3}$ | $NO_2$ μg N $m^{-3}$ | $O_3$ μg $m^{-3}$ |
|---|---|---|---|---|
| | Preila | | Rucava | |
| N (number of samples) | 1683 | 1756 | 1782 | 1637 |
| 10% | 0.6 | 31.5 | 0.2 | 29.5 |
| 25% | 0.8 | 46.5 | 0.4 | 38.6 |
| 50% | 1.1 | 62.6 | 0.6 | 50.9 |
| 75% | 1.7 | 74.5 | 0.9 | 62.1 |
| 90% | 2.7 | 85.1 | 1.3 | 71.5 |
| 99% | 6.1 | 97.9 | 2.2 | 90.5 |

## *Conceptualization of the model*

The investigations of the relation between ozone and nitrogen dioxide at the Preila station showed (Girgzdiene et al., 2002) the opposite trend of these pollutants during the measurement period of 1983–2001: $NO_2$ concentration decrease of 0.20 μg N $m^{-3}$per year ($p < 0.0001$) and ozone increase of 1.12 μg $m^{-3}$per year ($p < 0.001$). The detailed investigations revealed distinct ozone diurnal courses, and herewith the separate diurnal mean, at different $NO_2$ concentrations. In order to ascertain what influence the nitrogen dioxide level has on the ozone diurnal course, two groups of days with different ozone daily maximum were chosen in June 2000. 25% of days with the highest ozone daily maximum were attributed to the first group and 25% with the lowest ozone values to the second group. The obtained averaged diurnal courses of these groups were compared with the average ozone diurnal course in June (Fig. 4). The results revealed that the ozone diurnal course at low nitrogen dioxide concentration (average of 0.64 μg N $m^{-3}$) had very small amplitude. The diurnal course of ozone showed the well defined maximum in the afternoon and minimum during morning hours when nitrogen dioxide concentrations were high (average of 1.28 μg N $m^{-3}$). The average diurnal course of ozone concentration revealed a small steady increase (4 μg $m^{-3}$ per hour) between 8.00 and 16.00 (local time). A daytime ozone concentration increase was not observed on "clean", with low $NO_2$ concentration, days.

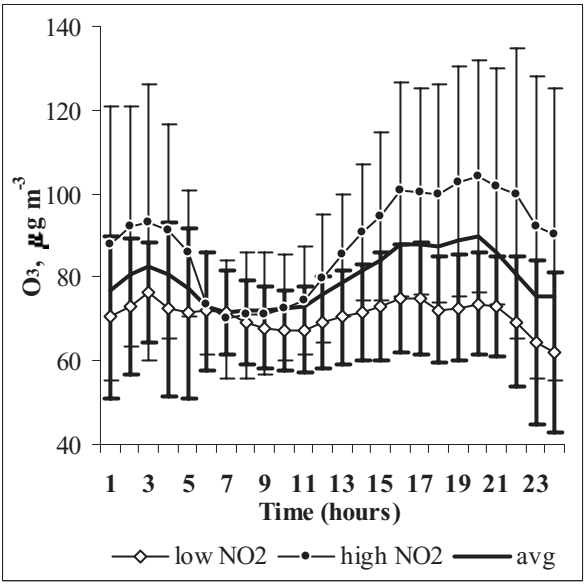


Fig. 4. Ozone diurnal cycles in June 2000: at high (average 1.28 mg N $m^{-3}$) and low nitrogen dioxide concentrations (average 0.64 mg N $m^{-3}$).

The VOC concentrations were not measured at the Preila and Rucava stations. As these stations are located in the rural $NO_x$ limited areas where the biogenic VOC emissions are dominant, the controll of $NO_x$ can reduce ozone concentrations.

Ozone maximum concentrations are measured during the warm period. Contrary to ozone, the maximum concentrations of $NO_2$ are found in the winter period when the photo dissociation process is abated. Thus, logically a time variant dynamic model is likely to be a better representation of the ozone-nitrogen dioxide process. The functional form of such a process can be described as,

$$S_t = f(N_t, N_{t-1}, N_{t-2}, ..., S_{t-1}, S_{t-2}, ..., S_{t-n}), \quad (1)$$

where $S$ is the daily ozone concentration, $N$ is the daily nitrogen dioxide concentration and subscripts *t, t-1,* etc. denote the time at respective lags in days.

## Results and discussion

### *Development and calibration of model*

The 3-year (January 1999–2001 December) data series of ozone and nitrogen dioxide concentrations were used for the model calibration. The measurements of $S_i$, $i$=1, 2,..., $n$ are the 24 h averages of $O_3$ concentrations in μg $m^{-3}$; $N_i$, $i$=1, 2, ..., $n$ are the daily $NO_2$ concentrations in μg N $m^{-3}$. In this case, the annual cycle (independently of the year) is given by a linear regression on the deterministic length of day.

