



Daytime ozone loss term in the mesopause region

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Abstract. For the retrieval of atomic oxygen via ozone observations in the extended mesopause region under sunlight conditions, two assumptions are used: first, the photochemical equilibrium of ozone and, second, that the ozone losses are dominated by ozone's dissociation from solar UV radiation, silently ignoring the O₃ destruction by atomic hydrogen. We verify both by 3-D modeling. We found that ozone approaches photochemical equilibrium at 75–100 km for daytime conditions. Hence, the first assumption is valid. However, the reaction of ozone with atomic hydrogen was found to be an important loss process and should not be omitted in retrieving atomic oxygen.

Keywords. Atmospheric composition and structure (middle atmosphere – composition and chemistry)

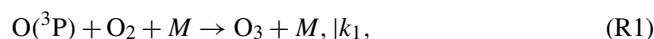
1 Introduction

Satellite measurements of atomic oxygen in the MLT (mesosphere–lower thermosphere) region are based on two major assumptions: (1) about the ozone's photochemical equilibrium and (2) about the solar UV dissociation as the main ozone loss at these levels. For several decades, these assumptions have been used to determine the distributions of atomic oxygen at specific heights of the MLT via satellite and rocket measurements of ozone and airglow emissions (e.g., Pendleton et al., 1983; Evans and Llewellyn, 1973; Evans et al., 1988; Thomas, 1990; Mlynchak et al., 2007, 2013a, b, 2014; Smith et al., 2010; Siskind et al., 2015). Kulikov et al. (2006, 2009) proposed algorithms for the simultaneous retrieval of O, H, HO₂ and H₂O by joint OH and

O₃ satellite measurements by implementing the assumption about the photochemical equilibrium of ozone. Mlynchak et al. (2013b) also used this assumption to derive exothermic chemical heat in the MLT region. Grygalashvyly et al. (2014) and Sonnemann et al. (2015) used these assumptions in their derivation of analytical solutions and in an analysis of OH* layer morphology.

The problems involved in the deviations from photochemical equilibrium that ozone experiences during the night were discussed in Kulikov et al. (2017). Under sunlight conditions, the photochemical lifetime of ozone is assumed to be ~2 min in this region due to photodissociation in the UV Hartley band. At almost all daytime zenith angles (except periods near terminators), the photochemical lifetime is much smaller than the characteristic transport times by advection and diffusion. Hence, the photochemical equilibrium of ozone holds in the mesopause during the daytime. However, ozone losses during the daytime are not so obvious.

The balance of photochemical ozone at these altitudes is determined by three primary reactions:



where k_1 and k_2 are corresponding reaction rates and J_{O_3} is the total dissociation rate of ozone, which is a sum of two branches, J_1 and J_2 , and M is air number density. The reaction rate of O₃ with O is several orders smaller than that of k_2 in the extended mesopause region; therefore, the reaction of ozone with atomic oxygen amounts to less than 10 % of the total ozone loss (Smith et al., 2008). Consequently, we can leave it out of the total ozone balance.

Under photochemical equilibrium of ozone (assuming it to be valid),

$$O_3 \cong \frac{k_1 \cdot O \cdot O_2 \cdot M}{J_{O_3} + k_2 H} \quad (R4)$$

Hence, for O retrieval by ozone observation via Reaction (R1), additional information about H is required. In Evans and Llewellyn (1973) and Thomas (1990), atomic hydrogen concentration is determined by OH* airglow emission, since Reaction (R3) is a primary source for excited hydroxyl. Kulikov et al. (2006, 2009) determines the values of O and H jointly as the result of an algebraic equations system that is solved under the conditions of the joint photochemical equilibrium of O₃, OH and HO₂.

Nevertheless, in the majority of investigations (e.g., Pendleton et al., 1983; Evans et al., 1988; Mlynczak et al., 2007, 2013a, b, 2014; Smith et al., 2010; Siskind et al., 2015), the second term in the denominator of Reaction (R1) is omitted (i.e., $O_3 = k_1 \cdot O \cdot O_2 \cdot M / J_{O_3}$) and only ozone observations are utilized to estimate atomic oxygen concentrations.

In this case, Reaction (R3) is supposed to be small relative to the dissociation of ozone: $k_2 \cdot H \cdot O_3 \ll J_{O_3} \cdot O_3$ (e.g., Smith and Marsh, 2005); this is, according to Pendleton et al. (1983), equivalent to $H \ll 5 \times 10^8 \text{ cm}^{-3}$. In these cases the uncertainty of atomic O density is assumed to be primarily the result of uncertainties regarding ozone measurements and reaction rates of Reaction (R1). For example, in the case of the SABER (Sounding of the Atmosphere using Broadband Emission Radiometry) instrument, such uncertainty amounts to 30 % (Mlynczak et al., 2013).

