

Recent Global Warming from CFC Destruction of Ozone!

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Abstract

There has been a lot of discussion about global warming. Some say carbon dioxide (CO₂) emissions caused the earth to warm. Others say there is no abnormality at all, that it is just natural warming. As you will see from the data and analysis presented, both sides of the debate are only partially right in this argument. A greater than normal warming did occur lately but it was not from CO₂ emissions. Chlorofluorocarbon (CFC) destruction of ozone provides answers to all of the unnatural global temperature anomalies seen over the last four decades.

CFCs have caused both unnatural atmospheric cooling and warming based on these facts:

- CFCs have destroyed ozone in the lower stratosphere/upper troposphere causing these zones in the atmosphere to cool 1.37 °C from 1966 to 1998, a time span selected to eliminate the effect of the natural solar irradiance (cooling-warming) cycle effect on the earth's temperature.
- The loss of ozone allowed more UV light to pass through the stratosphere to hit the earth and warm it up 0.48 °C from 1966 to 1998.
- Mass and energy balances show that the energy that used to be absorbed in the lower stratosphere /upper troposphere is now hitting the lower troposphere/earth at a sustainable level of 1.69×10^{18} Btu more in 1998 than it was in 1966.
- Greater ozone depletion in the Polar Regions has caused these areas to warm over twice that of the average earth temperature (1.15 °C vs. 0.48 °C). This has caused permafrost to melt, which is releasing copious quantities of methane, estimated at 100 times that of manmade CO₂ release, to the atmosphere. Methane in the atmosphere slowly converts to CO₂ and water vapor and its release has created higher CO₂ concentrations in the atmosphere.
- There is a temperature anomaly in Antarctica. The Signey Island landmass further north warmed like the rest of the Polar Regions; but south at Vostok, there has been a cooling effect. Although the cooling at Vostok needs to be analyzed in detail, because of the large ozone hole there, black body radiation from Vostok (some 11,400 feet above sea level) to outer space is most likely the cause. Especially, since this phenomenon occurred over the same period that stratospheric ozone destruction took place.

Greenhouse Gases

The Kyoto Protocol requires that the nations of the world reduce greenhouse gas emissions. What would the benefit be from following the Kyoto Protocol? T.M.L. Wigley¹, a senior scientist at the U.S. National Center for Atmospheric Research, calculated the "saved" warming that would accrue if every nation met its obligations (U.S. reduction of 43%). By 2050, it would drop the earth's temperature by 0.07 °C. This change is so small it could never be reliably measured with ground-based thermometers. This being the case, with others confirming similar drops, one wonders why scientists are even talking about CO₂ warming. In support of Wigley's analysis, even with the significant increase in CO₂ concentration in the atmosphere² that occurred since the year 1650 (+160 ppmv), the recorded data plot in Figure 1 shows no discernible correlation of CO₂ concentration with the earth's temperature.

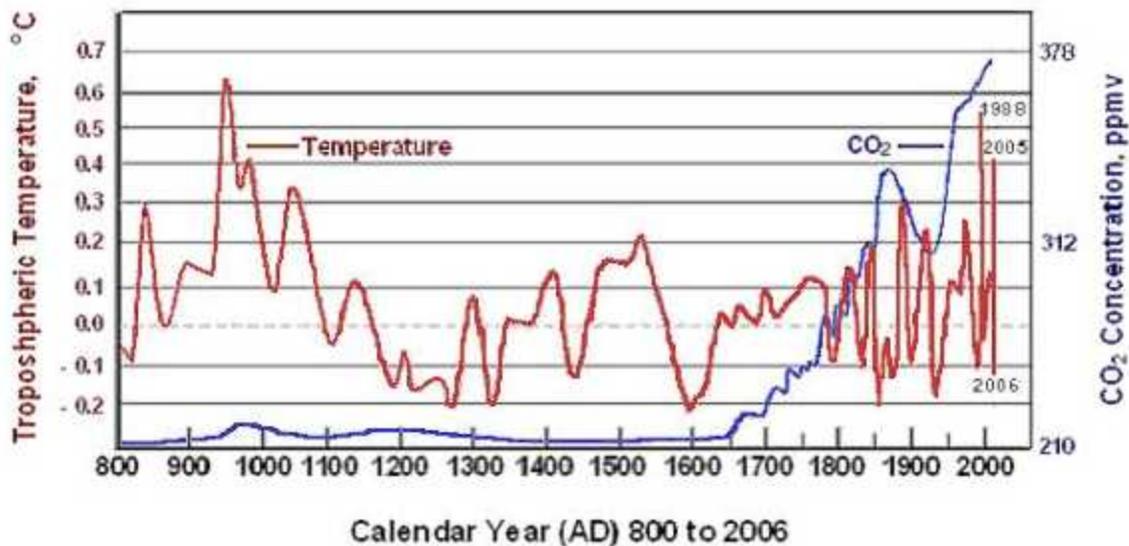


Figure 1. CO₂ concentration and temperature change with time from 800 to 2006 AD.

