

The natural greenhouse effect of atmospheric oxygen (O₂) and nitrogen (N₂)

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[1] The effect of collision-induced absorption by molecular oxygen (O₂) and nitrogen (N₂) on the outgoing longwave radiation (OLR) of the Earth's atmosphere has been quantified. We have found that on global average under clear-sky conditions the OLR is reduced due to O₂ by 0.11 Wm⁻² and due to N₂ by 0.17 Wm⁻². Together this amounts to 15% of the OLR-reduction caused by CH₄ at present atmospheric concentrations. Over Antarctica the combined effect of O₂ and N₂ increases on average to about 38% of CH₄ with single values reaching up to 80%. This is explained by less interference of H₂O spectral bands on the absorption features of O₂ and N₂ for dry atmospheric conditions. **Citation:** Höpfner, M., M. Milz, S. Buehler, J. Orphal, and G. Stiller (2012), The natural greenhouse effect of atmospheric oxygen (O₂) and nitrogen (N₂), *Geophys. Res. Lett.*, 39, L10706, doi:10.1029/2012GL051409.

1. Introduction

[2] It is a widespread notion that both main constituents of the atmosphere, molecular nitrogen (N₂) and molecular oxygen (O₂) 'exert almost no greenhouse effect' [Le Treut *et al.*, 2007]. Their contribution is mainly ascribed to indirect effects like the pressure-broadening of CO₂-lines in the infrared [Lacis *et al.*, 2010; Goldblatt *et al.*, 2009]. Thus, N₂ and O₂ are sometimes not considered as natural greenhouse gases even in case of low water vapor conditions [Lacis *et al.*, 2010].

[3] Due to their symmetry, homonuclear diatomic molecules like N₂ and O₂ do not exhibit a static electric dipole moment, such as H₂O, nor is there the possibility to induce vibrationally a dipole moment, as in the case of CO₂. Thus, there are no strong infrared absorption bands due to dipole transitions as in the case of the major greenhouse gases. However, as discovered by Crawford *et al.* [1949], collision-induced absorption leads to weak absorption features of N₂ and O₂ in the infrared [e.g., Hartmann *et al.*, 2008].

[4] Due to the atmospheric concentration of atmospheric N₂ (O₂) that is about 2000 (550) times higher than that of CO₂ and about 4.4×10^5 (1.2×10^5) times more abundant

than CH₄, even the weak infrared absorption of N₂ (O₂) can become radiatively important.

[5] The collision-induced fundamental vibration-rotation band at 6.4 μm is the major absorption signature of O₂ in the thermal infrared. Timofeyev and Tonkov [1978] reported that at distinct wavelengths near the band center, O₂ absorption may affect the atmospheric zenith transmission by up to 9% for dry atmospheric conditions. This effect is strongly modulated by the atmospheric water vapor content since the O₂ spectral signature is situated in the same spectral region as one of the most important H₂O infrared absorption bands (ν_2 bending). In the atmosphere the infrared signal of O₂ has first been detected through balloon-borne limb-sounding observations [Rinsland *et al.*, 1982].

[6] N₂ has two major bands influencing the infrared radiation: the collision-induced rotovibrational fundamental band at 2400 cm⁻¹ and the collision-induced rototranslational band at 100 cm⁻¹. In the atmosphere, the mid-infrared absorption of N₂ was first observed by Susskind and Searl [1977] by use of ground-based FTIR measurements. Rinsland *et al.* [1981] confirmed these observations by analysis of balloon-borne limb solar occultation spectra. A further detailed analysis of the mid-infrared continuum signals of O₂ and N₂ has been performed on basis of space-borne observations by Rinsland *et al.* [1989].

[7] The N₂ absorption band in the sub-mm range has been analysed in atmospheric measurements by Pardo *et al.* [2001]. They used ground-based Fourier transform spectroscopy at Mauna Kea to determine the continuum like absorption up to frequencies exceeding 1 THz.

[8] In various line-by-line radiative transfer calculations for the validation of radiation codes used within climate models [e.g., Fomin *et al.*, 2004; Collins *et al.*, 2006; Iacono *et al.*, 2008] or for the exact modeling of outgoing longwave radiation [Buehler *et al.*, 2006] the effects of collision-induced continua of N₂ and O₂ have mostly been taken into account by use of continuum parameterizations like the Mlawer, Tobin, Clough, Kneizys, and Davis (MT_CKD) model [Clough *et al.*, 2005]. However, we are not aware of any publications on the quantification of the effect of O₂ and N₂ on the outgoing longwave radiation flux (OLR). In the following, after a description of the used radiative transfer model we show spectrally resolved typical simulations of atmospheric transmission and OLR for a standard atmospheric situation. Then, the globally resolved net effects of O₂ and N₂ on OLR are discussed and at the end a comparison with an independent line-by-line model is presented.

