

## **Introduction**

Ozone gas has absorption bands in both the solar (shortwave) and terrestrial (longwave) radiation bands. In general, the solar absorption bands (UV) are saturated such that all of the downwelling solar radiation is absorbed in the atmosphere and none penetrates to the Earth's surface. One might therefore think that changes in ozone concentration would have no shortwave effect on climate since there is no change in the amount of solar radiation absorbed in the atmosphere provided the ozone absorption bands remain saturated. In contrast, the ozone longwave radiation bands are unsaturated such that a portion of the terrestrial radiation in this band does escape to space. One might therefore expect that ozone primarily affects climate as a greenhouse gas, similar to carbon dioxide's effect on climate.

Column integrated ozone concentrations have decreased since pre-industrial times. Yet, the net radiative forcing of ozone is positive, implying a warming affect on climate. This clearly violates the aforementioned intuition that ozone acts primarily as a greenhouse gas for which the radiative forcing should be of the same sign as the concentration change. We explore this apparent logical discrepancy here.

## **Changes in Ozone Concentrations Since the Pre-industrial**

Anthropogenic emissions have caused a decrease in stratospheric ozone and an increase in tropospheric ozone relative to the pre-industrial atmosphere. The observed global decrease in stratospheric ozone concentrations between 1980 and 2000 were approximately 4% of the total column ozone (WMO 2003), corresponding to decrease of 12.2 Dobson Units (DU). This global change is non-spatially uniform and essentially reflects very large (40-50%, WMO 2003) decreases in the Antarctic column integrated ozone during the spring, smaller but substantial decreases in the Arctic region (Newman et al. 1997), and virtually no long term trend in the tropics (WMO 2003). The global ozone trend since pre-industrial times primarily reflects large changes in the 1980's and early 1990's with an apparent recovery since 1995 (Newman et al. 2006), although the statistical significance of the upward trend as well as its physical attribution is ambiguous (IPCC 2007). The large decreases in polar stratospheric ozone during the 1980's and early 1990's has been largely attributed to anthropogenic emissions of Montreal Protocol

gases (Ramaswamy et al. 2001) which lead to catalytic ozone destruction (Molina and Rowland, 1974). Consistent with this attribution mechanism for stratospheric ozone loss, an ensemble of chemical transport models forced with Montreal Protocol gases simulate a stratospheric ozone decrease of 14-28 DU (Gauss et al. 2006). Thus, it is widely accepted that anthropogenic activities have led to decreased stratospheric ozone concentrations.

Tropospheric ozone has a lifetime of order one week; it is not well mixed in the atmosphere. Therefore, the assessment of global tropospheric ozone requires an extensive observation network of ozonsondes (Oltmans et al. 2006). Observations of tropospheric ozone are too scarce, both spatially and temporally, to determine the anthropogenic contribution to concentrations changes, especially in regards to changes extending back to pre-industrial times. Despite the lack of adequate observations, it is widely accepted that anthropogenic fossil fuel combustion and the associated increase in ozone precursor species ( $\text{NO}_x$  and hydrocarbons) has led to a substantial increase in tropospheric ozone concentrations since pre-industrial times (Haagen-Smit 1952). Surface ozone observations also suggest that lower atmosphere ozone concentrations increased substantially during the 20<sup>th</sup> century (Bojkov 1986). In order to assess the anthropogenic contribution to tropospheric ozone changes in their calculations of radiative forcing, the IPCC assessments have relied on chemical transport models forced with emissions of ozone precursors. Unfortunately, the IPCC does not assess the global change in tropospheric ozone concentrations, despite giving the radiative forcing value a medium level of scientific understanding. Chemical transport models calculate a tropospheric ozone concentration enhancement of between 7.9 and 13.8 DU relative to pre-industrial times (Gauss et al. 2006). Though the emissions of ozone precursor species are limited to the surface, models suggest that tropospheric ozone has increased at all levels extending up to the tropopause (Bernsten et al. 1997).