From the year 850 until 1650, the CO₂ concentration was relatively the same (~215 ppmv); however, the earth's temperature varied from +0.6 to -0.2 °C over that same time. In 2006, the CO₂ concentration was 375 ppmv and there is still no correlation of temperature with CO₂. Contrary to the actual climate data, some say that increased CO₂ levels in the atmosphere has caused global warming. They cite the Vostok, Antarctica ice core data³, as proof of that. However, the data show just the opposite, global warming comes first. After a global spike in temperature, the earth warms and the oceans start liberating more CO₂ because the solubility of CO₂ in seawater decreases as temperature rises. There is a lag of some 800 years from a global warming spike (850) until CO₂ concentration in the atmosphere starts to increase (1650).

Ozone Loss Effect

In 1994, ozone in the lower stratosphere in Antarctica had dropped to less than one-third of normal. Although not as severe, ozone concentration north of the Arctic Circle sank to 45% of normal in the winter of 1996.

The legendary hypotheses⁴ of Paul Crutzen, Sherwood Rowland, and Mario Molina led to CFCs being banned (Montreal Protocol) because they were destroying stratospheric ozone. Although it unleashed a storm of criticism and controversy at the time, they were vindicated by receipt of the 1995 Nobel Prize in Chemistry. In 1978, the USA banned the use of CFCs in hair sprays and other aerosols. In 1987, the governments of the world through the United Nations Environment Programme (UNEP), agreed to limit the production and release of a variety of CFCs. The protocol to accomplish this was put forward at a meeting in Montreal, Canada and has since become known as the Montreal Protocol. Since the original protocol, its provisions were amended in mid-1998; the amendments were then ratified or accepted by 120 and 78 countries, respectively.

CFCs will be produced in China and other developing countries until 2010. In July 2007, China shut down five of its six remaining CFC production plants ahead of schedule and now is only producing 550 metric tons per year.

It is well known that warming of the stratosphere is caused by ozone absorbing ultraviolet radiation. Since ozone keeps the stratosphere warm, using straightforward logic, loss of ozone would cause the stratosphere to cool. Because of ozone loss, more UV light passes through the stratosphere to hit earth. This effect is clearly shown by temperature versus ozone concentration in Dobson Units (DU) in the stratosphere that was measured by NASA⁵ (Figure 2).

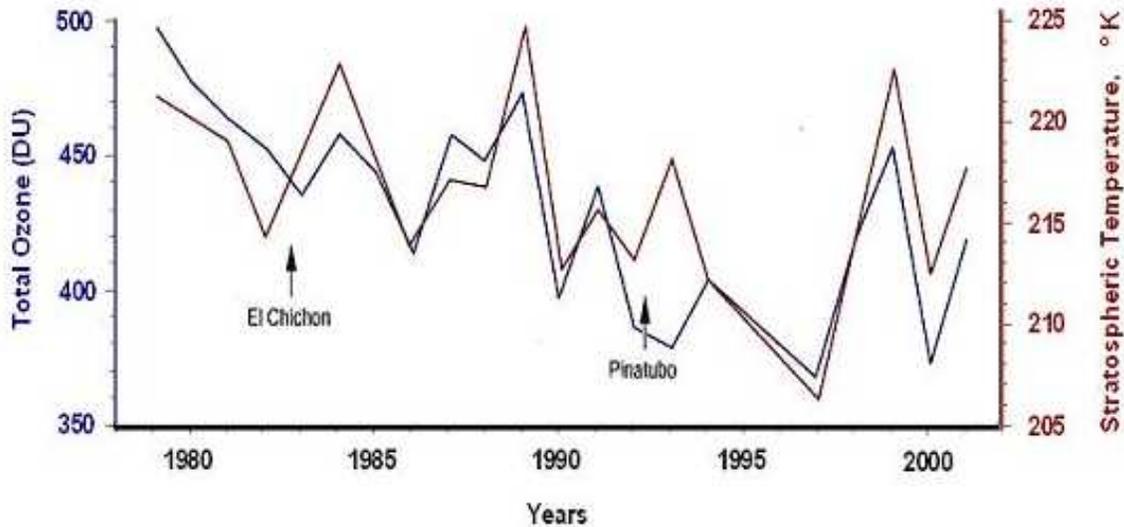


Figure 2. Ozone concentration versus stratospheric temperature.

