Sources and variations of tropospheric ozone in central Siberia: observations and model simulations

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Abstract. Impact of climatically significant anthropogenic and natural emissions to seasonal ozone ($O_3$) variations observed at the Zotino Tall Tower Observatory (ZOTTO) in central Siberia in 2007–2012 have quantitatively been estimated using GEOS-Chem chemical transport model. It is shown that the formation of a stable continental pollution plume from sources in Western Europe, European Russia, and southern Siberia plays an important role in regional balance of near-surface ozone and allows to explain up to 15%–17% of the amplitude of $O_3$ annual cycle observed at ZOTTO (~5–6 ppb).

1. Introduction

Large amount of observations and numerical simulations data shows that the effect of atmospheric emissions of photochemically active compounds on air composition in industrial regions is nonlocal and in many cases can be traced on regional and transcontinental scales [1]. Typical examples of this influence are large-scale plumes of polluted air from industrial areas of South-East Asia, North America and Europe, defined by satellite monitoring data, aircraft observations of tracer (long-lived) species (CO, NO$_x$, a number of organic species) during measurement campaigns and as the results of numerical simulations. In terms of influence on background (anthropogenically undisturbed) tropospheric photochemical system of many regions of Northern Eurasia the plume of polluted air from industrial regions of Western Europe, European territory of Russia (ETR) and southern Siberia traced in CO and O$_3$ surface fields up to ~120E in middle latitudes is of interest [2], [3]. The influence of "windward" industrial regions on air chemical composition in remote areas of Siberia is clearly visible, for example, in ZOTTO background monitoring station observational data at seasonal fluctuations in CO near-surface concentration with a maximum of ~200 ppb in late winter and a minimum of ~90 ppb in mid-summer, as well as short-term episodes of raised CO, O$_3$ and NO$_x$ concentrations during advection of anthropogenically polluted air from sources in southern Siberia [1], [2].

Quantitative estimates of regional and remote atmospheric pollution sources contribution to regional balance of near-surface ozone can be performed using chemical-transport models (CTM) with realistic emission fields. Despite the importance of such studies, reliable quantitative estimates of the role of regional and long-range transport in the balance of near-surface ozone in regions of Russia with increased anthropogenic load are currently practically does not exist.
2. ZOTTO station and GEOS-Chem model

ZOTTO (Zotino Tall Tower Observatory, 60.80° N, 89.35° E, 300 asl) is located on the eastern edge of West Siberian plain 30 km west of Yenisei river in boreal forest zone 450 km north of Krasnoyarsk. During the cold period of the year, the station is approximately on climatological boundary of polar front, which in the warm period of the year locates much to the north. This feature is important from the standpoint of long-range air transport study, because area of the station, depending on specific regime of atmospheric circulation, can be under the influence of air masses from North Atlantic, passing over the European continent and Western Siberia, and Arctic air masses coming from the Arctic and North-Eastern Siberia [2].

Interest in ZOTTO data in surface air composition studies is due to climatological features of the station location area. The tropospheric photochemical system in the region has a distinct continental type, which allows, with some caution, to generalize the results to continental areas of Siberia as a whole [1].

The gas analyzer DASIBI-1008 is used to measure the ozone concentration in instrument complex at the station. The principle of operation of this device is based on measurement of attenuation of ultraviolet (UV) radiation at a wavelength of 253 nm during passage of latter through a cell with a sample of test air. To improve the accuracy of the device measurements, a comparison method is applied: the measuring cell is consistently filled with a sample of analyzed air, and a sample of the air that has passed through the so-called zero filter, completely destroying all the ozone contained in the sample. Measured values of UV radiation attenuation are analyzed by microprocessor of the device, then ozone concentration is calculated by Baer equation, taking into account corrections for temperature and air pressure, also measured by sensors available in the device.

The results of near-surface ozone concentration measurements at an altitude of 5 m in 2007–2012 are presented in Fig.1.

Figure 1. Monthly averaged O₃ concentrations at an altitude of 5 m above the ground according ZOTTO observations in 2007–2012. Statistics by month are given: P_{10}, P_{50}, P_{90} – percentile, □ – average. Solid line – GEOS-Chem model calculation (monthly averaged concentrations, first model level ~58 m above the ground).

