

The heterogeneous reactions in the polar stratosphere (Molina et al., 1987; Isaksen, 1994) involving HCl, ClONO₂, HOCl, N₂O₅ and H₂O are responsible for the conversion of reservoir species into reactive forms of chlorine, and also for removal of reactive nitrogen species into more stable forms (such as HNO₃):



Due to the heterogeneous chemistry, active species of chlorine (and also bromine) accumulated in the polar vortex. Then, after polar sunrise, the re-appearing solar radiation starts the photochemical activity, which leads to intensive ozone depletion in polar stratosphere during the polar spring. Chlorine reservoirs (such as molecular chlorine - Cl₂) photodissociated rapidly by ultraviolet and visible radiation into chlorine atoms:



which initiates catalytic reaction chains, as chlorine atoms react with ozone to produce ClO. Due to the low solar elevation angles, atomic oxygen is not present in the polar stratosphere, therefore the ozone destruction occurs through the following catalytic chain:



Net:



Similar catalytic bromine cycles can occur involving Bromine compound:



Net:

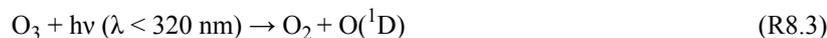


8.2 Tropospheric ozone

Tropospheric ozone is only about 10% of the total amount of ozone contained in a vertical column in the atmosphere. However, this relatively small amount of tropospheric ozone has a great importance because it's important role in the formation of photochemical air pollution and its oxidizing impact in the near surface layer (e.g. Krupa and Manning, 1988).

Tropospheric ozone is a direct greenhouse gas. Ozone abundances in the troposphere typically vary from less than 10 ppb over remote tropical oceans up to about 100 ppb in the upper troposphere, and often exceed 100 ppb downwind of polluted metropolitan regions (IPCC, 2001).

The absorption of solar ultraviolet radiation of wavelength shorter than 320 nm by ozone occurs in the troposphere similarly as in the stratosphere (see above). This photochemical reaction leads to the production of excited $O(^1D)$ atoms:



This excited $O(^1D)$ atoms have higher energy than ground state oxygen atoms, thus it has enough energy to react with water vapour to produce hydroxyl radicals (OH):



In this way, ozone is the precursor of OH, which is responsible for the oxidation of several species, such as carbon monoxide (CO) or alkanes (denoted as RH):



8.2.1. Global tropospheric ozone budget

Ozone is a secondary air pollutant that is not emitted directly to the atmosphere. Ozone can enter the troposphere from the stratosphere, where it forms by reactions (R8.1–R8.2). The most active regions of stratosphere-troposphere exchange of ozone are in cyclonic regions of the upper troposphere, near the disturbed tropopause. The major sources of tropospheric ozone, however, are chemical reactions, when it forms from its precursor compounds, such as reactive hydrocarbons and nitrogen oxides. Globally annual average of photochemical destruction of tropospheric ozone is comparable with the production. Another sink process of tropospheric ozone is dry deposition, when ozone is settling from the atmosphere to different surfaces (see Chapter 12). Globally averaged annual tropospheric ozone budget and major processes related to the life of tropospheric ozone can be seen in Figure 8.8.

