

A Theoretical Analysis of the Effect of Greenhouse Gases in the Atmosphere

Michael Hammer

A presentation to The Lavoisier Group's 2007 Workshop

'Rehabilitating Carbon Dioxide'

held in Melbourne on 29-30 June 2007

A Theoretical Analysis of the Effect of Greenhouse Gases in the Atmosphere

Michael Hammer

SUMMARY

A spectroscopic based analysis of the effect of greenhouse gases in the atmosphere is presented which takes into account both absorption and re-radiation of energy. The analysis predicts the energy radiated to space at the absorption wavelengths is reduced by the factor $1/(absorbance+1)$, very different from the factor $10^{-absorbance}$ predicted from a consideration of absorbance processes alone (absorbance is linearly related to concentration). The difference can be many orders of magnitude and offers a new perspective on the role of greenhouse gases in the atmosphere.

Differentiating the equation relating energy retention to greenhouse gas absorbance allows computation of the relative sensitivity (fractional change in energy retained for a given fraction change in concentration) and thus the additional heat retention for a fractional increase in a greenhouse gas concentration. Applying this computation to a doubling of the carbon dioxide concentration from 280 ppm to 560 ppm suggests the additional heat retention is about 1.2 watts/m² leading to a temperature rise of 0.22 degrees.

The analysis allows estimation of the relative sensitivity to water vapour and the estimate suggests that positive feedback from this source should be less than 15% of the direct impact from carbon dioxide. This is substantially lower than IPCC model based predictions.

The analysis also allows calculation of a temperature profile for the troposphere based on radiative processes alone and this computed profile closely matches the measured profile reported. The calculation also shows that an increase in greenhouse gas concentration should result in slight cooling of the upper troposphere around 10 km altitude which is in line with observations but contrary to some climate models which predict substantial warming of the upper troposphere.

CURRENT GLOBAL WARMING PREDICTIONS.

The IPCC fourth assessment report [www.ipcc.ch/SPM2fwb07.pdf] is used here as the reference point for current anthropogenic global warming claims. This provides the following information

- CO₂ has increased from 280 ppm in 1900 to 379 ppm in 2005 (p2)
- Temperature rise since 1950 is about 0.6 degrees but 0.4 degrees since 1940 due to 0.2 degrees cooling between 1940 and 1950 (fig SPM-3 p6)
- If CO₂ levels remain at 379 ppm the temperature is likely to continue to rise at 0.1 degrees per decade for the next 2 decades (p12,p13)
- Total additional rise by 2100 for CO₂ held at 379 ppm is 0.3 degrees (graph p14)

- The increase in CO₂ over the 20th century (280 ppm to 380 ppm) has directly increased radiative forcing by 1.66 watts/meter² (figure SPM-1 p3, SPM-2 p4)
- Total net anthropogenic forcing from all sources is 1.6 watts/meter² (fig SPM-2 p4)
- Doubling CO₂ concentrations (to 560 ppm) is likely to cause an increase of between 2 and 4.5 degrees above current temperatures. Best estimate 3 degrees although values substantially higher than 4.5 degrees cannot be excluded (p12)

ANALYSIS

Earth as a whole can only receive and lose energy by radiation. At thermal equilibrium the temperature will be such that the rate of energy loss by radiation matches the rate at which energy is received. The rate of energy loss is related to the temperature of the object via Stefan's law (given in most physics textbooks)

$$\text{Energy radiated} = k * T^4 \text{ where } k = 5.67 \text{ e-}8 \text{ watts meter}^{-2} \text{ Kelvin}^{-4}$$

T is Kelvin (= degrees C +273)

The energy input from the sun averages 245 watts per meter². Applying the above law suggests a surface temperature of 256.4 Kelvin or -16.6 C. The surface temperature of the Earth is however known to be about 287 Kelvin or +14C implying that some other factor must be affecting the energy balance. That source is the atmosphere. The atmosphere absorbs some of the energy radiated from the Earth's surface and in the process it is warmed. The warm atmosphere then itself becomes an emitter of energy some of which is emitted back onto the Earth's surface. At an average surface temperature of 287 Kelvin the energy loss is 385 watts/meter² implying that the atmosphere contributes 385 - 245 or 140 watts/meter². These numbers seem to be in agreement with numerous global warming papers.