GEOS-Chem (http://acmg.seas.harvard.edu/geos/, used version 11-01) - numerical Eulerian global chemical-transport model of atmospheric composition, taking into account all major natural and anthropogenic sources and sinks of chemically active gases and aerosols [4]. Meteorological fields and surface data with a time resolution of 3 (two-dimensional fields) and 6 (three-dimensional fields) hours are taken from the GEOS-GMAO global data assimilation system (Goddard Earth Observing System - NASA Global Modeling Assimilation Office, http://gmao.gsfc.nasa.gov/GEOS/) and are reprojected to model grid. In this work EDGAR 4.3.1 [5] data were used for anthropogenic
emissions in the model, MEGAN 2.1 [6] data - for emissions of biogenic VOCs. We used 4°×5° model grid, for comparison with ZOTTO measurements were used first level output with a height ~58 m above the ground. Calculations of chemical evolution were carried out in standard mode “NOx-Ox-hydrocarbon-aerosol” (the so-called “full chemistry” mode for the troposphere, 236 reactions, time step 60 min.)

Generally, the results of calculations for ZOTTO, based on monthly averaged data, was in good agreement with the observations (Fig. 1) despite the limited spatial resolution of the model. The mean bias $\delta = \bar{O} - \bar{C}$, standard error $\text{RMSE} = \left( \frac{(\bar{O} - \bar{C})^2}{\sigma_O\sigma_C} \right)^{1/2}$, and correlation coefficient $\text{COR} = \frac{(\bar{O} - \bar{O})(\bar{C} - \bar{C})}{\sigma_O \sigma_C}$ were used as consistency criteria. $\bar{O}$ and $\bar{C}$ are observed and calculated by the model monthly mean concentrations of $O_3$, $\sigma_O$, $\sigma_C$ - corresponding standard deviations, and the upper line means averaging over all values. It was obtained: $\delta=-3.5 \, (-4.8 \, -2.2)$ ppb, $\text{RMSE}=6.2 \, (5.3 \, 7.2)$ ppb and $\text{COR}=0.79 \, (0.67 \, 0.87)$, where the boundaries of the 95% confidence interval are indicated in parentheses.

3. Influence of regional anthropogenic NOx and biogenic VOCs emissions on ozone concentration in ZOTTO

The influence of polluted air plume is not only in increase of anthropogenic pollutants concentration, but also in formation of secondary pollutants, the most important of which is tropospheric ozone [7]. The main sources of tropospheric ozone are its transport from the stratosphere and photochemical production by nitrogen oxides (NOx) in the presence of CO and volatile organic compounds (VOCs) [3],[8], and nitrogen oxides are mainly of anthropogenic origin. Model simulations have shown that contribution of anthropogenic CO emissions to near-surface ozone concentration is insignificant [3], therefore, anthropogenic NOx and biogenic VOCs emissions are considered as the main factors influencing near-surface ozone concentration in central Siberia.

3.1 Model simulations scenario

Quantitative estimates of near-surface ozone concentration sensitivity to biogenic VOCs and anthropogenic NOx emissions was made for three macroregions: Western Europe, European territory of Russia (ETR) and Siberia (Fig. 2), considered earlier in [1],[2] in the study of natural and anthropogenic emission sources contribution to the observed seasonal variability of CO. Anthropogenic emissions in these regions determine the conditions of photochemical ozone generation in most of Northern Eurasia, including remote areas of western and central Siberia. The predominance of zonal air transport determines the consistent increase in its role against the background of climatically significant regional pollution sources for considered "leeward" regions - ETR and Siberia.

For the model experiment was chosen 2007. For all selected regions this year is characterized as warm with normal rainfall. In middle latitudes of Eurasia, zonal air transport was more intense than usual, and meridional air transport was weakened (according to Russian Hydrometeorological center, http://meteoinfo.ru). NOx and VOCs emissions in all selected regions were reduced by 50% and then by 100% in a series of calculations. In this paper, only biogenic VOCs are considered, results of earlier calculations showed that the contribution of anthropogenic VOCs on background of NOx emissions is insignificant.

The atmospheric response ($AR_x$) values were calculated as the difference between concentration obtained from baseline model calculation with full emissions, $\chi(O_3)_0$, and concentration calculated by the model with reduced emissions according to used scenario, $\chi(O_3)_S$:

$$AO_x = \chi(O_3)_0 - \chi(O_3)_S$$

In carrying out quantitative estimates in this work, maximum daily values of $O_3$ are used in order to focus on the photochemical processes of ozone formation and destruction.
3.2 Annual ozone variations analysis
In this work we use a series of measurements of ozone concentrations at ZOTTO station at an altitude of 5 m above the ground for the period from 03.2007 to 12.2012 (Fig. 1). The annual ozone variations at the station, shown in Fig. 3, are typical for mid-latitude background continental conditions of the Northern hemisphere [8]. The maximum near-surface ozone concentration (40 – 45 ppb) is achieved in April due to increase of solar flux and decrease of snow cover. Rise in intake of biogenic VOCs into the atmosphere leads to the active generation of ozone [3]. Increase of stratospheric exchange and zonal air transport occurs at the same time. By autumn, the intensity of chemical generation and atmospheric transport weakens, and average annual minimum near-surface ozone concentration (15 – 25 ppb) falls on September-October. Snowfall and low temperatures significantly slow down the processes of dry deposition and chemical destruction and therefore in winter ozone concentration begins to rise.
3.3 Factors of near-surface ozone concentration seasonal variability