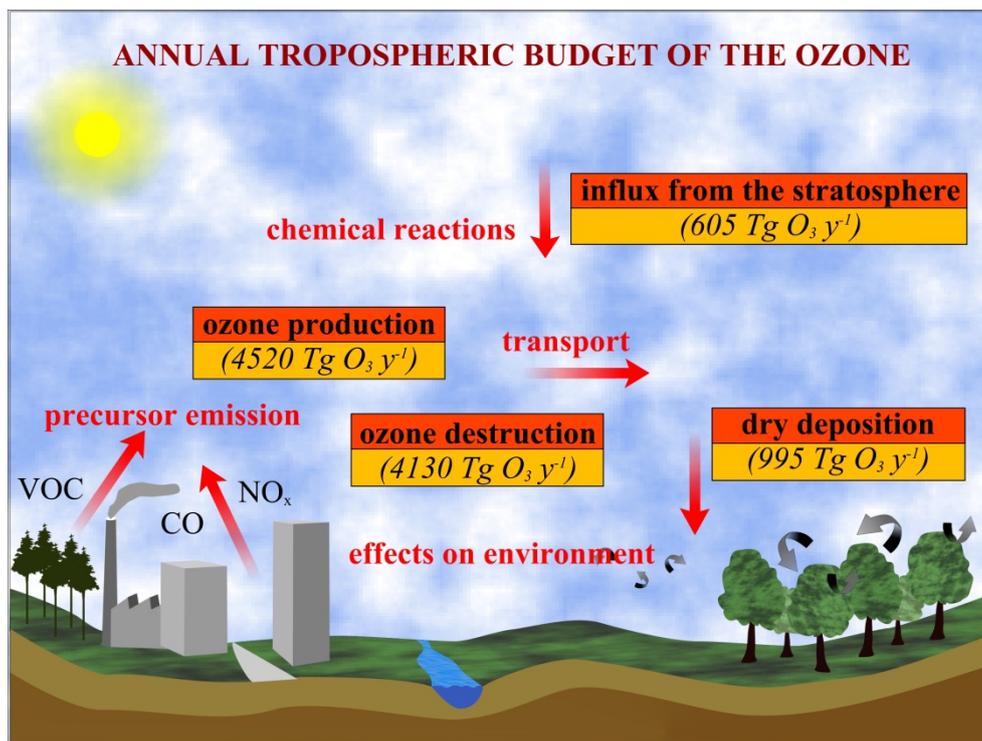
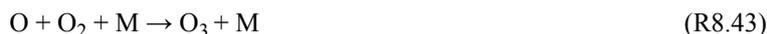


Figure 8.8: Annual tropospheric budget of the ozone. Source of data: Guicherit and Roemer, 2000.

8.2.2. Ozone production in the troposphere

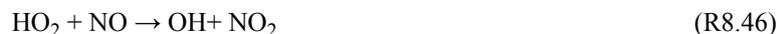
Ozone can form by the recombination of an oxygen molecule and an oxygen atom, similarly as in the stratosphere (reaction R8.1). Nevertheless, O atom cannot form in the troposphere by the photodissociation of molecular oxygen (reaction R8.2), because this reaction requires short wavelength ($\lambda < 242$ nm) which is not available in the troposphere (due to the absorption by stratospheric ozone). In the troposphere, nitrogen dioxide is the only known compound that can produce O atom during its photodissociation at available radiation:



In the presence of NO, O₃ reacts with it, which reaction destroys the ozone and reproduces the NO₂:



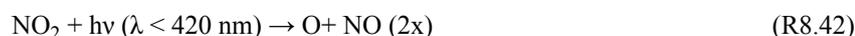
This means that reaction (R8.42)–(R8.44) themselves do not result net ozone production, because these reactions only recycle O₃ and NO_x. Net ozone production occurs, when other precursors, such as carbon monoxide (CO), methane (CH₄), non-methane hydrocarbons (NMHC) or certain other organic compounds (volatile organic compounds – VOC) are present in the atmosphere. Ozone production can be simulated by a simple reaction scheme, through the oxidation of carbon monoxide, when nitric oxide is available. In this reaction chain OH, HO₂, NO and NO₂ participate as catalysts:



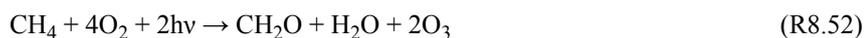
net:



Similar reactions chain occurs with the oxidation of methane in NO rich environment, when ozone and formaldehyde (CH₂O) are formed rapidly:



net:



Formaldehyde photodissociates to generate other radicals, which can participate further ozone productions.

Instead of methane, other organic compounds (NMHC, VOC) can also be participated in this reaction chain, where carbonyl species or a ketone formed next to the ozone. A schematic pattern of tropospheric ozone production can be seen if Figure 8.9.