However, the concentration of H may exceed the value of 10^8 cm^{-3} in the mesopause. For example, according to SME (Solar Mesosphere Explorer) satellite observations, the maximum level of atomic hydrogen is $\sim 2\text{--}5 \times 10^8 \text{ cm}^{-3}$ at 80–93 km (Thomas, 1990). Thus, the error in O values due to omission of Reaction (R3) is comparable to or exceeds 30 % ($\frac{\delta O}{O} = \frac{k_2 \cdot H}{J_{O_3}}$). This is in agreement with previous theoretical works which show that at 80–90 km the losses of ozone due to Reaction (R3) are comparable (Moreels et al., 1977) or even exceed (Allen et al., 1984) ozone losses via photodissociation (Reaction R2). Thus, the problem of correct retrieval of atomic oxygen by ozone measurements is still unresolved and needs more detailed research with respect to seasonal and latitudinal variation.

In this work, we conducted a global investigation, based on the 3-D chemistry-transport model (CTM) of both assumptions: the photochemical equilibrium of ozone and the relative significance of different sources of ozone losses in the upper mesosphere–lower thermosphere region in the daytime. The paper is structured as follows: in the next section, the model is briefly described; Sect. 3 presents the results and discussion of our calculations, followed by concluding remarks in the last section.

2 Model and calculations

For our calculations, we used the global 3-D CTM of the middle atmosphere developed by the Leibniz Institute of Atmospheric Physics (IAP). The model was particularly designed to investigate the spatiotemporal structure of phenomena in the MLT region and, specifically, in the extended mesopause region. The model contains 3-D advective and vertical diffusive transport (turbulent and molecular). The grid-point model extends from the ground up to the lower thermosphere (0–150 km; 118 pressure-height levels). The horizontal resolution amounts to 5.625° latitudinally and 5.625° longitudinally. The chemistry module consists of 19 constituents, 49 chemical reactions, and 14 photodissociation reactions. The CTM has been described in numerous papers (e.g., Sonnemann et al., 1998; Körner and Sonnemann, 2001; Grygalashvyly et al., 2009, 2011, 2012). It was validated, particularly for ozone, in a number of papers with measurements (Hartogh et al., 2004, 2011; Sonnemann et al., 2006a, b, 2007). Three-dimensional fields of the temperature and winds are used from the Canadian Middle Atmosphere Model (CMAM) for the year 2000 (de Grandpre et al., 2000; Scinocca et al., 2008).

We calculated the annual variation of the spatiotemporal distributions of the relative deviation ($O_3 / O_{3\text{eq}} - 1$), where O_3 is the ozone value calculated by the model and $O_{3\text{eq}}$ is the value of ozone concentration in photochemical equilibrium from Reaction (R1). We also calculated the ratio of ozone losses in Reactions (R2) and (R3). In order to remove transition regions that correspond to sunset and sunrise, we take into account the local time when the solar zenith angle $\chi < 80^\circ$. Previous research, based on satellite measurements, most often shows the results at pressure heights, or “pseudo altitudes”. Following these, in the present paper we represent our results at pressure heights $z^* = -H \ln(p/p_0)$, where $H = 7 \text{ km}$ is the scale height, p is the pressure and $p_0 = 1013 \text{ hPa}$ is the pressure at the surface.

3 Results and discussion

Figure 1 shows monthly mean height–latitude cross sections of the relative deviation ($O_3 / O_{3\text{eq}} - 1$) for each month averaged over daytime hours. Through the entire year, ozone stays in photochemical equilibrium above $\sim 90 \text{ km}$ with the relative deviation of less than 1 %. Deviations of ozone from photochemical equilibrium in the extended mesopause region occur with a maximum of 3–4 % at 80–85 km. The height of this area has an annual variation, with a maximum deviation in the winter hemisphere and smooth transitions from one hemisphere to another during spring and autumn. Generally, through the entire region comprising 75–100 km, one can assume that ozone stays in photochemical equilibrium and the deviation does not exceed 3–4 % under daytime conditions.