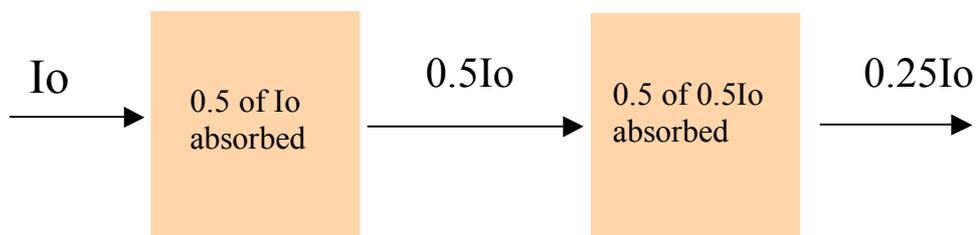
The significance of emissivity

All material substances both absorb radiant energy incident on them and emit radiant energy at a rate dependent on their temperature. However the degree to which they do both of these things also depends on their emissivity. The emissivity is a property of the substance, thus a highly polished surface has a lower emissivity than a dull surface and a white surface as a lower emissivity than a black surface. Absorption of radiant energy and emission of radiant energy are reciprocal processes, a material that does not absorb will also not emit and vice versa. The emissivity factor governs both to an equal extent.

Most of the atmosphere is made up of nitrogen and oxygen which do not significantly absorb infrared energy because their emissivity is exceptionally low. This means they also do not emit significant infrared – they are not greenhouse gases. Other gases however have a very strong ability to absorb energy at some wavelengths between 4 and 50 microns (the approximate range of emission wavelengths from earth's surface). They are the greenhouse gases and the most significant is water vapour followed by carbon dioxide and then methane and ozone. Because their emissivity is high at these absorption wavelengths and low at other wavelengths they also selectively radiate energy at these same absorption wavelengths.

Some basic spectroscopy

If a material absorbs light, one might intuitively expect the amount of light absorbed to be proportional to the concentration of the material, so that doubling the concentration doubles the amount of light absorbed. This is not the case as can be seen by a simple thought experiment. Imagine we have a piece of material which absorbs 50% of the light incident on it transmitting the other 50%. Doubling the concentration of material is exactly equivalent to adding a second identical piece of the material behind the first piece. We already agreed the first piece absorbs 50% of the light incident on it transmitting the remaining 50%. The second piece being identical does exactly the same, absorbing 50% of the light that passed through the first piece and transmitting 50%. Thus the net light passing through the two pieces is not 0 but 25%.



Thus the relationship between concentration and light absorbed is not linear, but exponential. Spectroscopists use the term absorbance to define the degree to which a sample absorbs a particular wavelength of light. This term is defined by the equation;

$$\begin{aligned} \text{Fraction of energy transmitted} &= 10^{-\text{absorbance}} \\ \text{and Fraction of energy absorbed} &= 1 - 10^{-\text{absorbance}} \end{aligned}$$

If a sample has an absorbance of 1, it means that it absorbs 90% of the light incident on it, transmitting the remaining 10%. The absorbance of a sample is directly and linearly proportional to the amount of absorbing material in the light path (Beers law). Thus if a particular sample has an absorbance of 1 then doubling the concentration of the absorbing species for the same path length or doubling the path length with the same concentration will change the absorbance to 2.

Application to an atmospheric greenhouse gas

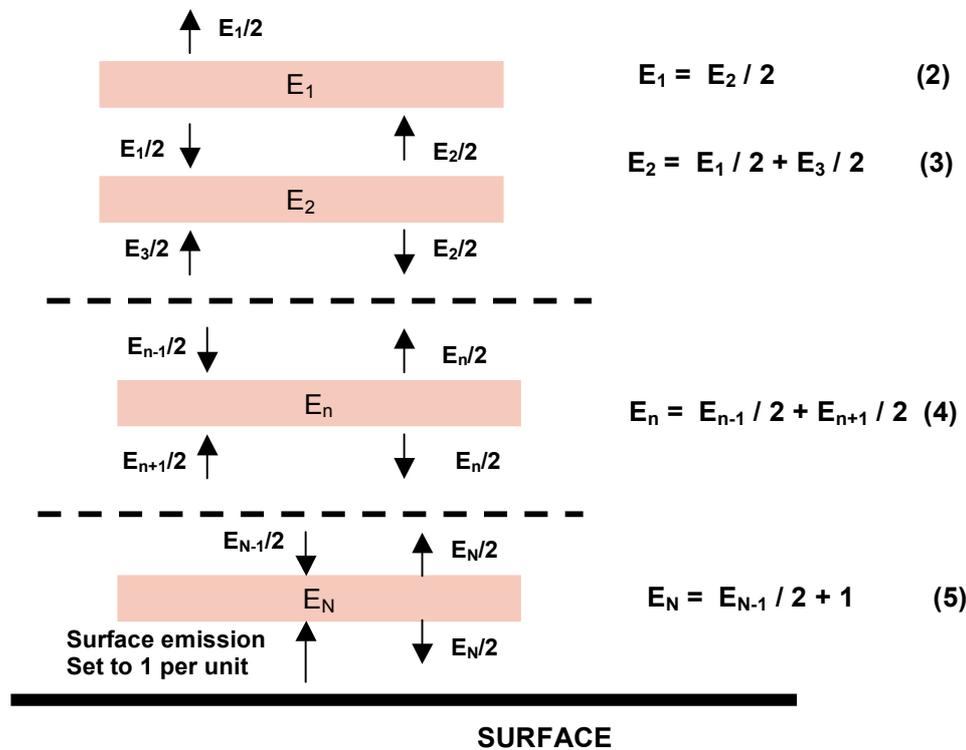
When the greenhouse gas absorbs energy it heats up and this heat is shared with other atmosphere components through collisions between gas molecules causing the entire gas volume to warm. As can be seen from Stefan's law, emission increases with temperature and the gas volume will warm up until the energy emitted matches the energy absorbed. This energy will be emitted in all directions but since the atmosphere is a thin continuous shell covering the entire earth it only has two surfaces, an inner surface adjacent the planet itself and an outer surface adjacent to space. Radiation can only leave the atmosphere through one of these surfaces. Thus, radiating in all directions in effect means 50% will be emitted towards space and 50% returned to the planetary surface.