A preliminary study to develop the conceived model for the Preila and Rucava stations data was performed. It has been observed that the ground-level ozone concentration is the combined effect of nitrogen dioxide concentration on that day, and ground-level ozone and nitrogen dioxide concentrations of five previous days. Accordingly, for these stations, a time lag of five days was chosen.

At first, for the development of the model (eqn. 1), we assumed that the model structure was considered to be linear. The basic structure of a linear dynamic model for a lag of five days is described below:

$$S_t = A_0 + \sum_{i=1}^{6} A_i N_{t+1-i} + \sum_{i=1}^{5} B_i S_{t-1}. \quad (2)$$

In the equation, $A_0$, $A_i$ and $B_i$ are the model coefficients. The values of these model coefficients and their respective level of significance were determined by using the techniques of multiple regression analysis. A linear dynamic model applicable at the 5% significance level was then obtained, which was of the following form:

$$S_t = 10.21 - 0.19N_t + 0.104N_{t-2} + 0.531S_{t-1} + 0.11S_{t-3} + 0.133S_{t-5} + e_t \quad (3)$$

and

$$S_t' = 11.29 - 0.19N_t' + 0.0824N_{t-2}' + 0.565S_{t-1}' + 0.093S_{t-5}' + e_t, \quad (4)$$

where $S$ and $S'$ are the daily ozone concentrations in μg $m^{-3}$ at the Preila and Rucava stations, respectively, $N$ and $N'$ are the daily nitrogen dioxide concentrations in μg N $m^{-3}$ at the Preila and Rucava stations, respectively. The coefficient $R^2$ of multiple determinations for the linear dynamic model in Eqn 3 was obtained to be 70% for Preila and 58% for Rucava (Eqn 4).

Furthermore, the model was calibrated for various scenarios. For example, the ozone concentration was estimated at nitrogen dioxide concentrations that were less than 2.7 μg N $m^{-3}$ (see Table 1). The obtained coefficient $R^2$ of multiple determinations was 63%. All modelled scenarios are presented in Table 2.

The results showed that the model generated and measured values of daily ozone concentrations coincided well only for scenarios No 1 and No 2 and the coefficients $R^2$ are statistically significant at p = 0.05 (Table 2).

T a b l e 2. The various scenarios for the ozone concentration modelling.

| No. | Scenario | $R^2$ Preila | $R^2$ Rucava |
|---|---|---|---|
| 1 | $NO_2$ values < 90% | 0.63 | 0.58 |
| 2 | $NO_2$ values > 50% | 0.69 | 0.66 |
| 3 | $NO_2$ values < 25% | 0.55 | 0.81 |
| 4 | $O_3$ values < 25% | 0.15 | 0.06 |
| 5 | $O_3$ values > 75% | 0.21 | 0.05 |

*Error component ( $e_t$ )*

The developed model can be divided into two components, namely, the deterministic and stochastic ones. The deterministic component consists of terms obtained through a multiple regression analysis, and the stochastic component represents the value $e_t$, which could be occurred due to faults during sampling, measurement and recording of the data. The magnitude of independence and randomness of values for $e_t$ were tested by computing the auto-correlation functions (*ACF*) (Hipel, McLeod, 1994). The series are considered to be a randomly distributed and independent white noise series when the ACF are not significantly different from zero, or are within the limits of twice the standard error (*SE*) of the series. The results, i.e., the difference between measured and predicted values of daily ozone concentrations, and their ACFs at different lags were calculated. It was observed that the values of calculated ACFs were within the limits of twice the standard error value of the residual ozone concentration series at the 5% significance level. This highlighted that the series for $e_t$ is independent, randomly distributed and cannot be modelled. Therefore, the error component was eliminated from the main model, and the final model, which represents the ozone-nitrogen dioxide process, was expressed as:

$$S_t = 10.21 - 0.19N_t + 0.104N_{t-2} + 0.531S_{t-1} + 0.11S_{t-3} + 0.133S_{t-5} \quad (5)$$

and

$$S_t^{'} = 11.29 - 0.19N_t^{'} + 0.0824N_{t-2}^{'} + 0.565S_{t-1}^{'} + 0.093S_{t-5}^{'} \; . \quad (6)$$