2. Radiative Transfer Simulations

[9] For the simulation of broadband infrared spectra at the top of the atmosphere the radiative transfer model KOPRA [Stiller, 2000] has been applied. KOPRA is an accurate and

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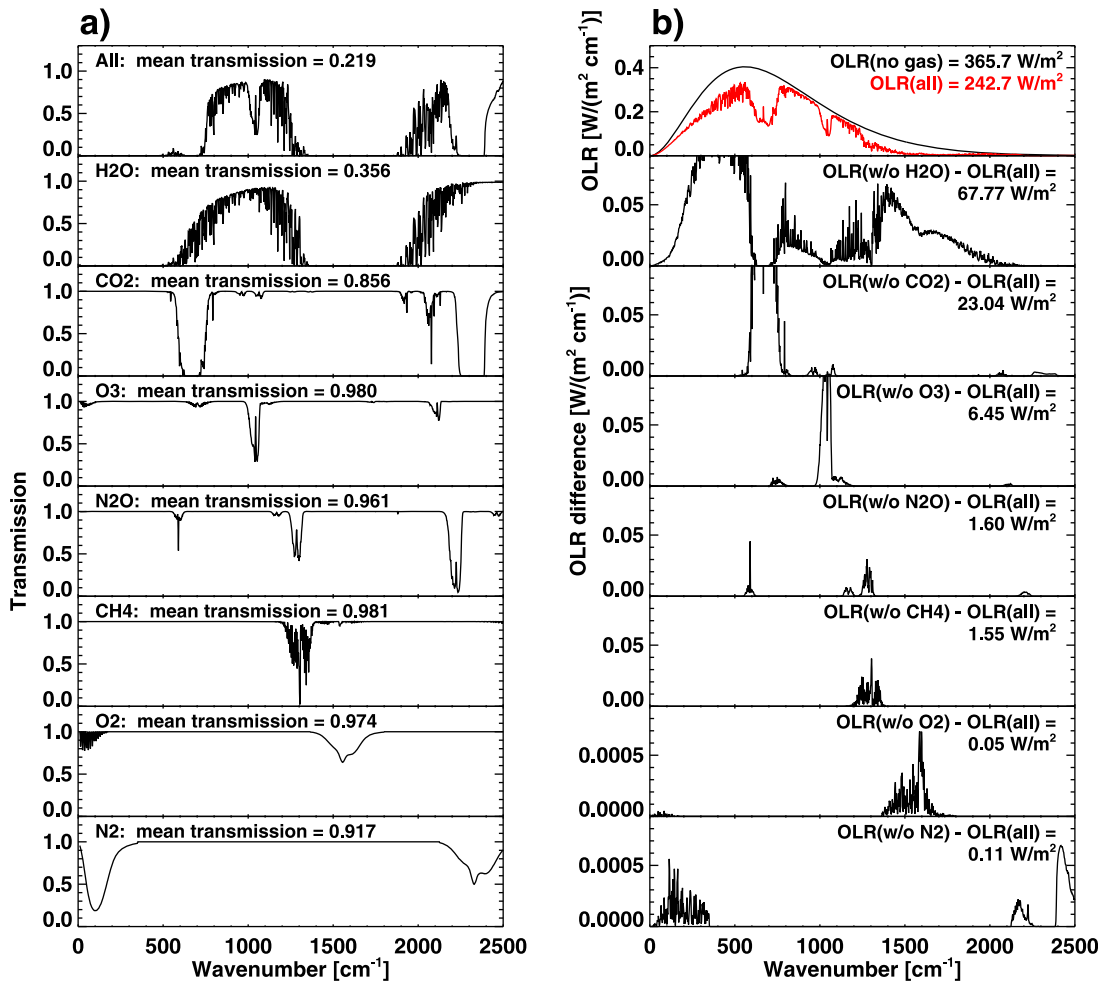


Figure 1. (a) Atmospheric zenith transmission between 10 and 2500 cm⁻¹ (1 mm–4 μm) in case of mid-latitude conditions for all gases (top) and single gas atmospheres. (b) Spectral OLR difference between the OLR where a single gas has been omitted and the OLR where all gases are included. Mind the different range of the y-axis for O₂ and N₂.