Column total ozone concentrations can be measured from land by use of a Total Ozone Mapping Spectrometer or from space with a Solar Backscatter Ultraviolet instrument. Both techniques give comparable results and indicate a total ozone column decrease of order 9 DU from 1964-2003 (WMO 2003). This result corresponds well with the separate stratosphere and troposphere estimates given above, although the different

time periods of each trend estimate coupled with the presumption that the stratospheric changes all occurred over a small time period in the late twentieth century while the tropospheric changes were most likely spread more uniformly over the century and a half since the pre-industrial (maybe biased towards the early twentieth century when emissions were “dirtier”) confuses the matter. It seems fairly well established that stratospheric ozone decrease since the pre-industrial have been substantially larger magnitude than tropospheric ozone increases over the same time period although this is not stated explicitly in any of the assessment reports.

### **Radiative Properties of Ozone**

Ozone has absorption bands in both the solar (shortwave) and terrestrial (longwave) radiative bands. The strongest absorption band is the Hartley band which is centered at 255 nanometers, corresponding to electronic transitions of ozone (Liou 2002), and is responsible for shielding the Earth’s surface from UVB and UVC radiation. While this absorption band is critical to life on Earth which would otherwise be damaged by harmful UV radiation (Wallace and Hobbs 2006), it is generally thought to have very little climate impact because these absorption bands are completely saturated in the Earth’s atmosphere in the sense that all solar radiation within this band is absorbed within the atmosphere (predominantly in the stratosphere and mesosphere). We will reexamine this assumption in the next Section. There is also a weak shortwave absorption band between 300 and 360 nanometers which has minimal climate effects. Because ozone is a tri-atomic molecule with a structure similar to water vapor, it has three radiatively active vibrational bands which fall at 9, 9.6, and 14.4 micrometers (Petty 2006). The 14.4 micrometer band coincides with the strong absorption band of carbon dioxide and therefore has very little climate impact. On the other hand, the 9 and 9.6 micrometer bands fall in the atmospheric window, where the Earth’s atmosphere is otherwise transparent to outgoing radiation and the Plank function corresponding to the Earth’s surface temperature is near its maximum; these absorption bands have a large climatic impact.