*Model testing and validation*

The developed linear dynamic model (Eqn 5 and Eqn 6) was tested based on the daily data series of the years 1999–2001 to check its performance. The estimated values of daily ozone concentration from the model were compared with the corresponding values of measured daily ozone concentration in those years. Applying this to the data series of 1998 and 2002 the applicability of the model was checked. Graphical comparison of the measured predicted and synthetically generated values of daily ozone concentration for the year 2002 is shown in Figs 5 and 6. It was observed that the model predicted and generated values of daily ozone concentrations coincided fairly well with the corresponding measured values of daily ozone concentrations. For the Preila station the coefficient of multiple determination of the model was found to be 70%, which indicated that the model could explain about 70% of the variability in the ozone concentration estimation. For the Rucava station the coefficient of multiple determination of the model was found to be 50%. Thus, the model was considered to be a better representation of the ground-level ozone and nitrogen dioxide process of the Preila station than for the Rucava station.

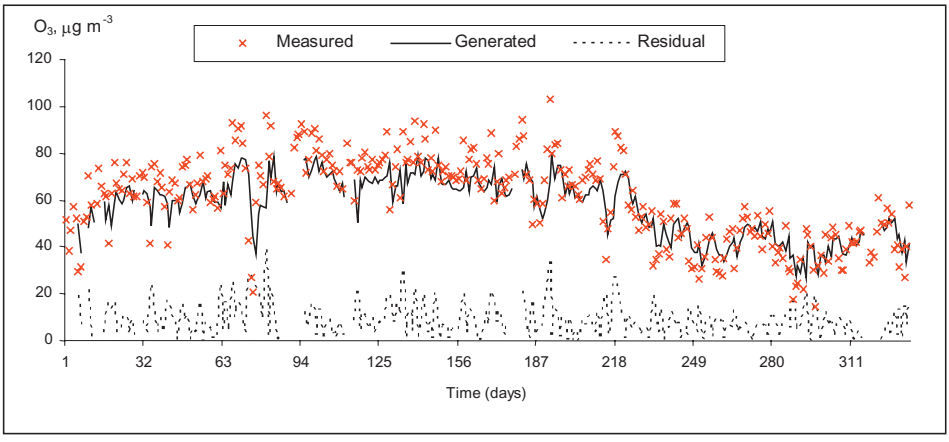


Fig. 5. Measured, generated and residual daily ozone concentrations at the Preila station for the year 2002.

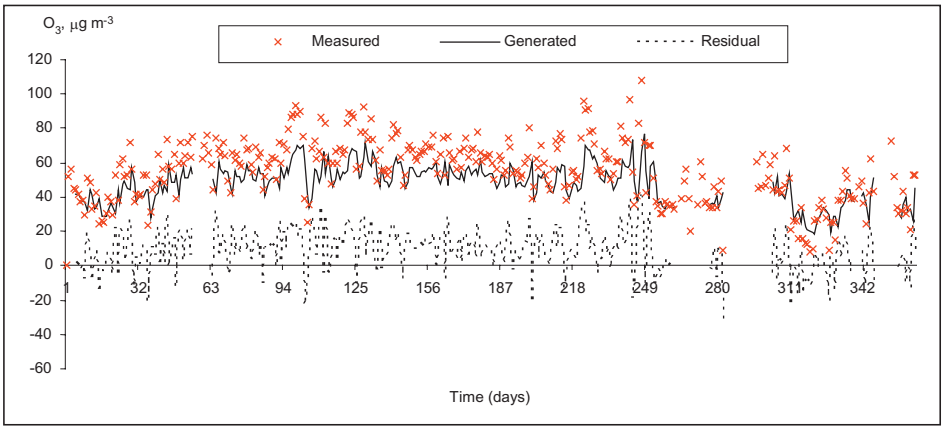


Fig. 6. Measured, generated and residual daily ozone concentrations at the Rucava station for the year 2002.

## Conclusion

The $O_3$ concentration data were analysed in order to identify possible relationship with $NO_2$ data. An input-output time invariant dynamic model was developed to represent the daily ozone-nitrogen dioxide process at the background stations. The coefficient of multiple determinations for the model was found to be 70% for the Preila station (Lithuania) and 58% for the Rucava station (Latvia). The model estimated and synthetically generated values of daily ozone concentrations were found to be in agreement with the corresponding measured values. The error component present in the model has been found to be an independent and randomly distributed white noise.

Referring to the results obtained by the regression model, the prediction of $O_3$ concentration at the Preila station was more accurate than at the Rucava station. One of the reasons for this result could be the influence of the surrounding conditions that are somewhat different for these stations. Atmospheric circulations conditioned by the surroundings (e.g., topography, presence of pollutant sources, such as towns or roads) and meteorological conditions (e.g., wind regime, air temperature, relative humidity and radiation) are important factors affecting the ozone levels at a given site.

*Translated by the authors*

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