Application of spectral analysis to investigation of surface ozone variations over Europe

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The paper presents preliminary results of spectral-cluster analysis of variations of the surface ozone concentration measured at the EMEP European ozone network. The energy contributions of different processes ranging from local to large-scale in four selected period groups from 91 to 1 day were analyzed. It has been shown that the energy spectral contributions of the large-scale processes are growing from the north to the south with the decrease of the contributions from shorter-term processes. Clustering of the energy contributions reveals the substantial spatial non-uniformity of the processes governing surface ozone regime over Europe.

Introduction

The increased interest in the problems of the quality of the environment is inseparably linked to the problem of change in the gas composition of the surface air. The role of surface ozone among other gases of potential health hazard cannot be overestimated.

In recent decades, investigators all over the world pay the particular attention to variability of the surface ozone. This attention is mostly caused by the following main factors:

1) ozone is a toxic atmospheric pollutant, whose concentration often exceeds the maximum permissible level, due to which the World Health Organization (WHO) included ozone in the list of five primary pollutants, whose content should be monitored in determining the air quality;

2) ozone plays the key role in tropospheric chemical and photochemical processes, taking an active part in the atmospheric transformation of trace gases and causing its oxidizing ability;

3) the positive trend of tropospheric and surface ozone, as well as the increase in the occurrence of events of the highly enhanced ozone concentration has been observed until recently over the vast continental areas of the Northern Hemisphere.[1]

Despite the situation has changed in the last decade,[2,3] that is, the peak concentrations decreased, it is still unclear what processes govern the variations of the surface ozone. Among the governing processes, one can separate, first of all, the horizontal and vertical transport and photochemical generation and destruction.[4] Dry sedimentation onto the surface, precipitation scavenging of aerosol, and some other processes also give a certain contribution. If the dynamic processes have natural variability, then the level of ozone precursors in the atmosphere is directly connected with the human activity. The separation of natural and anthropogenic components of variations and trends of the surface ozone concentration at different points of the globe can hardly be achieved because of limited experimental data and cannot be achieved mathematically (directly) because of nonlinear relations between the ozone variations and the governing processes.

In this paper, we attempt to consider this problem from the viewpoint of scaling the atmospheric processes governing the variations of the surface ozone concentration. The technique developed is used to study the variability of the surface ozone over Europe based on EMEP (Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe) data using spectral-cluster methods for analysis of data.

1. Selection of governing processes

The scales of atmospheric processes governing variations in the gas composition are significantly different and can be from hours (days) to years and even decades.[5] Among the most characteristic scales of the annual variability associated with various processes, it is proposed to separate four time ranges: 90–31, 30–19, 18–8, and 7–1 days. Some of these periods were found in the surface ozone variations at the stations involved in the TOR-2 Project.[6]

The longest-period (hereinafter, large-scale) group partly represents the seasonal variability of the ozone concentration. The main governing factor in this group is variation of the radiative and thermal conditions in the lower atmospheric layer, which affects, in the first turn, the activity of photochemical processes.

The periods of 19–30 days are usually associated with global atmospheric oscillations (for example, planetary waves, long and superlong waves, Rossby waves).[7] The planetary waves affect the surface ozone due to vertical motions accompanied by ozone transport from the higher levels (for example, from the upper troposphere, where the ozone concentration is higher). The planetary waves were also found in

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TOC,[8] and their relation to global climate changes was confirmed.[9]

The periods of 18–8 days represent the oscillations of the concentration caused by the large-scale synoptic processes (large-scale baric systems, air mass alternation, etc.).[7] The effects of various baric systems on the ozone variations have been estimated in many studies, and it has been shown that the passages of frontal zones, cyclones, and anticyclones are accompanied by characteristic changes in the ozone concentration.[10]

The periods of 1–7 days characterize the short-period, local processes (including local synoptic processes), which are caused by both the local characteristics of the territory, for example, the distribution of sources and the presence of local circulations, and by the effect of the internal gravitational waves, etc. This range does not include the diurnal variability of the surface ozone concentration.