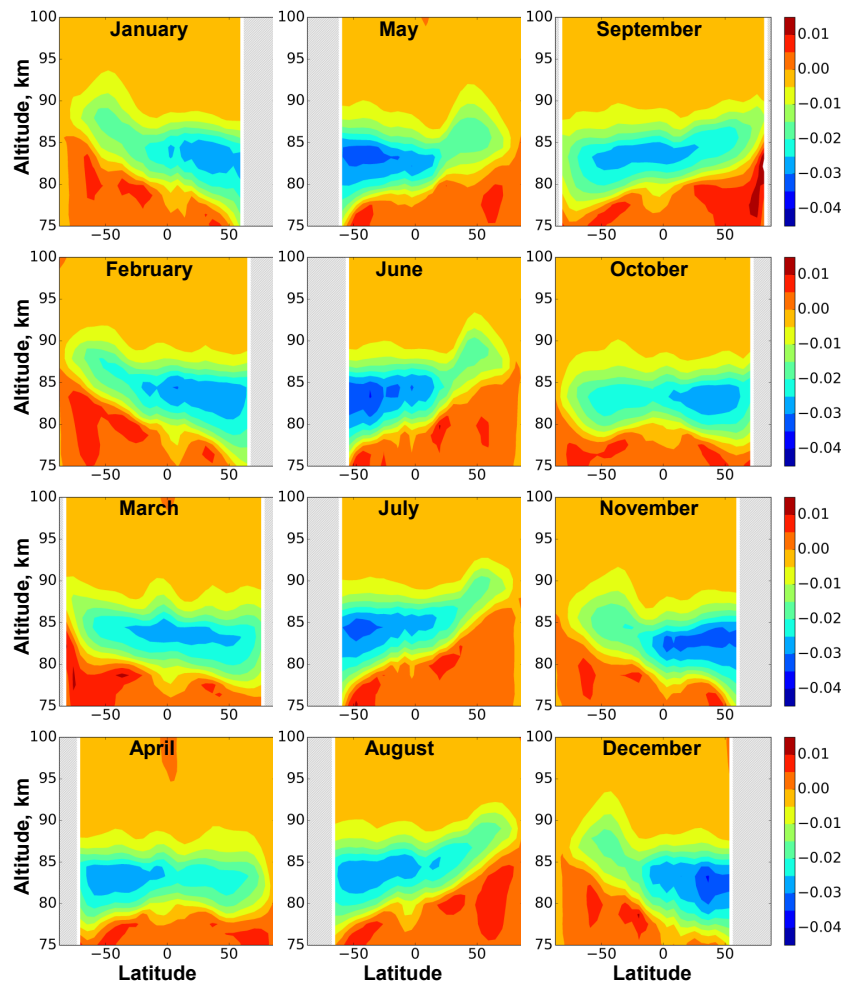


Figure 1. Daytime mean monthly averaged $O_3 / O_{3eq} - 1$.

Figure 2 shows daytime mean monthly averaged height–latitude cross sections for the ratio of Reactions (R2) and (R3), i.e., $R = k_2 \cdot H / J_{O_3}$. The black solid line and dashed line designate areas where this ratio equals 0.1 and 0.3, respectively, i.e., where the loss of ozone due to reactions with atomic hydrogen amounts to 10 and 30 % of the dissociation loss of ozone, respectively. Evidently, the area where $R > 0.1$ is essential for all seasons and composes more than half of the total area between 75 and 100 km. The maxima of the ratio are placed at 85–90 km in equatorial and low latitudes and amount to 0.2–0.7, depending on the season. The ratio is greatest in January–February and in June–July because the level of net dissociation is reduced near the solstices. The lowest values of the ratio appear in April and October, where the daily net incoming solar radiation is maximized and tides in the equatorial mesopause produce high values of atomic hydrogen. One can see that Reaction (R3) composes the essential branch of ozone losses and should not be omitted for daytime conditions at all latitudes throughout the entire year.

Figure 3 shows daytime averaged annual mean height–latitude cross sections for the ratio R . Comparison of this figure with the SABER results demonstrates how the uncertainty due to omitting Reaction (R3) may modify the observed values. For example, according to SABER (Fig. 5 in Mlynarczyk et al., 2013), atomic oxygen concentration below ~ 92 km has an almost uniform meridional distribution. But taking Reaction (R3) into account, one can see that the maximum of O concentration should exist at 84–92 km for low and equatorial latitudes. This may result in corrections to the reported levels of exothermic chemical heat, which are calculated through the retrieval of atomic oxygen (Mlynarczyk et al., 2007), as well as in higher values for the night-to-day ratio and diurnal variation of atomic oxygen (Fig. 5, Smith et al., 2010). More detailed analysis is needed for each particular measurement and is beyond the scope of this work.