fast line-by-line model being used for the analysis of spectrally high resolved satellite remote sensing observations like the IR-limb emission sounder MIPAS [Fischer *et al.*, 2008] or the IR-nadir instrument IASI [Keim *et al.*, 2009]. Beside the indirect model validation via the validation of the retrieved atmospheric parameters, KOPRA has successfully been compared to various independent radiative transfer models [e.g., Tjemkes *et al.*, 2003]. For the calculations shown within this paper we have used spectroscopic data from HITRAN 2008 [Rothman *et al.*, 2009]. Continuum contributions for water vapor and CO₂ are parameterized according to the MT_CKD model version 2.5.2 [Clough *et al.*, 2005]. The collision induced continuum by O₂ is based on the empirical model by Thibault *et al.* [1997]. The continuum by N₂ near 2300 cm⁻¹ is calculated according to Lafferty *et al.* [1996]. The collision induced rototranslational absorption by N₂ at around 100 cm⁻¹ is taken from the MT_CKD version 2.5.2 implementation which is based on Borysow and Frommhold [1986] and Boissoles *et al.* [2003]. All following KOPRA radiative transfer calculations have been performed on a spectrally high resolved variable wavenumber grid with a grid width down to 0.0005 cm⁻¹ [Kuntz and Höpfner, 1999]. For the figures the high-resolved

spectra have been smoothed with a 2 cm⁻¹ wide boxcar function.

3. Calculation for a Standard Atmosphere

[10] Figure 1a shows the atmospheric zenith transmission between 10 cm⁻¹ and 2500 cm⁻¹ (4 μm–1000 μm) for single gases H₂O, CO₂, O₃, N₂O, CH₄, O₂ and N₂ and their combination for a typical atmospheric mid-latitude situation [Remedios *et al.*, 2007] as calculated with KOPRA. It is obvious that in case of O₂ a maximum reduction of the atmospheric transmission by 40% (around 1550 cm⁻¹) and in case of N₂ by 50% at 2330 cm⁻¹ and 80% at 100 cm⁻¹ is reached. The mean zenith transmission of single gas atmospheres is reduced by 2.6% due to O₂ and by 8.3% due to N₂, in comparison to 1.9% by e.g. CH₄. For a zenith angle of 80° an atmosphere consisting only of N₂ and O₂ would even be opaque by O₂ absorption between 1500–1650 cm⁻¹, and by N₂ absorption in the regions 20–200 cm⁻¹ and 2230–2470 cm⁻¹. The mean transmission would be reduced by 14.2% due to O₂ and by 25.7% due to N₂, compared to 6.9% by CH₄ and 92.5% by H₂O.

[11] The effect of O₂ and N₂ on the outgoing longwave radiation flux (OLR) at the top of the atmosphere (assumed at