Except for the periods of the two volcanic eruptions, temperature and ozone concentration rise and fall together. From 1997 to 2001, the temperature of the stratosphere averaged a 1 °C change for every 6.45 DU increase or decrease in the stratospheric ozone concentration.

A colder winter results in more polar stratospheric clouds, a greater destruction of ozone, and a larger ozone hole. However, the primal cause is not colder temperature, it is loss of ozone that created the colder temperature in the first place. Colder temperatures make more ice crystals that create more ozone depleting chemicals to exacerbate the destruction of ozone.

In addition, the cold air over the Polar Regions in winter creates vortices of fast-moving air. These vortices effectively insulate the Polar Regions from the rest of the atmosphere. They sit there, are very stable, and keep the outside higher-ozone air from coming in. Most stratospheric ozone is created in the tropics because of the greater intensity of solar radiation that creates ozone. The ozone is then transported by stratospheric air currents to the Arctic and Antarctica. However, these strong and stable vortices hinder the migration of ozone into the stratospheres over the poles and more UV light passes through to hit earth.

Besides the more pronounced solar heating-cooling cycle variations that occur every 80,000 to 110,000 years shown in the Vostok ice core data, the sun's thermostat also increases and decreases in a normal short term cooling-warming cycle⁶, see Figure 3. To eliminate the short-term solar irradiance warming-cooling cycle effect on global warming, the period from 1966 to approximately 1998 was chosen for analysis.

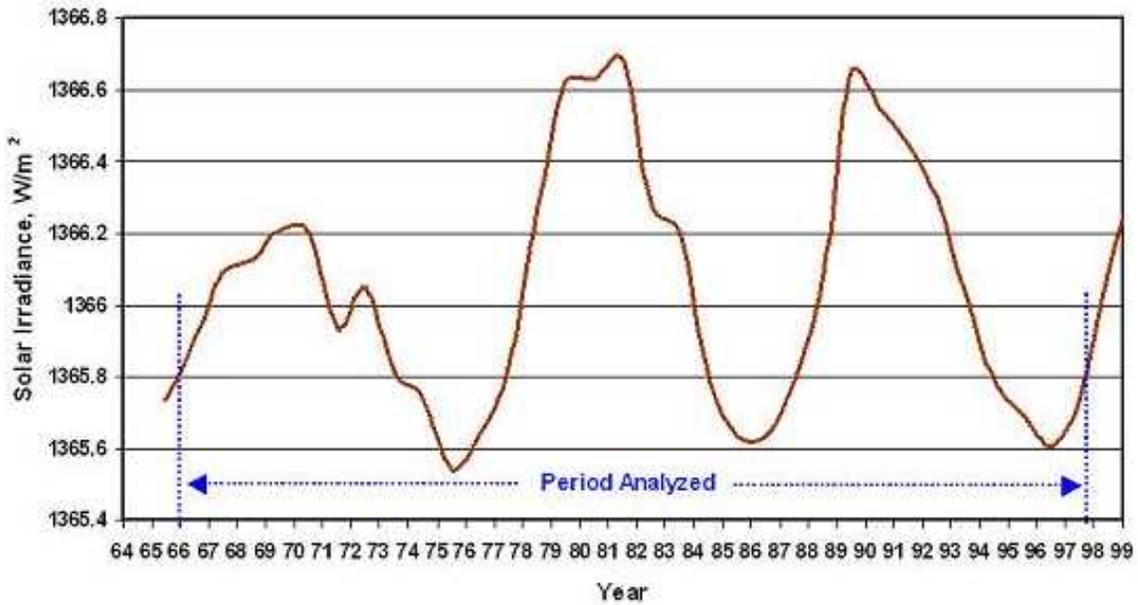


Figure 3. Solar irradiance cycle effect on earth.