For very low green house gas absorbance, well below 1, the fraction of energy absorbed will be small and to first order we can ignore energy emitted by the gas being re-absorbed within the gas column. In that case the energy returned to the earth's surface is half the energy absorbed;

$$0.5 * (1 - 10^{-\text{absorbance}}) \quad (1)$$

The possibility of energy emitted by the gas being re-absorbed by the gas becomes more significant as the absorbance rises. In this context we must again remember that the same emissivity covers both absorption and emission so that emitted energy will be at the absorption wavelengths thus facilitating repeated absorption and re-emission. By the time the atmospheric absorbance has reached 1, 90% of the energy at the absorption wavelengths is being absorbed which also means that much of the energy emitted by the atmosphere will be re-absorbed within the atmosphere, possibly going through several absorption re-emission cycles within the atmosphere. In that case, equation (1) will not apply.

To analyse this situation, imagine we treat the entire gas column as stack of 1 absorbance layers. As a first order approximation, assume that each layer absorbs all the energy it receives from above or below and maintains itself in thermal equilibrium by emitting an equal amount of energy, half towards the surface and half away from the surface. The result is shown diagrammatically below for an N absorbance atmosphere.



Where E_1 is the total energy absorbed by layer 1
 E_2 is the total energy absorbed by layer
 E_n is the total energy absorbed by layer n
 E_N is the total energy absorbed by layer N

Fig 1

Equations (2) to (5) are obtained by summing energy into each layer.

$$\text{Substituting (2) into (3) gives } E_2 = 2 * E_3 / 3 \quad (6)$$

$$\text{Substituting (6) into (4) gives } E_3 = 3 * E_4 / 4 \quad (7)$$

$$\text{In general for the } n\text{th layer } E_n = n/n+1 * E_{n+1} \quad (8)$$

$$\text{replacing } n \text{ by } n-1 \text{ in (8) gives } E_{n-1} = n-1/n * E_n \quad (9)$$

$$\text{rearranging (8) gives } E_{n+1} = n+1/n * E_n$$

$$\text{confirming } E_{n-1}/2 + E_{n+1}/2 = ((n-1)/2n + (n+1)/2n) * E_n = E_n$$

$$\text{From (9) } E_{N-1} = N-1/N * E_N$$

$$\text{Substituting into (5) gives } E_N = (N-1)/2N * E_{N+1}$$

$$\text{And rearranging } E_N = 2N/(N+1) \quad (10)$$

Repeated substitution in (8) yields;

$$E_n = n/n+1 * E_{n+1} = n/n+1 * n+1/n+2 * E_{n+2} * \dots * N-1/N * E_N$$

$$\text{Cancelling common terms gives } E_n = n/N * E_N \quad (11)$$

$$\text{The energy radiated away to space is } 0.5 * E_1 = 1/(N+1) \quad (12)$$

$$\text{The energy returned to the earths surface is } 0.5 * E_N = N/(N+1) \quad (13)$$

Equations 1 and 13 are plotted below. Interestingly, even below 1 absorbance equation 13 gives essentially the same result as equation 1 and can thus be treated as a reasonable approximation over the entire absorbance range.