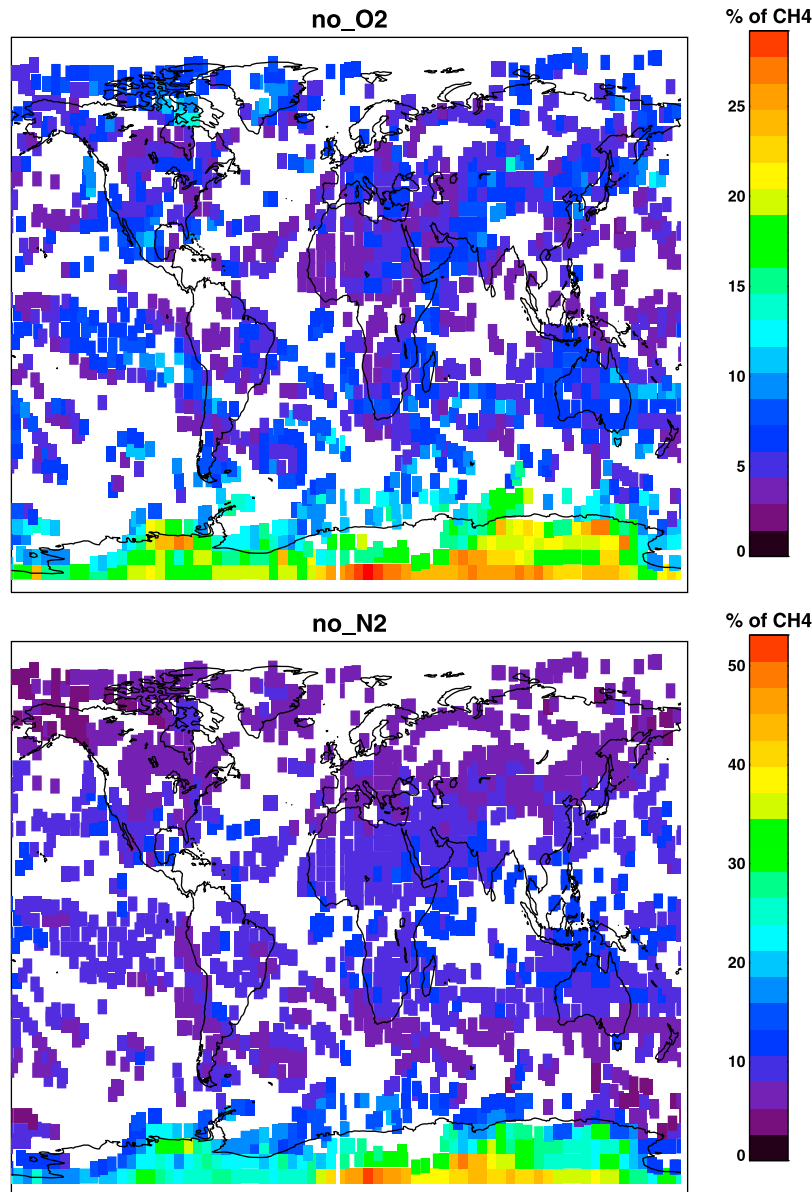


Figure 2. Cloud-free global distribution of the values of OLR reduction due to (top) O₂ and (bottom) N₂ relative to that of CH₄ for realistic all-gas atmospheres: $\frac{\Delta\text{OLR}(\text{O}_2\text{orN}_2)}{\Delta\text{OLR}(\text{CH}_4)} \times 100$.

80 km altitude) is estimated by integrating radiance calculations at different nadir angles (0°, 20°, 40°, 60°, 81°) taking into account Earth's sphericity. (The radiances between 81° and 90° have been neglected since those lines-of-sight do not hit the earth any more but correspond to limb views).

[12] In the following we discuss the net contribution to the OLR by different gases with respect to an atmosphere composed of the full set of species. This means that a gas with an absorption band in the same spectral region as a strong band of another species has less effect on the OLR than in case of less overlapping spectral signatures. As can be seen in Figure 1a, the collision induced absorption band of O₂ is covered by the ν_2 H₂O absorption, the rovibrational band of N₂ at 2400 cm⁻¹ by the strong 4.3 μm CO₂ absorption and the rototranslational band of N₂ at 100 cm⁻¹ by absorption mainly due to H₂O.

[13] Results are presented in Figure 1b as the difference between OLR calculations where a single gas has been

omitted and the OLR values where all gases are included ($\Delta\text{OLR}(\text{gas } x) = \text{OLR}(\text{all without gas } x) - \text{OLR}(\text{all})$). Mind that 'omitted' and 'without gas x' here mean that the gas is set to be infrared-inactive but still contributes to the atmospheric density and pressure.

[14] As indicated in Figure 1b, $\Delta\text{OLR}(\text{O}_2) = 0.05 \text{ Wm}^{-2}$ and $\Delta\text{OLR}(\text{N}_2) = 0.11 \text{ Wm}^{-2}$. Thus, the natural greenhouse effect of oxygen and nitrogen together are about 10% of that of CH₄ ($\Delta\text{OLR}(\text{CH}_4) = 1.55 \text{ Wm}^{-2}$). Mind that the mean tropospheric concentration of CH₄ used in these calculations was 1.8 ppmv.

[15] To evaluate the effect of overlapping spectral signatures on the relative contribution to OLR reduction we simulated the pure hypothetical case of single gas atmospheres. Here, compared to the flux for an infrared-inactive atmosphere (365.7 Wm⁻²), each of N₂ and O₂ reduces the OLR by 2.8 Wm⁻² and CH₄ by 4.3 Wm⁻². The effect of both major atmospheric constituents together would exceed the

Table 1. Cloud-Free Global and Antarctic (70°–90°S) Means of the OLR, the Absolute OLR Reduction and the OLR Reduction Relative to That of CH₄ for Realistic All-Gas Atmospheres^a