The above scaling of the periods has been already used earlier in analyzing the temporal variability of total ozone column.[8]

2. The data involved

In this work, we used the data on the ozone concentration obtained at the EMEP European network of measurement stations. The surface ozone measurements are accessible on the Internet (http://www.nilu.no/projects/ccc/).

The EMEP network of stations has been arranged in 1979 to study variations in the gas and aerosol composition of the atmosphere over Europe and to assess the transborder pollutant transport. These stations measure the concentrations of ozone and some its precursors. The network covers quite densely the territory of the Central and Northern Europe; three stations are located on the territory of Russia (the network is partly shown in Fig. 3).

In our analysis we used the series of measurements of the surface ozone concentration with 1-hour time resolution. The data are of high quality. The filling percentage is from 79 to 99%. The standard device for measurement of the ozone concentration was DASIBI, which provides the accuracy of 1 ppbv.

To study peculiarities in the surface ozone distribution, we have selected 90 stations with the maximum duration of measurement series equal to 10 years and longer.

3. Methods

The processing of the data has been carried out in several stages. First, the data of the selected stations were filtered in order to find the spectral range containing the selected ranges of variations (separation of variations from 3 months to 1 day). Preliminary filtering of the data is needed to reject the annual and diurnal periods, which are responsible for more than 50% of surface ozone variation. The filtering was performed by the method of moving average with subtraction. This procedure allowed us to reject variations longer than 3 months, as well as short-period (one day and shorter) variations. The filtered series were then used to assess the spectrum of variability of the surface ozone at the network of stations considered.

The spectral analysis was conducted with the use of the correlogram method.[11] The Fourier transform was obtained using Matematica 3.0 software package. Then the percentage contributions of the studied processes to the energy spectrum were estimated.

In our analysis we used the above mentioned periods of 91–31, 30–19, 18–8, and 7–1 days. The energy contribution of each period to the total spectrum was calculated by the following equation:

$$S = \frac{\sum\limits_{i=n_{\text{start}}}^{n_{\text{end}}} (\text{Re}(b_i)^2 + \text{Im}(b_i)^2)}{\sum\limits_{i=0}^{N} (\text{Re}(b_i)^2 + \text{Im}(b_i)^2)} 100\%,$$

where b_i are the Fourier transform coefficients; N is the total number of harmonics in the analyzed spectrum; n_{start} and n_{end} are the start and the end numbers of harmonics of the analyzed periods.

This processing of measurements was performed for every station and then systematized.

We have considered the latitudinal distribution of the obtained estimates and performed their cluster analysis both in terms of the vector of energy contributions and with the additional account for the latitude and longitude of a station. It was found that the latter approach is not fully correct from the mathematical point of view, because naturally groups the stations with respect to the parameter having the prevailing effect, that is, the latitude and longitude.

The method of k-average was used for classification of the vectors of energy contributions. The principles of this method are described in the literature in a sufficient detail (see, for example, Ref. 12). The cluster analysis was carried out in the SPSS 8.0 package of statistical programs.

4. Results

First of all, in this work we studied the contribution of different mechanisms to variability of surface ozone depending on the latitude of the observation station. The latitudinal distribution of energy contributions of different processes is shown in Fig. 1.

As can be seen from Fig. 1, low-frequency large-scale processes are responsible for the maximum energy in the spectrum. It has the significant latitudinal gradient from north to the south, smoothly decreasing from 54% in the region of 45–50° to 44% in the region of 60–65°N. Since the large-scale processes partly reflect the seasonal behavior, this latitudinal gradient demonstrates the natural variability of irradiance and, consequently, the activity of photochemical processes of ozone generation from precursors. A slight increase in the last latitudinal group is likely connected with a random burst due to poor statistics in the high-latitude zone (only four stations).