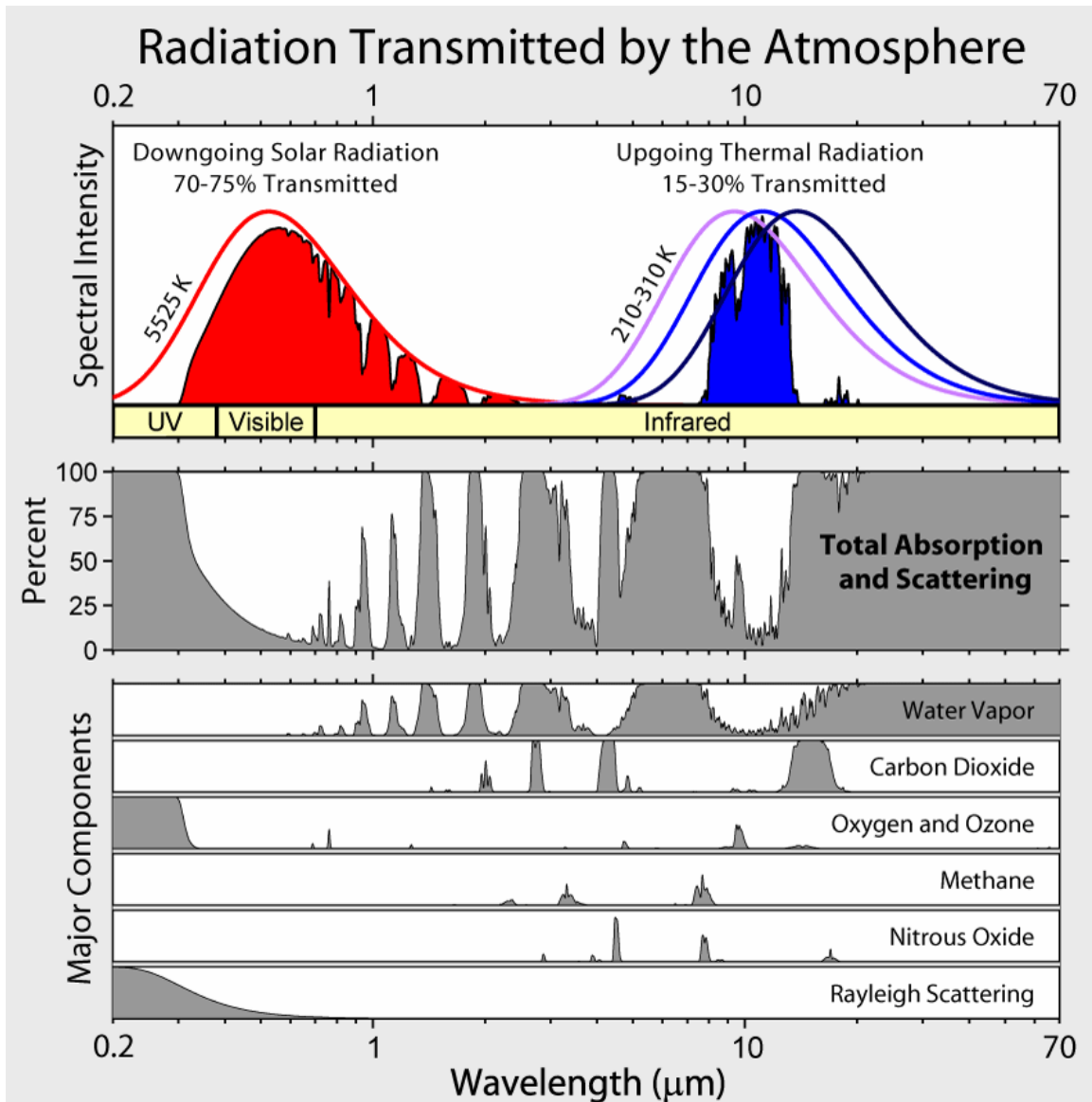


Figure 1. Incoming radiation to the Earth's surface and outgoing radiation at the top of the atmosphere (shaded red and blue curves respectively) coplotted with the Sun and Earth's blackbody radiation curve (red and blue lines). The Sun's blackbody curve has been rescaled by a geometric factor ( $R_E^2/4 \cdot R_{SE}^2$ ) so that it represents the solar flux arriving at the top of the Earth's atmosphere. The lower panels show the absorption bands of the radiatively active species in the Earth's atmosphere. (Source: Wikimedia commons)

### Radiative Forcing Definition

Given the concentration changes (relative to the pre-industrial) of ozone in the troposphere and stratosphere and the radiative properties of ozone, what would we expect

the net radiative forcing of ozone to be? Before answering this question, we have to look at the definition of radiative forcing, and the physical basis for this definition.

IPCC defines radiative forcing as the net (shortwave down minus longwave up) radiative flux at the tropopause due to change of concentration of an atmospheric constituent after the stratosphere temperatures have adjusted to the composition change, with the tropospheric temperatures held constant (IPCC 2007). The rationale for this definition is that the stratospheric temperatures adjust to a radiative imbalance on a time scale of several months as opposed to several decades for the troposphere (Hansen et al. 1985). More explicitly, this definition of radiative forcing relies on the assumption that the stratosphere is in radiative equilibrium whereas the troposphere is in radiative convective equilibrium. Therefore, after an atmospheric composition change, the stratospheric temperatures must adjust so that there is zero net radiative flux convergence and the net radiative flux is vertically invariant in the stratosphere. In other words, once the stratospheric temperatures have adjusted, the radiative flux at the tropopause is identical to the radiative flux at the top of the atmosphere and represents the change in energy leaving the system due to the composition change.