	OLR (Wm ⁻²)	ΔOLR (Wm ⁻²)	ΔOLR _{relCH4}
Global			
All gases	259.1		
No gas	381.5		
All w/o H2O	322.8	63.7	34.1
All w/o CO2	285.9	26.8	14.4
All w/o O3	266.3	7.2	3.87
All w/o N2O	261.0	1.88	1.01
All w/o CH4	261.0	1.87	1.0
All w/o O2	259.2	0.11	0.060
All w/o N2	259.3	0.17	0.092
Antarctic			
All gases	176.8		
No gas	199.7		
All w/o H2O	188.8	11.94	17.7
All w/o CO2	185.5	8.63	12.8
All w/o O3	177.3	0.44	0.646
All w/o N2O	177.6	0.75	1.12
All w/o CH4	177.5	0.67	1.0
All w/o O2	177.0	0.11	0.161
All w/o N2	177.0	0.15	0.219

$$^a \Delta \text{OLR}(\text{gas } x) = \text{OLR}(\text{all without gas } x) - \text{OLR}(\text{all}), \Delta \text{OLR}_{\text{relCH}_4}(\text{gas } x) = \frac{\Delta \text{OLR}(\text{gas } x)}{\Delta \text{OLR}(\text{CH}_4)}$$

OLR-reduction due to CH₄ by a factor of 1.3. This drop from a factor of 1.3 to 10% in relative importance of N₂ and O₂ compared to CH₄ is caused by the overlapping bands of H₂O and CO₂ in a real atmosphere. To demonstrate how strong this importance is modulated by temperature and water-vapor content of the atmosphere a realistic global situation is described in the following.

4. Global Picture

[16] In this section we investigate the OLR reduction by N₂ and O₂ in relation to CH₄ globally for a real atmospheric situation. As an example, October 16th, 2007 has been chosen arbitrarily. ECMWF T106 analysis for 6 UT of temperature and humidity has been applied to produce altitude profiles at cloud-free locations. To reduce the number of broad-band line-by-line calculations globally a 5° longitude × 5° latitude grid has been used. Within each grid-cell we have chosen the cloud-free profile nearest to the grid center. In case there has been no cloud-free situation, no calculation has been

performed for the related grid cell. For all other gases (CO₂, O₃, N₂O, CH₄, O₂, and N₂), standard profiles have been used [Remedios *et al.*, 2007].

[17] The calculations for an atmosphere containing the full set of gases are presented in Figure 2 and in Table 1. In Figure 2 (top) the OLR reduction due to oxygen relative to that of methane ΔOLR(O₂)/ΔOLR(CH₄) is shown, and Figure 2 (bottom) demonstrates the similar effect for nitrogen ΔOLR(N₂)/ΔOLR(CH₄). With exception of the southern polar region the values vary around 6% for O₂ and 9% for N₂. Global mean relative OLR reductions are 6.0% and 9.2% for O₂ and N₂, respectively (Table 1).

[18] Over Antarctica, maximum values for ΔOLR(O₂)/ΔOLR(CH₄) of around 30% and for N₂ of up to 50% are reached. Mean values for latitudes poleward of 70°S are 16.1% for O₂ and 21.9% for N₂ as listed in Table 1. This large contribution to the natural greenhouse effect relative to the one exhibited by CH₄ is due to the extremely low humidity over the southern polar region, such that spectral signatures of water vapor interfere less with those of O₂ and N₂.

5. Model Evaluation

[19] The accuracy of KOPRA simulations of the OLR reduction due to O₂ and N₂ relative to CH₄ has been evaluated by comparison with independent calculations performed with the ARTS radiative transfer model [Buehler *et al.*, 2005; Eriksson *et al.*, 2011]. Like KOPRA, ARTS is a line-by-line model which has been applied recently for the modeling of OLR at the top of the atmosphere [Buehler *et al.*, 2006]. For nadir view, a comparison dataset has been calculated on basis of 42 altitude profiles of pressure/temperature and trace gases (H₂O, O₃, CO₂, N₂O, CH₄, O₂, N₂) [Garand *et al.*, 2001]. Figure 3 shows the comparison for ΔOLR(O₂)/ΔOLR(CH₄), ΔOLR(N₂)/ΔOLR(CH₄) and the sum of both.