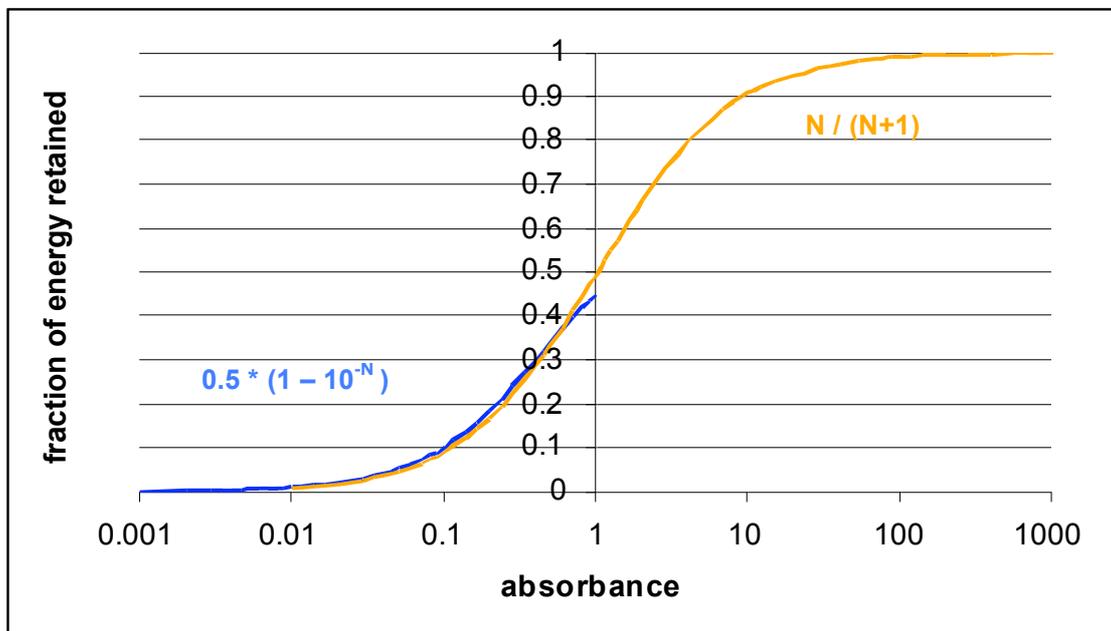


Fig 2

Equation (11) gives the relationship between energy absorbed by a layer versus the position of the layer within the gas column or atmosphere and as can be seen it is a linear relationship.

The fraction of the atmosphere column above any given altitude (ie: n/N) is simply given by the per unit pressure at that altitude (pressure = 1 per unit at the surface) and if the greenhouse gas is a constant fraction of the atmosphere (probably true for carbon dioxide but not for water vapour) the energy absorbed and thus also the energy radiated upwards at the greenhouse absorbing wavelengths will be directly proportional to this pressure. Using the pressure versus altitude data from the CRC handbook of Chemistry and Physics 63rd edition allows the upwards radiation as a function of altitude to be computed