The thermodynamic balance in the troposphere is very different as the atmosphere is continually cooled by radiation whereas the surface is radiatively warmed. Thermodynamic equilibrium is maintained by a combination of latent and sensible heat fluxes from the surface to the atmosphere with the latent heat fluxes providing the lion share of the requisite atmospheric heating. The implicit assumption that makes radiative forcing a useful concept is that the entire troposphere (and the surface heat fluxes) will adjust as a unit to maintain radiative-convective equilibrium *with a fixed lapse rate*, regardless of the vertical heating profile changes induced by the composition change. In other words, any radiative heating changes within the troposphere leads to uniform tropospheric heating. Although this definition of radiative forcing has a well justified physical basis, it removes a lot of intuition from radiative transfer calculations because there is no a priori reason that the instantaneous forcing (disallowing the stratospheric temperatures to adjust) and the adjusted forcing even need to be the same sign (Fu, Qiang. Personal communication, 03 March 2009) and the adjusted temperature profiles are often complicated functions of the vertical radiative heating profiles.

The IPCC gives separate estimates of for tropospheric and stratospheric ozone radiative forcing. The stratospheric ozone radiative forcing is assessed to be  $-0.05 \pm 0.1 \text{ W/m}^2$  which is a substantial modification from the third assessment reports central value of  $-0.15 \text{ W/m}^2$ ; even the sign of stratospheric ozone radiative forcing is ambiguous in the most recent assessment. Tropospheric ozone radiative forcing is assessed to be between  $+0.25$  and  $+0.65 \text{ W/m}^2$  with a central value of  $0.35 \text{ W/m}^2$ , unchanged from the third assessment report (IPCC 2007). Given the tropospheric and stratospheric ozone changes discussed in the first section, this result implies that ozone radiative forcing is a strong function of its vertical location. Most notably, while the column average ozone has decreased since pre-industrial times, the net radiative forcing is assessed to be significantly positive; this sign difference is counter-intuitive to our understanding of ozone as a greenhouse gas and this result has surprised some experts in radiative transfer (Gauss et al. 2006). We will try to understand the physical mechanism underlying this result in the remainder of this work.

### **Shortwave Radiative Forcing**

At first thought, the fact that a negligible fraction of the ultraviolet solar radiation in ozone's Hartley bands reaches the Earth's surface might imply that the band is saturated and changes in ozone would have no climate effect at these wavelengths. This logic is flawed, however, because the definition of radiative forcing does not treat the atmosphere as a whole as a closed system, but rather considers the atmosphere below the tropopause a closed system. In other words (from the radiative forcing perspective), radiation that is absorbed in the troposphere adds energy to the lower atmosphere as a collective unit where as radiation absorbed in the stratosphere is dynamically decoupled from the lower atmosphere and the Earth's surface<sup>1</sup>. Therefore, if a decrease in ozone concentration in the stratosphere causes more intense solar radiation to penetrate through the tropopause and be absorbed in the troposphere, this will act to heat the surface of the Earth even if there is a negligible change in radiative flux there.

Atmospheric heating by ozone shortwave absorption in the stratosphere is an order of magnitude larger an effect than any other radiative absorption process in the

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<sup>1</sup> The stratosphere is not radiatively decoupled from the troposphere in the sense the radiative absorption in the stratosphere will lead to temperature adjustments that, in turn, modify the radiative forcing at the tropopause. This process is briefly discussed in the penultimate section.