Since the early seventies, the loss of ozone has caused the stratosphere to cool, see Figure 4. The exceptions to cooling caused by ozone destruction occurred at the times of the major eruptions of El Chichon and Mt. Pinatubo volcanoes that caused some warming. In 1998, the stratosphere was 1.37 °C cooler than it was in 1966. This period was chosen to negate the solar irradiance cycle and the volcanic eruption periods. The cooling over this time span was due solely to loss of ozone.

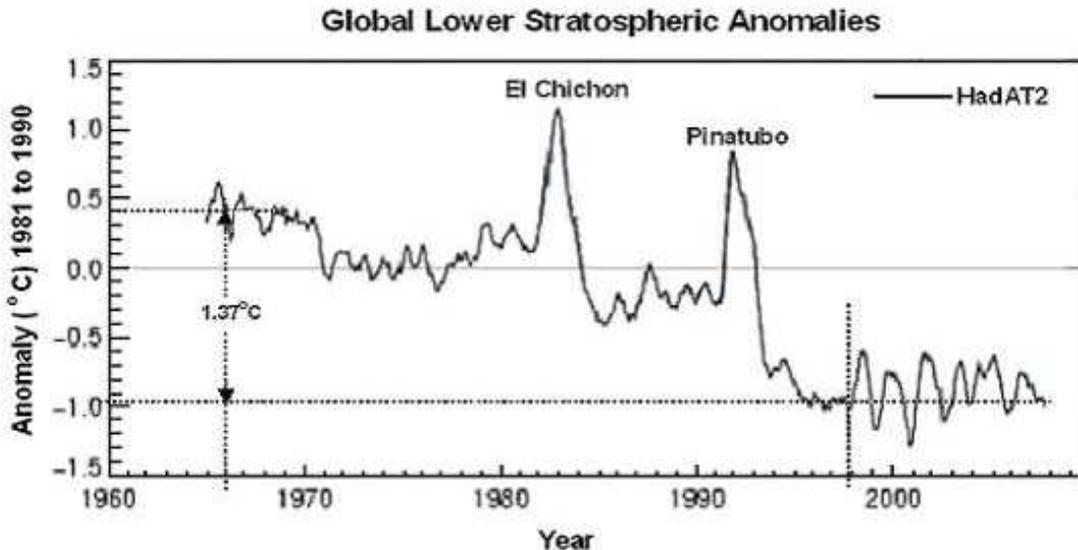


Figure 4. Lower stratosphere temperature change with time ⁷.

As can be seen in Figure 4, stratospheric cooling started to stabilize in 1996 when much of the CFC ⁸ production had been curtailed. The change in ozone depletion chemicals in the stratosphere versus time is shown in Figure 5 and they started leveling out at the same time.

The contribution of methyl bromide is split into anthropogenic (A) and natural (N) components and the natural ozone-depleting substance methyl chloride is included. The line at 2 ppb corresponds to the time when ozone depletion was first detected (about 1980).

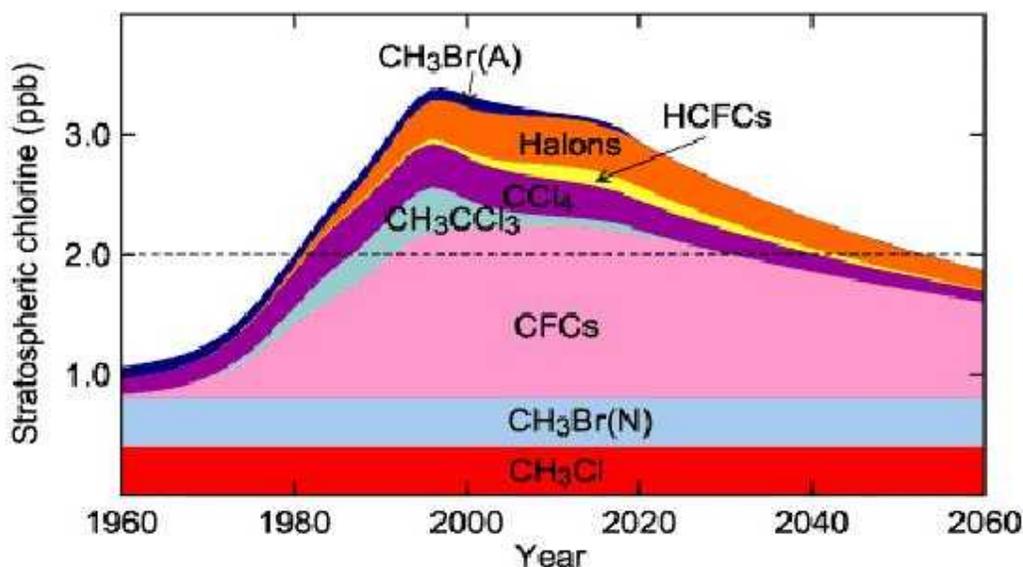


Figure 5. Ozone depletion chemicals in the stratosphere.