□

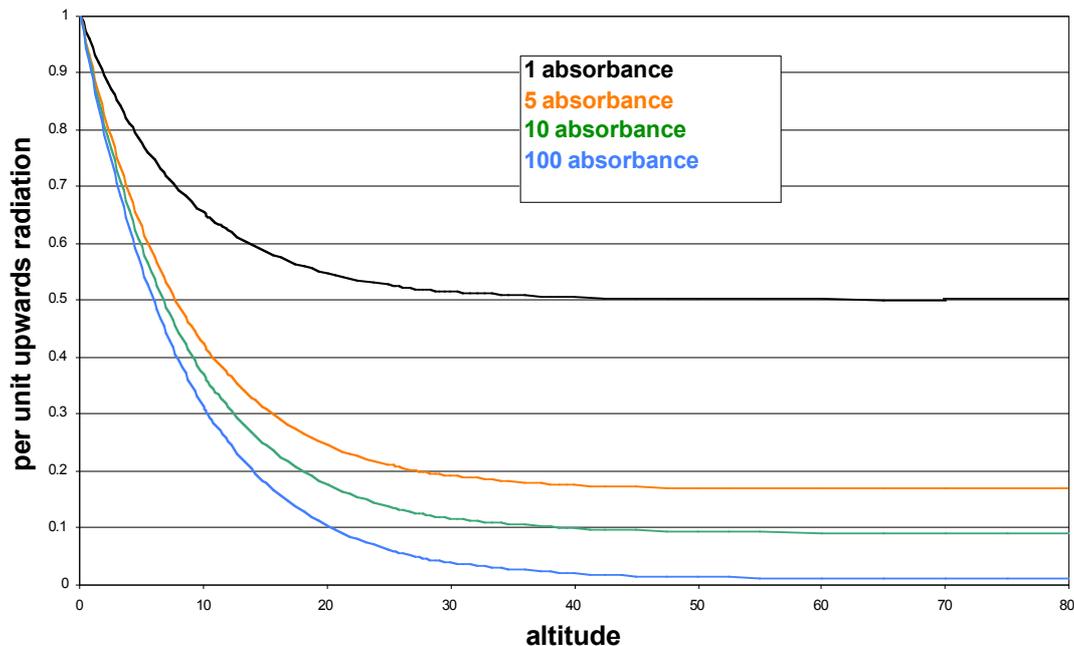


Fig 3

Prediction of temperature profiles in the troposphere

Stefans law applies to black body radiators. At the temperatures of interest most of the black body radiation will be between 4 and 50 microns and, given that the greenhouse gases have many absorbing lines spread over this wavelength range, the T^4 relation between energy and temperature should be reasonably applicable.

Applying this relationship yields a radiation based prediction of temperature versus altitude for the troposphere. Above the troposphere this analysis is not relevant because of the large effect of direct absorption of solar energy especially UV energy by Ozone.

The scale factor was adjusted to make the lowest layer of the atmosphere have the same temperature as the earth's surface. Figure 4 shows the result for several different total absorbances. These total absorbance will be of course the weighted mean contribution of all greenhouse gas absorbers across all wavelengths.

Energy will also be transported upwards in the atmosphere by convection which has been ignored here. Including convective heating should result in less cooling with altitude than the radiation alone suggesting that the true absorbance will be higher than the plot below suggests.

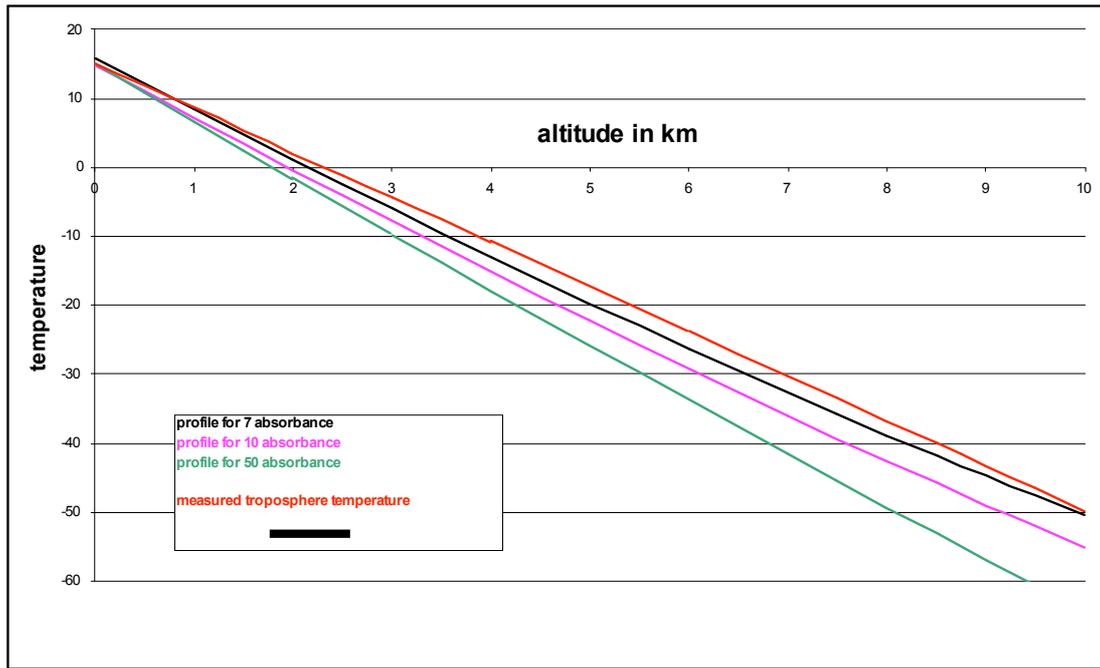


Fig 4

Comparing the curves for 7 abs and 10 abs shows that increasing greenhouse gas concentration leads to increased cooling with altitude. Assuming an increase in surface temperatures either through greenhouse effect or other natural effects plus an increase in greenhouse gas the result is some warming of the lower troposphere (but less than surface warming) together with cooling of the upper troposphere. This result is in line with the experimental findings reported by D.H. Douglass et al [Altitude dependence of atmospheric temperature trends Geophysical research letters vol 31 L13208 2004) but contrary to the scenarios predicted by global warming models.

Sensitivity analysis

It would be very nice to be able to determine the rate at which the retained energy changes with greenhouse gas concentration or in other words the sensitivity of the system to changes in greenhouse gas concentration. This is given by the slope (or first derivative) of the concentration versus energy retained graph (fig 2). Since equation 13 is a good fit over the entire absorbnace range I have used it as the basis of this calculation. The first derivative of equation 13 with respect to absorbnace (N) is;

$$d(\text{energy})/d(\text{absorbnace}) = d(N/(N+1))/dN = 1/(N+1)^2$$

This gives the per unit rate of change in energy retained versus absorbnace at an absorbnace = N.