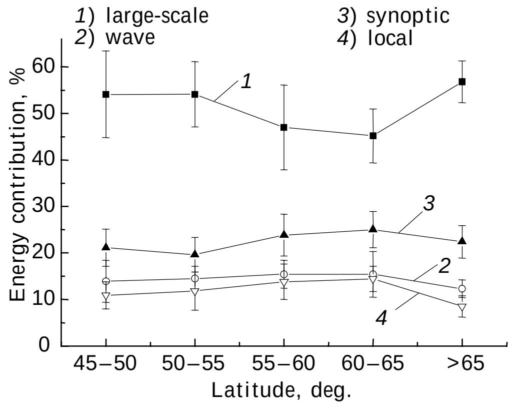

Fig. 1. Latitudinal distribution of the energy contribution of different components according to the data of spectral analysis of surface ozone measurements at the EMEP network.

The component of planetary wave processes has a low energy spectral maximum in the region of 60–65°N, which can be attributed to passage of a planetary frontal zone in this region with possible intensification of the stratosphere–troposphere exchange, in particular, by means of the planetary waves. However, this maximum is not well pronounced. On the average, the contribution of the planetary-wave component to the energy spectrum of variations is about 15%.

The energy contribution of the synoptic component has a small latitudinal gradient with a weakly pronounced maximum in the mid-latitudes. On the average, the energy contribution of the synoptic component does not exceed 20%.

The energy contribution of the short-period component also has a weak latitudinal gradient, inverse to that of the large-scale processes. In higher latitudes, the energy contribution of the short-period component increases. The energy contribution of local processes is the smallest among all the considered groups (about 10%).

The obtained spatial gradients indicate that, when going on from low to high latitudes, a smaller part of the energy is transported by long-period variations, which is connected with the change in the irradiance and, consequently, in the activity of photochemical ozone generation.

To estimate the possible spatial variability of the energy contributions of different processes to the spectrum of surface ozone variations, we have conducted the cluster analysis of the vectors of energy contributions.

Clusterization of the energy contributions is shown in Fig. 2. The geographic distribution of clusters is shown in Fig. 3. Clusters are ordered in accordance with the increase of the latitude of the cluster center. The first (southernmost) cluster incorporates three stations, located in Portugal, Austria, and Slovakia. The features of this cluster are the maximum contribution of the large-scale component to the observed spectra of variations and, consequently, the significant influence of the seasonal behavior on the observed variations.

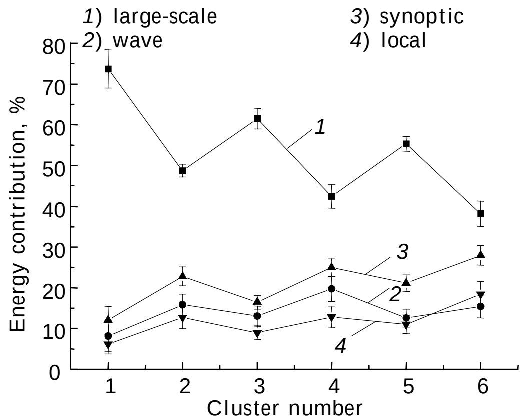

Fig. 2. Cluster distribution of the energy contribution of different components from the data of spectral analysis of surface ozone measurements at EMEP network. Centers of the clusters: 1) 45.06°N, 10.05°E; 2) 50.58°N, 5.49°E; 3) 51.9°N, 10.89°E; 4) 52.45°N, 14.54°E; 5) 54.24°N, 10.76°E; 6) 54.35°N, 7.6 °E.