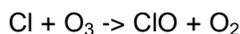
It also shows when major ozone recovery is anticipated (2050 to 2060). Although not shown, chloroform (CHCl_3), dichloromethane (CH_2Cl_2), and a range of other chlorinated solvents contribute a further 0.1 ppb to the stratospheric chlorine. CFC's and CCl_4 are nearly inert in the troposphere and have lifetimes of 50-200+ years. The hydrogen-containing halocarbons like HCl are more reactive, and tend to be removed in the troposphere by reactions with OH radicals. This process is slow and they live long enough for a large fraction to reach the stratosphere. Total tropospheric organic chlorine amounts to over 3 ppbv, and this concentration is nearly independent of altitude throughout the troposphere. Methyl Chloride (CH_3Cl) is the only ozone-depleting chlorocarbon from a major natural source and makes up around 0.5 ppbv of the total. Organic bromides and iodides also destroy ozone.

It is different in the stratosphere; the major source of CFC decomposition there is photolysis⁹, reaction with ultraviolet (UV) light radiation. Ultraviolet light has wavelengths in the 200-400 nm region. UV-A light is a low energy UV light with wavelengths between 320-400 nm. Only about 5% of the UV-A light is absorbed by ozone and most reaches the surface of the Earth. UV-B light is of moderate energy and has wavelengths between 290-320 nm. Ozone absorbs most of the UV-B light before it reaches the surface of the Earth. UV-C light is a higher energy UV light with wavelengths in the range of 200-290 nm. Ozone and oxygen molecules both absorb the UV-C light before it can reach the Earth's surface. Therefore, where there is low stratospheric ozone, more UV-B light from the sun passes through the atmosphere to hit earth and heat it up.

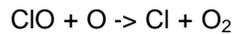
The initial products from high energy UV-C light hitting a CFC molecule are a chlorine atom and an organic radical, considering CFC-11 (trichlorofluoromethane):



The free chlorine atom can then react with ozone to form ClO:



The ClO in turn will react with nascent oxygen (O) to release a chlorine atom; thus, a continuous destruction of ozone occurs because the chlorine atoms are not sequestered into stable compounds:



The CFC chlorine can take other reaction paths, but this is believed to be the predominant ozone destruction cycle. It has been estimated that one CFC molecule in the stratosphere will destroy 100,000 molecules of ozone over its natural lifetime there. Though the concentration of CFCs is only 3 ppbv, they have the ozone destruction effect of a concentration of 0.03% based on one reaction per ozone molecule.

During winter, the air temperature drops and clouds of ice crystals, with mixtures of hydrochloric, sulfuric and nitric acids, form in the stratosphere. These ice crystals provide a surface for chemical reactions that change chlorine compounds that do not affect ozone (e.g. hydrogen chloride) into more active forms that do destroy ozone, such as:



The temperature changes before 1966 are predominantly the result of the natural change in the rate of solar energy hitting earth. However, after CFC refrigerants and aerosols started to be produced and released to the atmosphere, greater warming of the earth has occurred. The troposphere/earth from 1966 to 1998 has warmed around 0.48 °C see Figure 6.