In practice, it is far more useful if the derivative can be expressed in terms of a fractional change in current energy retained for a fractional change in green house gas concentration (for example: if a green house gas currently contributes say 20 watts per square meter of warming how much will that increase for a 20% increase in greenhouse gas concentration). This could be termed the relative sensitivity and can be derived by;

$$\frac{d(\text{energy})/\text{energy}}{d(\text{absorbance})/\text{absorbance}} = \frac{d(\text{energy})}{d(\text{absorbance})} * \frac{\text{absorbance}}{\text{energy}}$$

The absorbance is N and the per unit energy retained is N/(N+1) so the relative sensitivity is

$$1/(N+1)^2 * N * (N+1)/N = 1/(N+1)$$

This relative sensitivity is plotted below as a function of absorbance

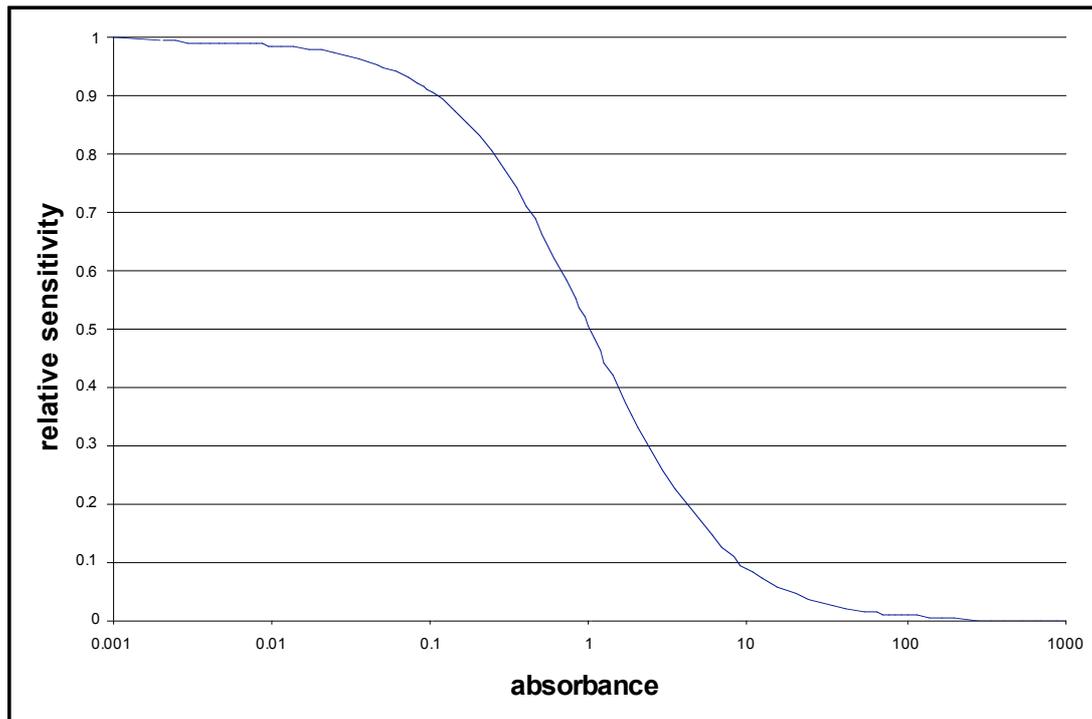


Fig 5

For a gas absorbing energy at several wavelengths the overall relative sensitivity observed will be the weighted sum of the contributions from each wavelength. Where there are strongly absorbed wavelengths, these will have large weighting functions because they result in significant energy retention but very low relative sensitivity and will thus very significantly dilute the effect of weaker lines, lowering the overall relative sensitivity observed.

Looking at the situation for carbon dioxide, experimental data published by Dr Heinz Hug [www.john-daly.com/artefact.htm] shows total atmospheric absorbance of CO₂ at 15 microns of 2100 abs @ 357 ppm (1630 abs at 280 ppm). This is the strongest absorbing line in the wavelength of interest. The HITRAN spectral data [vpl.ipac.caltech.edu/spectra/co2hitran2004imagesmicrons.htm] shows numerous narrow lines between 14.5 and 15.5 microns and using Dr Hug's results to scale these indicates virtually all are above 500 abs (relative sensitivity <0.002). In addition there are many other weaker lines extending down to 13.3 microns and up to 16.7 microns virtually all of which scale to above 16 abs (relative sensitivity < 0.06). There are some (but many fewer) still weaker lines out to 20 microns and while some of these will have high relative sensitivities they will have very small weighting functions.