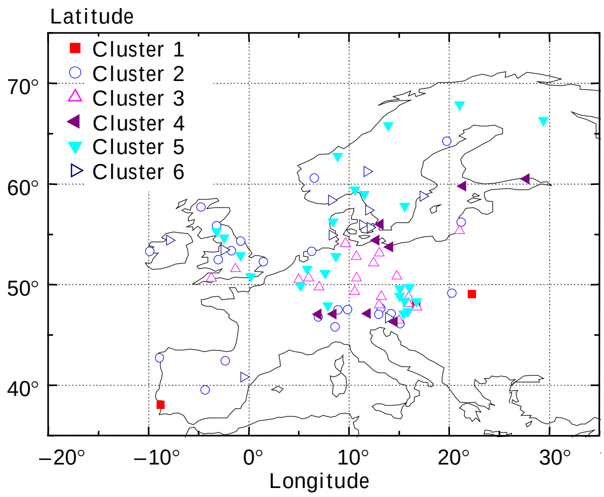

Fig. 3. Geographic distribution of clusters in terms of the energy contributions of different components.

As can be seen from Fig. 2, the results of cluster analysis are in a good agreement with the results of latitudinal analysis of energy contributions. The minimum contribution (38%) of large-scale processes in observed in the sixth (northernmost) cluster. The maximum contribution of the wave component (about 20%) is observed in the fourth cluster. A feature of the fourth cluster is that it incorporates both four stations located in Alps along 48°N and the stations located on the Baltic Sea coast. In this cluster, the contribution of synoptic processes is relatively high (about 25%). The significant contribution of the synoptic component in this cluster as compared with other clusters is most likely connected with the fact that it includes coastal stations. The relatively high energy contribution of the long-period component in the third cluster corresponds mostly to continental mid-latitudinal regions, though the stations in this cluster are not considerably localized. The maximum contribution of the local and synoptic components to the energy spectrum is observed in the northernmost group. An interesting fact is that almost all stations in this cluster are coastal. The only exclusion is the mountain AT38 station (1900 m above the sea level), where the large-scale synoptic processes determine 30% of the energy contribution in the chosen range of periods.

The noticed spatial inhomogeneities in arrangement of the clusters demonstrate a complex pattern of the distribution of the governing processes over Europe and the complicatedness of an unambiguous description of this spatial distribution. Detailed interpretation of the obtained results is possible if invoking the description of observation conditions at every station of a particular cluster.

Conclusion

The preliminary results of spectral-cluster analysis of variations of the surface ozone concentration over Europe observed at the EMEP network have been analyzed. The constructed estimates of energy contributions of different processes: from local to large-scale, have revealed some interesting features in the spatial variations of the surface ozone.

It has been shown that the energy spectral contributions of the large-scale component have the latitudinal gradient from the north to the south. This can be explained by the fact that this scale reflects to the maximum degree the activity of photochemical processes associated with the latitudinal gradient of irradiance among all the considered processes. In other considered components, this effect is much weaker. The energy approach has allowed us to separate the 55–60°N region as a zone of the most active influence of wave processes.

Due to application of clusterization to analysis of spatial inhomogeneities in surface ozone variations, we have separated some characteristic clusters on the territory of Europe. In particular, as in the case with latitudinal averaging, one cluster has incorporated the stations located in the southernmost and most continental regions of Europe, characterized by the maximum contribution of the large-scale component. The great number of continental stations with the significant contribution of the large-scale component has been localized in a separate cluster as well. The contributions of the components for different clusters can differ almost twice, which is especially pronounced in the variations of the contribution of large-scale synoptic processes. However, this analysis shows that the division into clusters significantly depends on the observation conditions, therefore, for further interpretation of the obtained spatial distribution of the energy contributions, it is necessary to obtain the information on the observation conditions.

This analysis has revealed the extremely complex mechanisms of formation of the surface ozone concentration under inhomogeneous physical-geographic conditions of pollution of the European territory.

The revealed regularities agree with the general ideas on the distribution of the mechanisms governing the surface ozone concentration. In particular, the characteristic increase of the effective contribution of the wave and sorter-period ranges in going on from 45 to 65°N corresponds to the model of the three-cell structure of the wind field in the zonal climatic model developed in Ref. 13. This model also demonstrates the estimated negative gradient of the energy contribution of the wave and shorter-period regions of the variability.

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