atmosphere and is responsible for the thermal structure of the stratosphere (McFarlane 2008). But how much of this heating penetrates into the troposphere? While the heating at tropopause level is reduced by over a factor of ten relative to the heating in the stratosphere, it still achieves a value of order .05 C/day (Petty 2006) which roughly translates to 5 W/m<sup>2</sup>. Linearizing the roughly 5% decrease in stratospheric ozone since the pre-industrial onto this climatology would suggest an approximately .25 W/m<sup>2</sup> warming due to stratospheric ozone loss; this back of the envelope result is roughly consistent with the ensemble mean values of +.18 W/m<sup>2</sup> (Gauss et al. 2006) and +.15 W/m<sup>2</sup> (Forster and Shine 1997) in a series of radiative transfer models forced with estimated ozone changes which presented results for shortwave and longwave radiative forcing (in each the stratosphere and troposphere) due to ozone changes separately. In contrast, there is little to no change in shortwave tropospheric radiative forcing due to ozone changes because the Hartley bands are saturated (in the climatology and all perturbation experiments that were considered in the studies) and all the solar radiation has been absorbed by the time it reaches the Earth's surface. Thus, column averaged shortwave radiative forcing due to ozone changes since the pre-industrial are positive, reflecting the stratospheric depletion only, and have comparable magnitude to the net (shortwave plus longwave) ozone radiative forcing given by the IPCC.

### **Longwave ozone radiative forcing**

From the perspective of radiative forcing at the tropopause due to a tropospheric composition change, a positive greenhouse effect can be understood as causing the effective emission temperature to decrease relative to the Earth's surface; if the upwelling radiation through the tropopause decreases relative to the radiation emitted by the Earth's surface, the system will gain energy and warm uniformly (spatially). Using Kirchoff's law and assuming the components behave as black bodies, it can be shown that the greenhouse effect will scale not only with the magnitude of the absorption but also as the difference of the temperature where the radiation is absorbed to the fourth and the surface temperature to the fourth. In other words, if the tropospheric temperature structure was isothermal, the greenhouse effect (within the troposphere) would disappear and if the lapse rate changed signs so would the greenhouse effect. These thought experiments are

largely irrelevant to the real atmosphere since the thermal structure of the troposphere is essentially determined by relaxation to a convectively neutral state and this is assumed to be fixed, *a priori*, when performing radiative transfer calculations. Nonetheless, this logic implies that radiative forcing is most sensitive to greenhouse gas changes in the vicinity of the tropopause, where the atmospheric temperature minimum occurs. These expectations are born out in radiative transfer calculations where it is found that radiative forcing is most sensitive to ozone concentration changes at the tropopause level (Wang et al. 1980) and changes at this level are an order of magnitude more effective at climate forcing than changes in the boundary layer (Lacis et al. 1990). This logic also implies that longwave radiative forcing is potentially most effective at low latitudes, where the thermal contrast between the surface and the tropopause is largest (Wallace and Hobbs 2006).

For greenhouse gas composition changes in the stratosphere, the instantaneous radiative forcing is most sensitive to absorption where the stratosphere is warmest; since composition changes in the stratosphere affect radiative forcing via altering downwelling longwave radiation, adding greenhouse gases in warm regions will lead to the largest changes in downwelling radiation per unit change in absorption<sup>2</sup>. However, we would expect ozone to be a less efficient absorber in the middle stratosphere due to both the opacity of the atmosphere in the Chappius band (much of the surface emissions in this band are absorbed in the lower atmosphere) and the lack of pressure broadening of the absorption bands (Ramanathan et al. 1976). In general, these latter two effects are stronger than the temperature effect and ozone is relatively ineffective greenhouse gas in the upper stratosphere, as compared to its effectiveness at the tropopause level (Gauss et al. 2006). Furthermore, the instantaneous longwave forcing expectations have little bearing on the final radiative forcing solution since the stratospheric temperature adjustment exerts a more profound effect on longwave forcing in the stratosphere (Hansen et al. 1997) than the instantaneous changes.

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<sup>2</sup> Qiang and I disagree on this point. I don't think either of us is confident in our reasoning though the logic presented here makes sense to me. If I were to make a bet on this, I might side with him.