Based on the above, the weighted mean relative sensitivity should be less than 0.05 for CO₂ concentrations between 280 and 560 ppm.

At +14 centigrade the earth's surface emits about 34 watts between 14 and 16 microns and, as indicated above, CO₂ absorbs a substantial fraction of this. The other lines extending out a further 0.7 microns each side of this central band will add somewhat more. Earlier IPCC data suggested that 280 ppm CO₂ contributes between 12% and 20% of the 140 watts/sq meters of atmospheric warming (17 to 28 watts/m²). This analysis is consistent with that, suggesting a figure closer to the upper end.

The change from 280 to 380 ppm is a 36% increase which, on the basis of the above, would translate to a $36 * 0.05 = 1.8$ % increase in retained energy. If the 280 ppm heat retention value was say 28 watts/m² that would correspond to 0.5 watts/m² increase which would contribute about 0.1 degrees of warming. An increase to 560 ppm represents a further 47% increase over 2005 levels and for the same sensitivity would cause a further increase of $47 * 0.05 * 28.5$ watts/m² or 0.67 watts/m² which would add a further 0.12 degrees of warming for a total of 0.22 degrees over 1900 levels.

The 4th IPCC report claims a 1.66 watt increase in CO₂ heat contribution over the 20th century corresponding to a 5.9% increase in the 28 watt total for a 36% increase in CO₂ concentration or a relative sensitivity of 0.16. This is significantly higher than the above analysis suggests. Even so, applying the 1.66 watts claimed by IPCC (an increase from 385 watts/m² to 386.66 watts/m²) results in a temperature increase of 0.28 degrees. Doubling the CO₂ concentration (from 280 to 560 ppm) represents a further increase of 560/380 or 47% above 2000 levels. Using the same relative sensitivity value (which ignores any decrease due to the increasing total absorbance) implies the additional heat retained is $47 * 0.16 = 7.7\%$ increase over 2000 levels = $0.077 * 29.5 = 2.3$ watts. Increasing from 386.7 w/m² to 389 watts/m² yields a further temperature increase of 0.43 degrees. IPCC however claim a most likely rise of 3 degrees C. A 3 degree increase in temperature translates to a 17 watt/m² increase in retained energy, far more than the above calculation suggests. The reason given for the discrepancy is that the temperature rise is not directly from CO₂, instead most comes via positive feedback from water vapour. Higher temperatures lead to more water vapour and thus greater energy retention from its greenhouse effect. This claim needs to be investigated further.

The role of water vapour

The CRC handbook of chemistry and physics 63rd edition gives the saturation partial pressure for water vapour as a function of temperature. The plot is shown below. When converted to a fractional increase per degree centigrade it translates to an almost constant 7% increase per degree C over the whole temperature range.

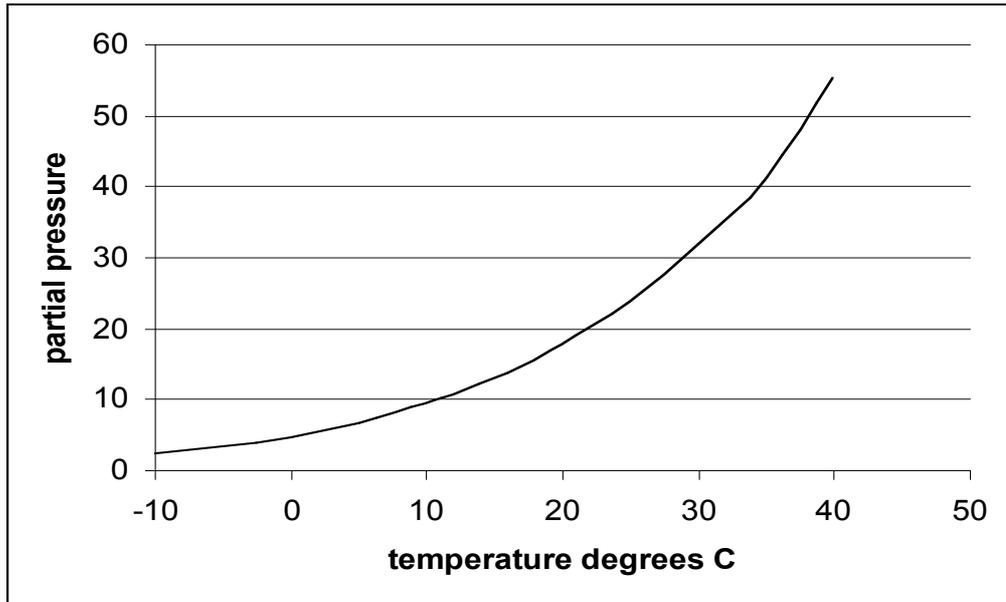


Fig 6

Earlier IPCC data suggests water vapour contributes between 50% and 70% of the total global warming effect or between 70 and 100 watts/m². For the following analysis a value of 85 watts/m² and constant humidity have been assumed.