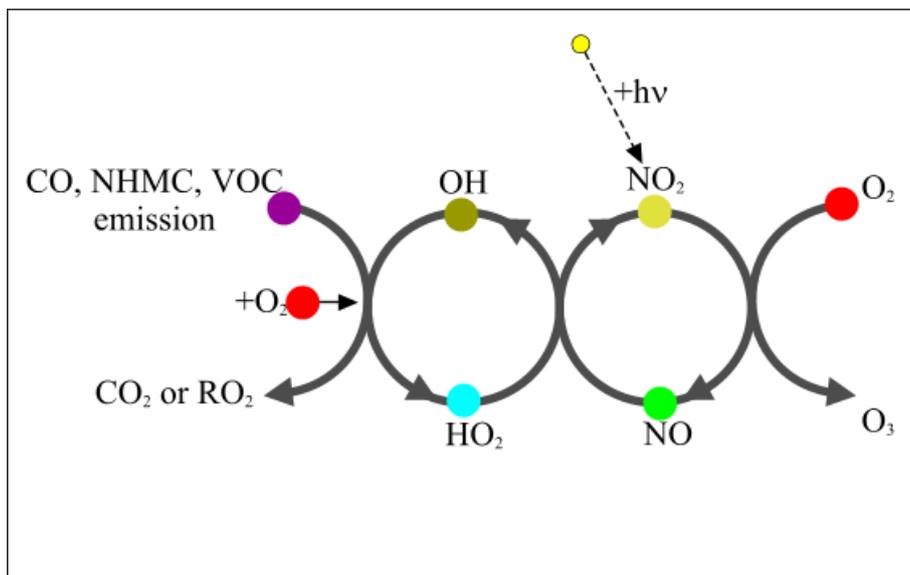


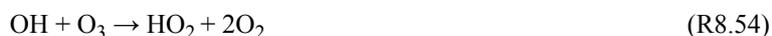
Figure 8.9: Schematic picture of photochemical ozone formation in the troposphere

8.2.3. Sinks of the tropospheric ozone

Primary loss processes of tropospheric ozone are the photochemical reaction (R8.3), when O₃ molecules dissociate by solar radiation. In NO rich environment, the reaction (R8.44) governs the ozone destruction. On the other hand, in NO-poor environment, the oxidation of carbon dioxide can lead to ozone loss. In that case, after the reactions (R8.40) and (R8.45) the generated HO₂ can react with ozone (instead of reaction R8.46):



Further ozone can be destroyed by the direct reaction with OH radical:



Next to chemical destructions ozone can be removed from the atmosphere by dry deposition. This process is more intense during unstable atmospheric stratification. After movement from near surface layer by turbulent diffusion, ozone can react with the receiving surface. Many plants are extremely sensitive to ozone and can be damaged (see details in Chapter 13).

8.2.4. Spatial and temporal variability of ozone in the near surface layer

The background surface ozone concentration increased steadily worldwide in the last decades of 20th century (Vingarzan, 2004). Spatial and temporal distributions of ozone concentrations, however, show large variability. Background ozone concentration at a given place and time results from a combination of formation, transport,

destruction and dry deposition and affected by elevation, too. Higher concentrations typically occur at sites located in the free troposphere (Figure 8.10).