[20] In general both models compare reasonably well: the mean values for O₂ are 6.4%(KOPRA) vs. 6.1%(ARTS) and for N₂ 8.1%(KOPRA) vs. 6.0%(ARTS), respectively. Differences are explained by different set-ups of the two models. First, the frequency grid of the ARTS simulations has been coarser (0.3 cm⁻¹) than that of KOPRA (min 5 × 10⁻⁴ cm⁻¹). A sensitivity analysis using a degraded frequency grid of 0.3 cm⁻¹ for KOPRA showed a reduction of the total effect from 14.5% to 13.5%, thus approaching the lower values of ARTS. Remaining differences are likely due to the application of different spectroscopic databases

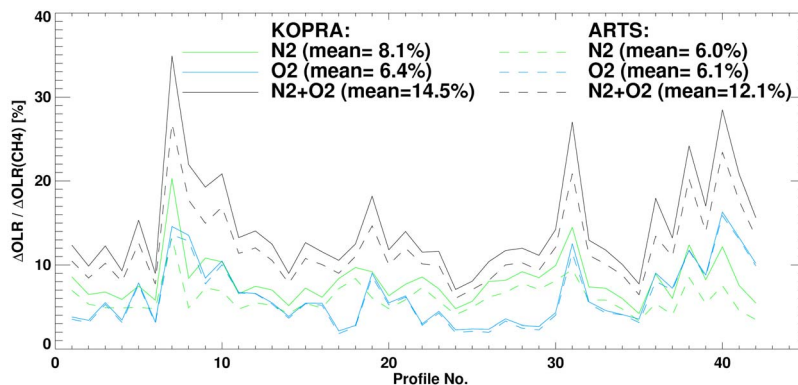


Figure 3. Comparison between OLR reductions by N₂, O₂ and N₂ + O₂ relative to those by CH₄ ($\frac{\Delta \text{OLR}(\text{gas } x)}{\Delta \text{OLR}(\text{CH}_4)} \times 100$) for KOPRA (solid lines) and ARTS (dashed lines) in case of different atmospheric situations (x-axis).

(ARTS: HITRAN 2004, KOPRA: HITRAN 2008) and continuum models (ARTS: MT_CKD_1.0, KOPRA: MT_CKD_2.5.2). An update within the MT_CKD_2.5.2 model concerns e.g. the increase of the N₂ continuum in the 0–350 cm⁻¹ range [Pardo *et al.*, 2001; Boissoles *et al.*, 2003; Pardo *et al.*, 2005]. This probably explains the stronger relative effect of N₂ compared to that of O₂ within the KOPRA simulations compared to ARTS. In summary, the model intercomparison confirms the relative large effects on OLR by O₂ and N₂ as deduced from KOPRA simulations.

6. Conclusions

[21] This work challenges a common perception on the negligible role of O₂ and N₂ as natural greenhouse gases in the Earth's atmosphere compared to species like CH₄ or N₂O. It is in fact the large abundance of oxygen and nitrogen which compensates for their only weak interaction with infrared radiation through collision-induced absorption bands. We have shown that for hypothetical atmospheres consisting of only single gases the natural greenhouse effect of O₂ and N₂ together would be larger than that of CH₄ by a factor of around 1.3. For a realistic atmospheric composition this effect is reduced through shading of O₂ and N₂ absorption bands mainly by spectral signatures of H₂O and, to a less extent, by CO₂. Still the net global OLR reduction of oxygen and nitrogen together is with 0.28 Wm⁻² about 15% of that due to CH₄. However, for dry atmospheric situations like over the Antarctic continent the effect of O₂ and N₂ even reach up to 80% of the influence of CH₄ for a realistic atmospheric composition.

[22] An atmospheric situation with increased values of N₂ has been proposed as possible solution for the 'Faint Young Sun' paradox by Goldblatt *et al.* [2009]. Repeating their calculation of longwave radiative forcing we obtained similar values for a doubling of N₂ concentrations (≈12 Wm⁻²). We investigated this effect for single absorbers and found reductions of the OLR by 9.4, 5.1, 4.6 and 1.9 Wm⁻² for H₂O, CO₂, N₂, and CH₄. The relatively large value in case of N₂ is due to collision-induced continuum absorption which scales with the square of concentration while the dependence of strong absorption bands on line-width is much smaller. Thus, we object to the view that the radiative forcing of N₂ increase operates only indirectly by broadening the absorption lines of other gases [Goldblatt *et al.*, 2009]. Actually it is a combination of this indirect effect and the direct impact through collision-induced absorption.

[23] Finally we would like to stress that this work concerns only the contribution of N₂ and O₂ to the natural greenhouse effect. In no way does it affect the importance of CH₄ and other anthropogenically affected gases with respect to global climate change.

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