If the temperature rises by T degrees the water vapour partial pressure (concentration) will rise to 1.07^T, an increase of 1.07^T - 1 per unit. If T is small this increase is approximately equal to 0.07 * T (eg: for a 3 degrees rise 0.07*3 = 0.21 compared to (1.07^T - 1) = 0.225)

If the relative sensitivity as defined earlier is S then the fractional increase in energy retained will be

$$0.07 * T * S$$

Since we assumed water vapour retains at present 85 watts/m² the incremental heat retained due to water vapour will be;

$$0.07 * 85 * T * S \text{ watts/m}^2 = 6 * T * S$$

The first derivative of Stefan's law gives a measure of the incremental energy per degree temperature rise (watts per degree)

$$= 5.67 \text{ e-}8 * 4 * T^3$$

At 288 K this equals 5.5 watts/(M² * degree) and again for small temperature changes this can be considered approximately constant.

Thus for a total temperature rise of T degrees the additional energy retained will be 5.5 * T watts/m². In the scenario previously outlined, this is made up of 2.3 watts/m² from CO₂ and 6*T*S watts/m² from water vapour

Thus: $2.3 + 6 \cdot T \cdot S = 5.5 \cdot T$; rearranging gives $T = 2.3 / (5.5 - 6 \cdot S)$

This allows us to readily compute the relationship between T and S, shown in the table below.

Relative sensitivity to water vapour (S)	Total temperature rise (T)
0	0.42
0.1	0.47
0.2	0.53
0.4	0.74
0.66	1.5
0.72	2
0.79	3
0.82	4
0.917	Thermal runaway

For a 3 degree total temperature rise the relative sensitivity to water vapour would have to be 0.79. From the earlier analysis, a relative sensitivity of 0.79 is only achieved for extremely weak absorbing lines, which is entirely inconsistent with the major greenhouse role played by water vapour.

Indeed the altitude versus temperature graph shown in figure 4 suggests that the average atmospheric absorbance is unlikely to be less than about 7 abs and could be very significantly greater when convective processes are taken into account. The average atmospheric absorbance is likely to be strongly dominated by water vapour since it is by far the most significant greenhouse gas. That would suggest a relative sensitivity for water vapour of no more than about 0.12 and possibly considerably less. As the table above shows, a sensitivity of 0.12 would increase the CO₂ induced temperature increase by about 15% to about 0.48 degrees.

Further, if the amplification effect of water vapour were true, it should have also amplified the IPCC claimed 1.66 watts/m² additional CO₂ contribution over the 20th century to the same degree ie: $1.66 + 0.79 \cdot 6 \cdot T = 5.5 \cdot T$ which yields a temperature rise of 2.2C. This has clearly not occurred and that would seem to be a significant inconsistency between historical analysis and future projections.

Of course, Earth's climate system has significant time constants and it could be claimed that the above apparent inconsistency is because we have yet to see much of the temperature rise consequent on the increase in carbon dioxide levels. However IPCC data predicts that if CO₂ levels were held at 379 ppm the temperature would only rise a further 0.3 degrees, with two thirds of that occurring in the next 20 years. That would imply a total temperature rise of 0.7 to 0.9 degrees depending on the start date chosen, still substantially smaller than the 2.2 degrees calculated above.

CONCLUSIONS

Evidence suggests that there has been an increase in average global temperature over the 20th century. An hypothesis has been strongly asserted that this is due to increasing carbon dioxide concentration predominantly due to human activity. A further hypothesis suggests that only a small portion of the temperature rise is due to the direct action of carbon dioxide with much of the remainder being due to positive feedback via water vapour. The total predicted temperature rise for an increase in CO₂ levels to 560 ppm is 2 – 4.5 degrees above current temperatures with 3 degrees most likely.

This spectroscopic based analysis suggests that sensitivity to both gases is likely to be far lower than would be required for such a scenario and does not support either hypothesis. It suggests that an increase in CO₂ concentration from the current 379 ppm to 560 ppm is likely to cause a temperature increase of about 0.12 degrees (0.22 degrees C for a change from 280 ppm to 560 ppm) and that the positive feedback effect from water vapour should be less than 15% of this direct effect. These results are about 20 times lower than the IPCC predictions.