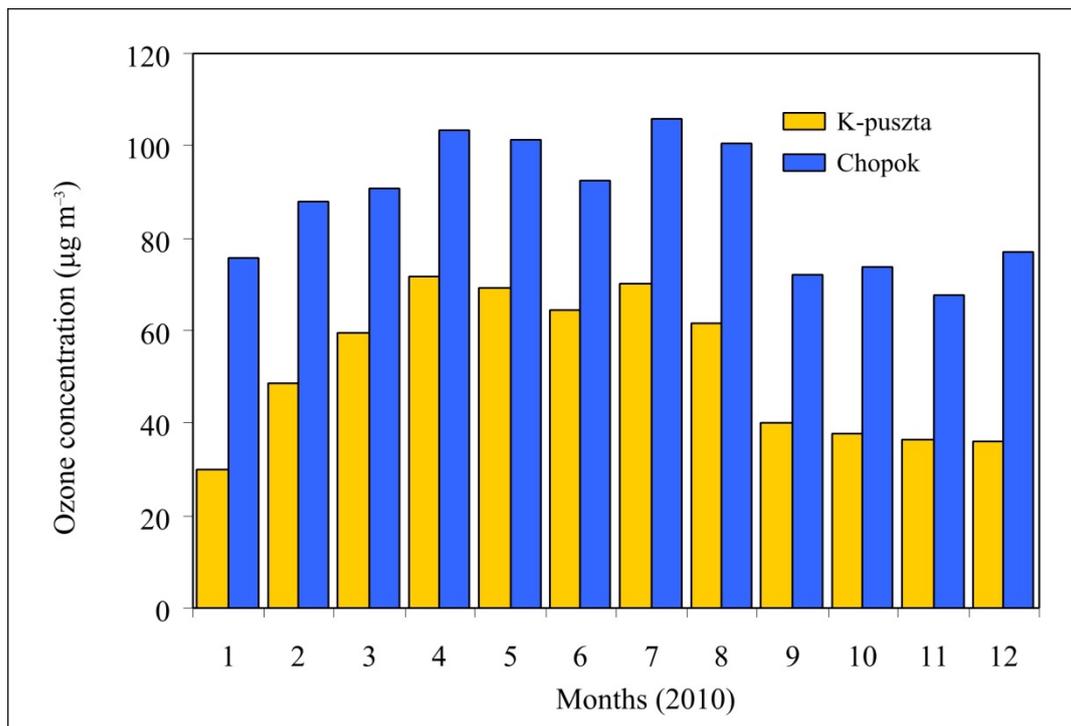


Figure 8.10: Average monthly ozone concentrations in 2010 at two EMEP (European Monitoring and Evaluation Programme) measuring station: K-puszta (Hungary, $\varphi = 46^{\circ}58'$, $\lambda = 19^{\circ}35'$, $h = 125$ m) and Chopok (Slovakia, $\varphi = 48^{\circ}56'$, $\lambda = 19^{\circ}35'$, $h = 2008$ m). Source of data: <http://www.nilu.no/projects/ccc/onlinedata/>

Seasonal cycle of tropospheric ozone is also well-defined in Figure 8.10. Higher values can be observable in summer period due to the more intense photochemical reactions.

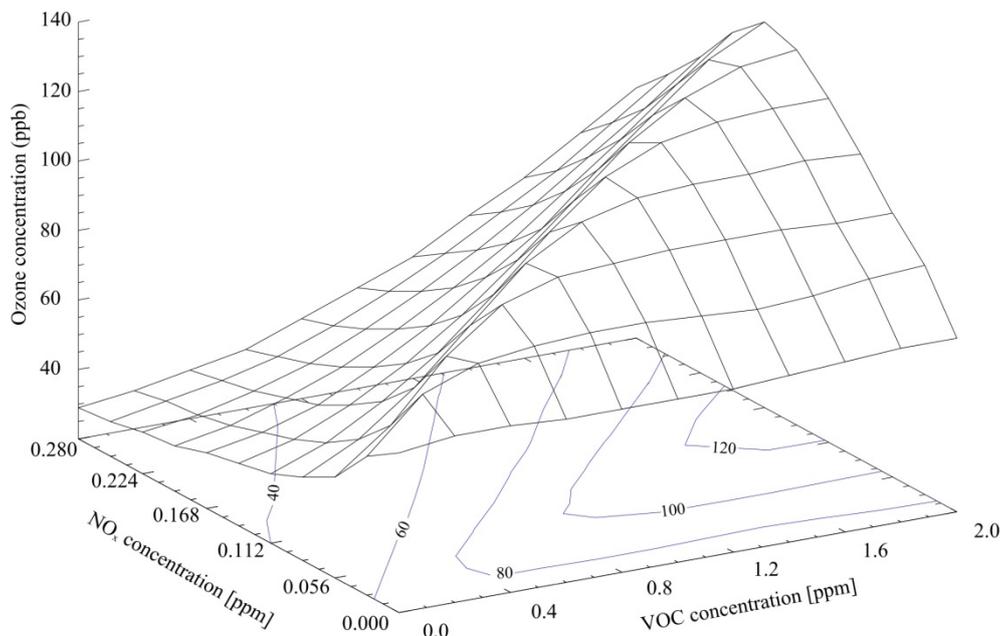


Figure 8.11: Modelled ozone concentration with different ratio of NO_x and VOC concentration

Near surface ozone is produced mainly in the urban environment due to the high emission of ozone precursor compounds. The ozone production depends on the rate of the precursors concentrations. Figure 8.11 shows a result

of a model simulation. The ozone concentrations were simulated by a simple box model in the function of NO_x and VOC concentrations. It seems that ozone concentration increasing with increase VOC concentration. Concentration of nitrogen compounds, however can affect both the ozone production and destruction. High NO emission in the city causes ozone destruction.