In summary, ozone longwave radiative is most sensitive to composition changes at the tropopause. Changes above that level are complicated by several competing effects including adjustment processes that will be discussed in the next section.

### **The role of stratospheric adjustment in radiative forcing**

Stratospheric ozone depletion leads to an (positive) instantaneous shortwave radiative forcing that is larger in magnitude than the (negative) instantaneous longwave radiative forcing (McFarlane 2008 and Forster and Shine 1997). Therefore, the instantaneous radiative forcing due to stratospheric ozone depletion is positive and differs in sign from IPCC's assessment of stratospheric ozone radiative forcing. To reconcile this apparent discrepancy, we must understand the role of stratospheric temperature adjustment.

In the stratosphere, ozone acts to heat the local atmosphere through both absorption of solar radiation (of order 2 K/day) and through absorption of terrestrial radiation (of order 0.2 K/day, Petty 2006). Therefore, stratospheric ozone depletion will lead to local cooling (stratospheric temperature adjustment), eventually decreasing the outgoing longwave radiation from the column and bringing the system back into radiative equilibrium. The cooler stratosphere will emit less down-welling longwave radiation, resulting in a diminished long wave radiative flux at the tropopause and a negative radiative forcing due to the adjustment process. The temperature adjustment has no effect on the shortwave radiative forcing. Thus, the radiative forcing due to stratospheric ozone composition changes alone (instantaneous forcing) leads to tropospheric warming, but the stratospheric temperature adjustment process works to cool the troposphere; there is no physical mechanism constraining the forcing due to adjustment to be smaller than instantaneous forcing. Thus, the adjusted forcing (the sum of the instantaneous forcing and forcing due to the stratospheric temperature adjustment) is not constrained in sign, and an ensemble of radiative transfer calculations disagree on the sign of the adjusted forcing due to stratospheric ozone changes (Gauss et al. 2006).

Radiative transfer models suggest that above 70 hPa, the instantaneous radiative forcing is larger than the forcing due to stratospheric temperature adjustment (Hansen et al. 1997) and the radiative forcing due to ozone depletion is positive, reflecting the role of

shortwave processes. Other model studies put this division line between positive and negative radiative forcing at 30 km elevation (Lacis et al. 1990).

The separation of ozone radiative forcing into longwave and shortwave components is not completely possible due to interaction of the different absorption bands through stratospheric temperature adjustment. In the stratosphere, the adjustment process has a radiative effect comparable in magnitude to the forcing due to composition changes alone.

## **Conclusions**

Anthropogenic activities have led to a depletion of stratospheric ozone and enhancement of tropospheric ozone, with a net decrease in column integrated ozone reflecting a greater contribution from stratospheric changes. However, the net radiative forcing of ozone is positive, reflecting a greater contribution from tropospheric changes. This suggests that ozone radiative forcing is sensitive to the vertical location of the composition changes and weights the tropospheric changes more heavily.

To first order, this apparent paradox can be explained by shortwave radiative forcing due to ozone concentration changes. Stratospheric ozone depletion allows more solar radiation to penetrate into the troposphere where it is absorbed and the resulting heating is dynamically coupled to the Earth's surface. Tropospheric ozone enhancement has a small shortwave warming effect on surface temperatures, leading to more solar absorption in the lower atmosphere. Thus, considering shortwave radiation alone, both stratospheric ozone depletion and tropospheric ozone enhancement lead to surface warming and thus lead to the net positive radiative forcing. The effectiveness of ozone as a greenhouse gas also has a vertical dependence, emphasizing concentration changes at the tropopause level. Above this level, stratospheric temperature adjustments play a larger role in longwave radiative forcing than instantaneous forcing and lead to negative radiative forcing. This tends to counter the positive shortwave radiative forcing due to stratospheric changes, leaving the net radiative forcing due to stratospheric composition changes fairly neutral. In contrast, the net radiative forcing due to tropospheric ozone changes reflects ozone's role as a greenhouse gas and is strongly positive.

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