For the seasonal variations of ozone, the phase and amplitude are explained by planetary atmospheric processes and seasonal dynamics of middle latitudes atmospheric photochemical system associated with the annual variations of solar radiation. This fact is clearly visible in observational data (Fig. 1, statistics by month). As can be seen from the figure, the amplitude of seasonal variations (~20-25 ppb, based on the difference between the mean values in different seasons) significantly exceeds short-period variations during cold and most of warm season. Typical magnitude of these variations, taken as a difference $P_{90}-P_{10}$, usually does not exceed 15 ppb.

ZOTTO is located at such a distance from anthropogenic sources of pollution that the emission plume is almost completely degraded. However, anthropogenic NO$_x$ emissions have a significant impact on the photochemical ozone production in area near the station. Generally, variations of ozone at the station is determined primarily by large-scale atmospheric circulation processes and global mid-latitude photochemistry, but with a shift closer to emission sources, the effect of ozone production in the presence of NO$_x$ increases by 2-3 times [3]. The average seasonal AR$_s$ values for ZOTTO for the chosen period are shown in table 1 and based on it summary diagram in Fig. 4. Maximum AR$_s$ values are observed in summer for all scenarios with 100% reduction of anthropogenic NO$_x$ emissions: 5.0 ppb at 100% and 50% of biogenic VOC emissions, 5.8 ppb at completely switched off emissions. At full anthropogenic and reduced by 100% biogenic emissions the response value does not exceed 2.2 ppb. In winter, the anthropogenic influence is also noticeable: with full NO$_x$ emissions for all scenarios, the maximum values of the AR, are close to zero, but with a decrease in anthropogenic emissions by 50% and 100%, negative response values are observed to -2.3 ppbv and -4.5 ppbv, respectively.

![Figure 4. Summary diagram of AR$_s$ for ZOTTO at different values of biogenic VOCs and NO$_x$ emissions in Siberia, ETR and Europe (Fig. 2). The average values for all seasons of 2007 are given.](image)

Based on the results presented in table 1, it can be argued that in the warm period (spring – summer – autumn) in area near the station is implemented NO$_x$-sensitive ozone generation regime: value of ARs in ozone field is determined by regional NO$_x$ emissions, controlling the intensity of ozone precursors oxidation reactions. In winter, HO$_x$-sensitive generation regime dominates: intense emissions of nitrogen oxides lead to ozone destruction in titration reaction with NO, which is the main volume of anthropogenic NO$_x$ emissions [3].
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### Table 1. Seasonally averaged maximum daily values of near-surface ozone concentration in area near ZOTTO. Seasonally averaged maximum daily values of atmospheric response to different types of emissions under different scenarios. All data are for 2007.

| Season  | O₃ ppb | 0% reducing NOₓ | 50% reducing NOₓ | 100% reducing NOₓ |
|---------|--------|------------------|-------------------|-------------------|
|         | Reducing VOCs | 50% | 100% | 0% | 50% | 100% | 0% | 50% | 100% |
| Winter  | 26.0   | 0.05             | 0.11              | -2.35            | -2.30           | -2.24          | -4.52          | -4.47          | -4.42          |
| Spring  | 37.4   | 0.26             | 0.64              | 0.98             | 1.13            | 1.40           | 3.77           | 3.80           | 3.90           |
| Summer  | 37.2   | 0.68             | 2.19              | 2.05             | 2.41            | 3.60           | 4.99           | 5.00           | 5.76           |
| Autumn  | 28.9   | 0.50             | 1.19              | 0.05             | 0.45            | 1.05           | 1.05           | 1.32           | 1.80           |

### 4. Summary
The result of model simulations indicate the important role of long-range air transport from climatically significant sources of atmospheric pollution in Europe, ETR and southern Siberia, as an important factor of seasonal and interannual variability of near-surface ozone concentration in Northern Eurasia. However, despite the fact that observed nonlocal effect of anthropogenic emissions plays a significant role, its contribution cannot be considered decisive. The observed seasonal variations of ozone at area near ZOTTO are caused primarily by large-scale chemical-transport processes in the Northern hemisphere, such as stratospheric-tropospheric exchange, atmospheric circulation in extratropical latitudes features and the global distribution of climatically significant natural and anthropogenic sources of ozone precursor emissions. According to modern concepts [3, 7] such a situation corresponds to background regime of the photochemical system in middle latitudes in regions with low anthropogenic load.

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