When the air mass from the city is transported to far away by the wind, higher ozone concentrations can be formed in rural NO-poor environment. Additionally biogenic emission of ozone precursors (e.g. isoprene emitted by trees) can cause further increase in ozone concentration. Hence, higher ozone concentrations most frequently occur in rural environment (Figure 8.12).

Surface ozone concentration has also a typical diurnal cycle. Highest values occur in the afternoon, when photochemical activity is more intense. The production during the day is also related to the daily course of precursor emissions. Typical diurnal cycle of the ozone concentration measured in an urban site is presented in Figure 8.13. This figure also shows a significant difference between a summer and a winter month. However, the daily variation of ozone concentration is similar in each period.

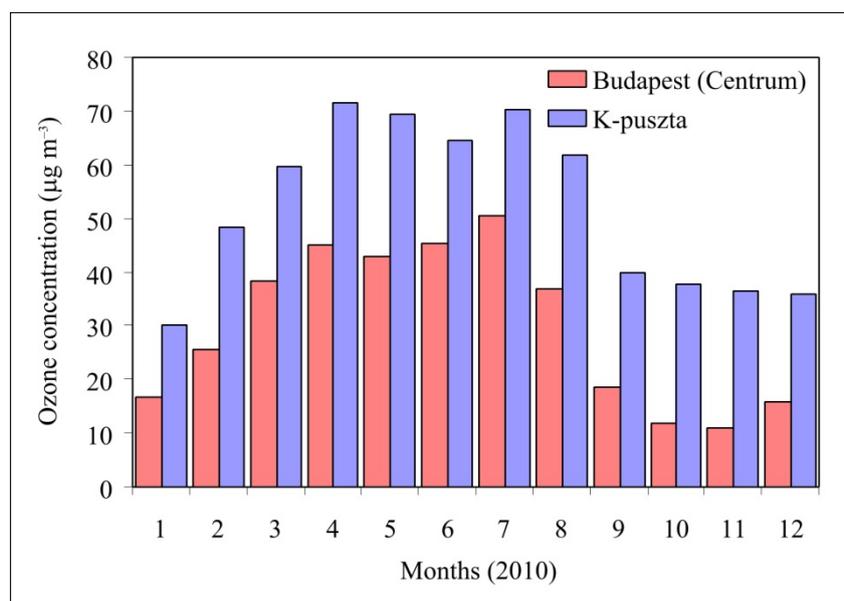


Figure 8.12: Average monthly ozone concentrations in 2010 in urban and rural environment. Data obtained from an urban measuring site of Hungarian Air Quality Monitoring System (Budapest centrum - Kosztolányi Dezső tér) and from a background measuring site of European Monitoring and Evaluation Programme (K-puszta) operated by Hungarian Meteorological Service. Sources of data: <http://www.nilu.no/projects/ccc/onlinedata/> and