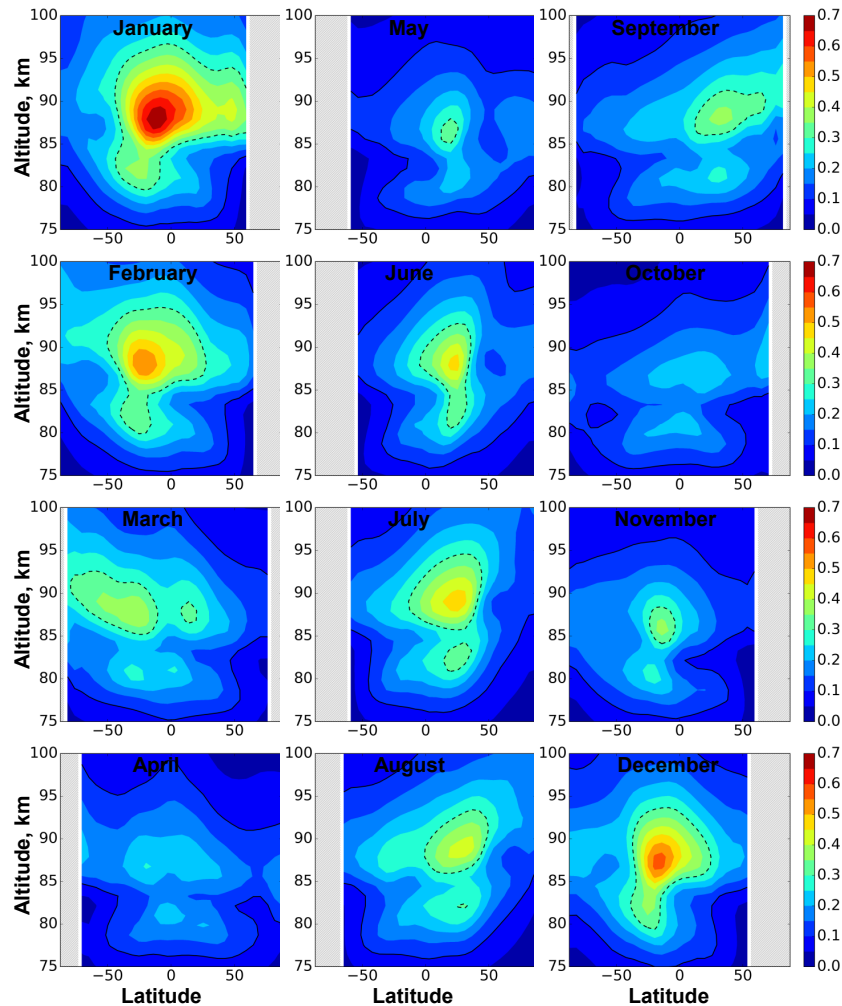


Figure 2. Daytime mean monthly averaged R .

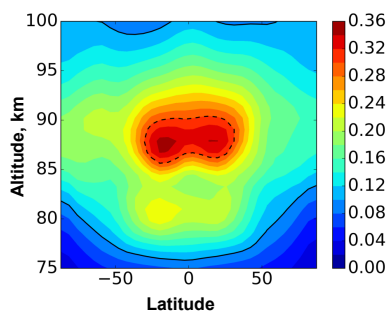


Figure 3. Daytime mean annually averaged R .

4 Conclusions

By 3-D modeling, we prove that ozone almost always stays in photochemical equilibrium in the extended mesopause region during daytime hours.

The results discussed in Sect. 3 allow us to draw the following conclusions on the relative significance of ozone losses and the atomic oxygen concentration uncertainty due to omitting Reaction (R3):

1. In most of the 75–100 km region, the uncertainty due to omitting Reaction (R3), $\delta O/O$, exceeds 10%; hence, it should not be ignored.
2. Areas where $\delta O/O$ is comparable to or higher than the uncertainty of ozone measurements and the rate of Reaction (R1) ($\sim 20\%$) exist throughout the entire year.
3. $\delta O/O$ amounts to 50–70% at maxima.

Hence, the reaction of ozone with atomic hydrogen is found to be an important loss process and should not be omitted.

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(Nizhny Novgorod, Russia) and inquiries about calculated distributions used for this paper can be addressed to Mikhail V. Belikovich (belikovich@ipfran.ru).

Competing interests. The authors declare that they have no conflict of interest.

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