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New Directions: A Chemical Tropopause Defined[☆]

Tropospheric ozone (O_3) has two main sources, namely import from the ozone-rich stratosphere and in-situ photochemical production involving precursors, being mainly nitrogen oxides ($NO_x = NO + NO_2$), carbon monoxide (CO), and hydrocarbons (HC). How these two sources partition, on local as well as global scales, and how they vary in time are important and hotly debated issues. An intrinsic problem is that the net tropospheric ozone production is the smallest difference ($\sim 10\%$) between the two very large fluxes of ozone production and destruction. The understanding and modeling of the tropospheric ozone production and loss terms is a major challenge for atmospheric chemists. Concerning the other source, i.e. import of ozone rich air from the stratosphere, there also are considerable challenges, although these are more of a dynamical nature.

The analysis of the relationship between CO and ozone variations constitutes a powerful tool to quantify the net photochemical ozone production in the troposphere in relation to the influx of stratospheric ozone. Here, we revisit this tool in the upper troposphere/lower stratosphere (UT/LS) in light of recently acquired passenger aircraft data, and show how it can be used to define a chemical tropopause.

Photochemistry preferentially results in positive O_3 –CO correlations, because CO acts as proxy for other pollutants or ozone precursors (notably NO_x), respectively, i.e., the more CO an air mass contains the more ozone can be produced. However, as reviewed in a previous New Directions column (Parrish et al., *Atmospheric Environment* 33, 5147–5149, 1999), especially during winter, nighttime chemistry can cause extended net losses of NO_x , in particular via its conversion to N_2O_5 and HNO_3 and subsequent irreversible removal by heterogeneous reaction with aerosols. This additional loss of NO_x may shift the ratio between O_3 production and loss to a net O_3 loss. Consequently, negative O_3 –CO correlations can appear.

In the UT, where these heterogeneous reactions are less relevant in this respect, negative O_3 –CO correlations

are almost only ever encountered in air masses influenced by or originating from the LS (Zahn et al., *Journal of Geophysical Research*, Vol. 107(17), 2002). These negative, often compact, correlations, are not formed by chemistry within the probed air masses, but are caused by transport, namely mixing among tropospheric and stratospheric air. LS air is rich in ozone and poor in CO (typically 10–20 ppbv, with methane oxidation being the only significant in-situ source). In contrast, tropospheric air is poor in ozone and rich in CO (with a fairly wide range of typically 50–300 ppbv due to the presence of major CO sources). Whilst the transport time scales around the extra-tropical tropopause (in the order of weeks) fall short of the chemical lifetime (τ) of ozone (τ =months) and of CO ($\tau \approx 2$ –5 months), the O_3 –CO relationship is primarily controlled by transport (and not by local chemistry). This has been confirmed using comparisons with long-lived transport tracers such as CH_4 or N_2O . So, when UT air and LS air mix at the tropopause, negative O_3 –CO correlation appear.

In a nutshell, the O_3 –CO relationship can be applied:

- in the UT over regional distances (< 500 km), to infer the partitioning between ozone produced photochemically in the troposphere—mostly yielding a positive correlation with CO, and ozone imported from the LS—giving a negative correlation with CO (see Zahn et al., 2002); and
- in the LS to learn about the mixing of tropospheric air, and about the physical processes (their time scales, seasonal and spatial distributions, etc.) that intermingle UT air with LS air.

These contrasting conditions in UT air and LS air often cause a marked change in the observed O_3 –CO relationship at the extra-tropical tropopause. Observations made by the CARIBIC project (Civil Aircraft for the Regular Investigation of the atmosphere Based on an Instrument Container) have revealed that the transition from a non, or a weak, O_3 –CO correlation in UT air, to a compact negative O_3 –CO in LS air, was often sufficiently abrupt to define a chemical tropopause (Fig. 1).

The CARIBIC O_3 –CO correlations recorded over nearly 5 years along three flight routes (Germany

[☆] Something to say? Comments on this article, or suggestions for other topics, are welcome. Please see <http://www.uea.ac.uk/~e044/apex/newdir2.html> for further details or contact newdirections@uea.ac.uk.

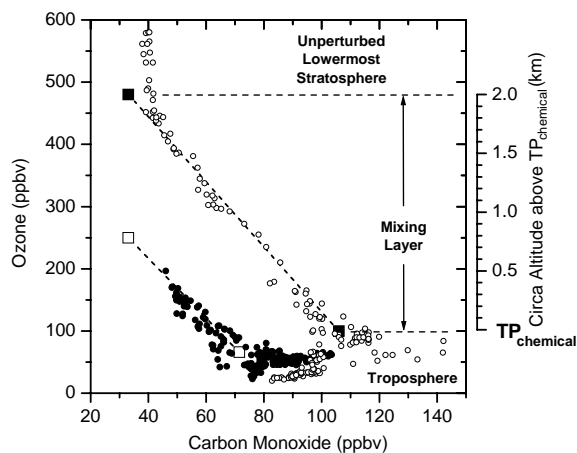


Fig. 1. O_3 -CO correlation around the tropopause observed over the North Atlantic on 14 May 2001 (open circles) and over Central Europe on 5 November 2000 (filled circles). The sloping lines are mixing lines between tropospheric and stratospheric air with the squares denoting the end members. The transition from tropospheric air to the compact mixing line is defined as the chemical tropopause. For the May flight, the mixing layer, that is the area embraced between the end members of the mixing line, is marked and the corresponding approximate altitude above the chemical tropopause is shown (right-hand y-axis). For the November flight, the chemical tropopause was found at lower ozone values, and the ozone concentrations within the mixing layer were also lower, although the mixing layer had again a vertical extent of about 2 km (not shown).

to southern India, to southern Africa, and to the Caribbean) at 9–12 km altitude north of 30°N, allow some new insights into the budget of ozone in the UT/LS.

Firstly the ozone mixing ratio undergoes a well-defined seasonal variation at the chemical tropopause, most clearly between 35° and 45°N over less polluted regions, such that:

$$O_3^{\text{tropopause}} = 97 + 26 \sin[2\pi(\text{Day of Year} - 30)/365] \quad (\text{in ppbv})$$

The maximum is in April/May, the minimum in October/November (see Fig. 1). This is due primarily to in-phase seasonal variation of downward ozone transport from the stratosphere.

Secondly we see that mixing between UT and LS air occurs primarily in a layer above the chemical tropopause, with a year-around vertical extent to this layer of about 2 km (Fig. 1), in agreement with the observations of Fischer and co-workers in Geophysical Research Letters (Vol. 27, 97–100, 2000).

Finally, it is clear that the origin of ozone in the UT changes markedly with season. In summer, photochemical production rules, whereas in winter, import of ozone from the stratosphere takes precedence. The well-known springtime ozone maximum is also observed in the CARIBIC measurements. Here the influx of stratospheric ozone and photochemical ozone production contribute equally to the observed maximum (see Zahn et al., 2002).

The CARIBIC data have helped us to further refine our understanding of the UT/LS ozone budget. The fact that civil aircraft happen to cruise optimally in a most interesting, relatively little explored, and always changing part of the atmosphere, has allowed us to explore some new directions. Although CARIBIC is pausing at the moment, an even more powerful instrument container is being constructed for deployment on a Lufthansa Airbus A340-600, starting in September 2003.

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