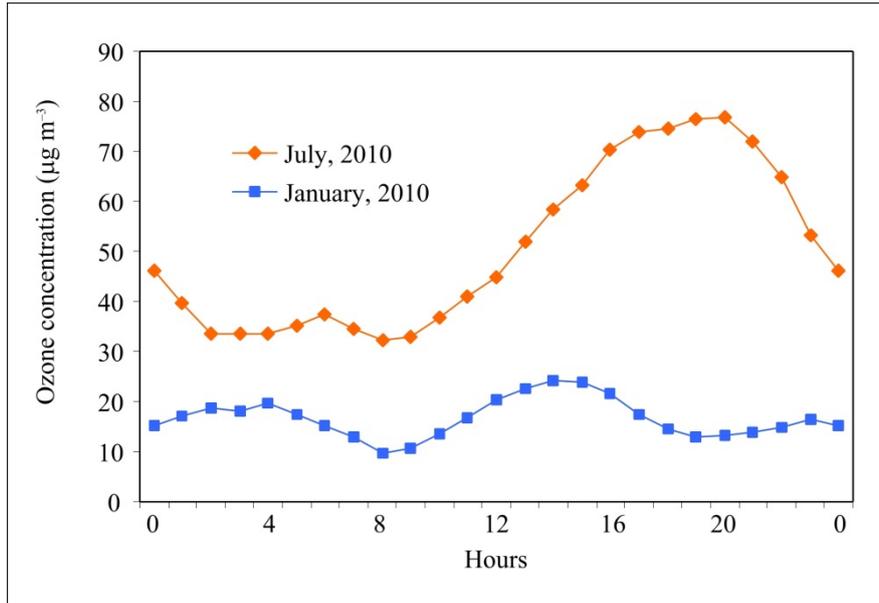


Figure 8.13: Average diurnal variation of ozone concentration in July and January, 2010. Data obtained from an urban measuring site of Hungarian Air Quality Monitoring System (Budapest centrum – Kosztolányi Dezső tér). Source of data:

Similar temporal variation can be found in background ozone concentration. The highest concentration values occur in spring and summer in the early afternoon hours, while the lowest ones in winter in the case of stable stratification (Figure 8.14).

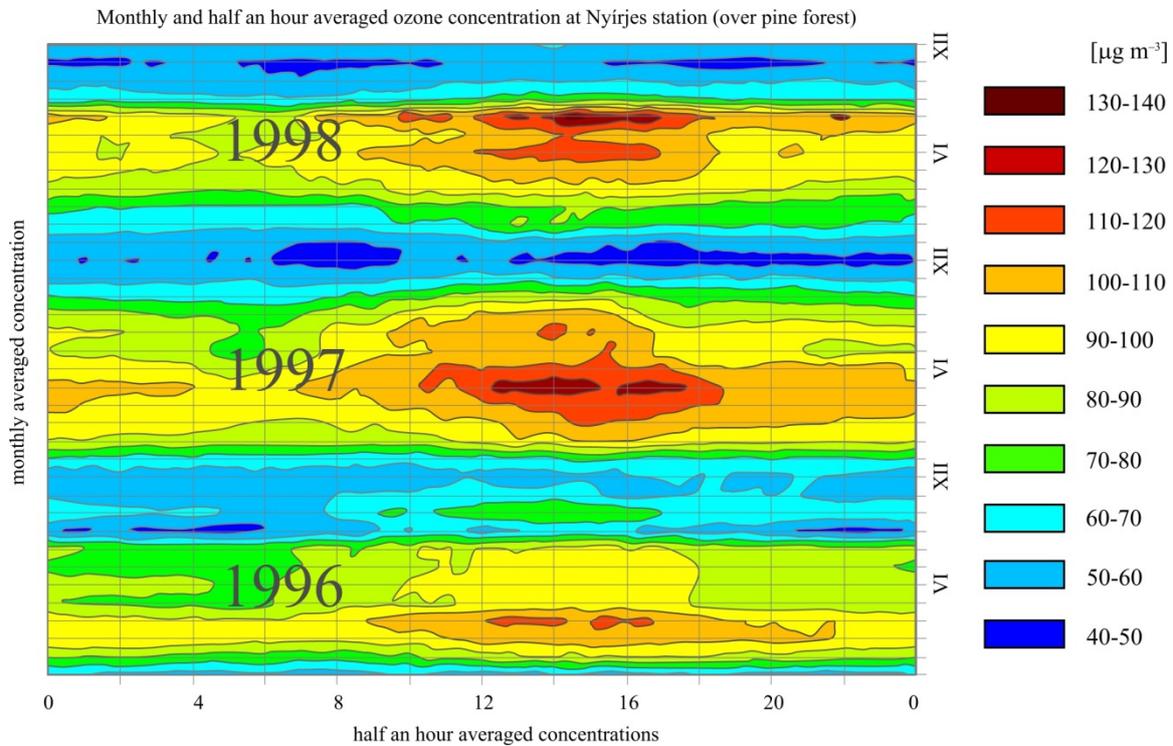


Figure 8.14: Temporal variability of background ozone concentration at Nyírjes station (Mátra Mountain) from 1996 to 1998.

References

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