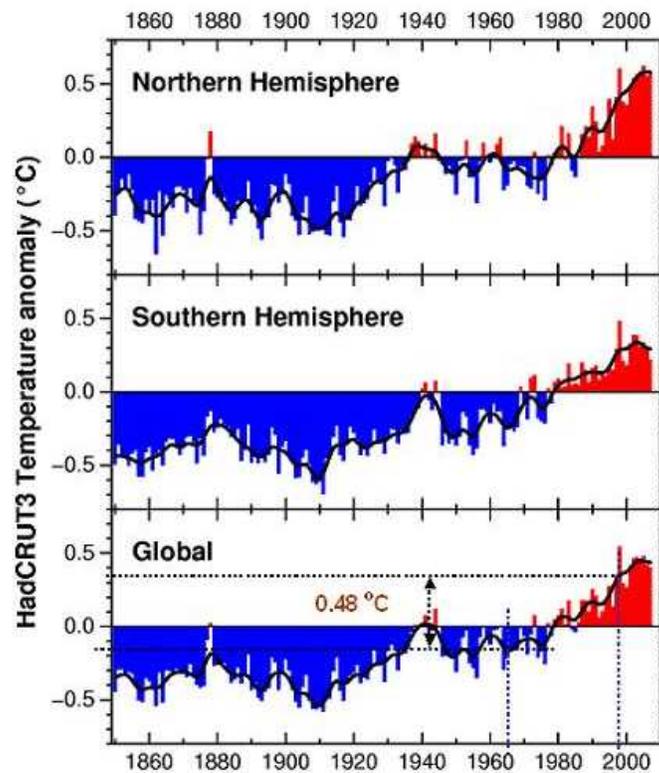


Figure 6. Near earth surface temperature global change with time¹⁰.

One can readily see that the Northern Hemisphere, Southern Hemisphere and the average Global Temperatures all started leveling out and then started to decline after the CFCs peaked and started to decline (Figure 5). This is seen more clearly in Figure 7 where CFC concentration, and average stratosphere and earth temperatures are plotted versus time. As shown by the arrows, in a logical sequence, CFC concentration started to drop first causing a reduction in stratospheric cooling and then a reduction in earth warming.

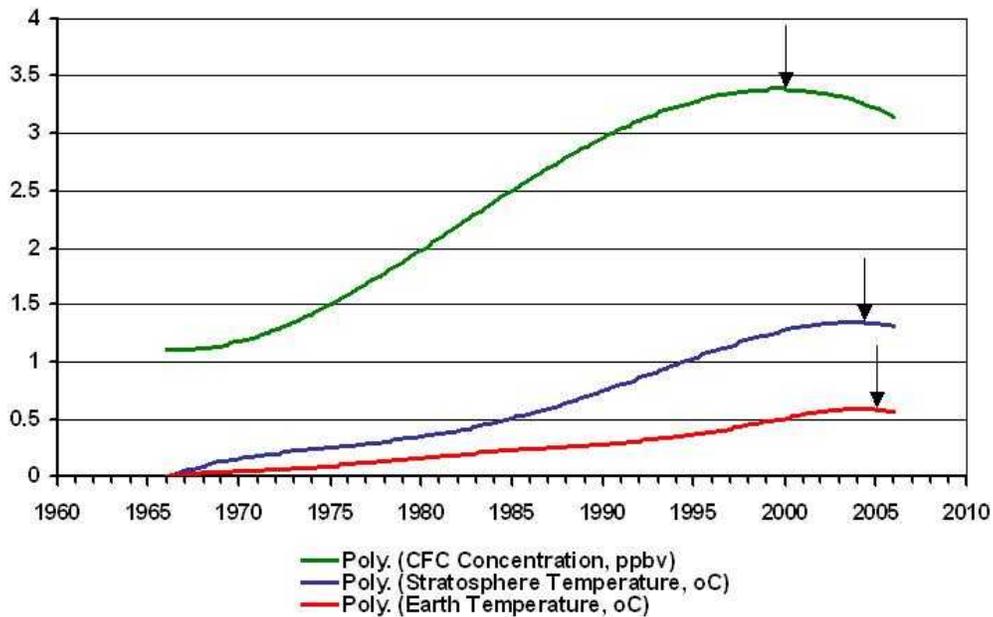


Figure 7. Stratospheric cooling, earth warming and CFC concentration.

According to NASA, the lower stratosphere and upper troposphere, both of which have cooled together¹¹, extends from 8 to 19 km above the surface of the earth with the lower troposphere being in the 0 to 8 km elevation zone. Knowing how much the lower stratosphere-upper troposphere cooled and how much the lower troposphere-earth warmed, mass and energy balances were made to determine how much more radiant energy is hitting the earth due to ozone destruction. Table 1 shows a mass and energy balance was completed around the lower stratosphere/upper troposphere (8-19 km above sea level) zone.

TABLE 1. UV-B LIGHT NOT ABSORBED IN UPPER TROPOSPHERE/LOWER STRATOSPHERE

Atmosphere 8 km to 19 km above Sea level Mass and Energy Balance						
Basis: 0°R & H2O(l)						
			TEMP. °R	LB	BTU/LB	BTU
INPUT: (1966)						
Upper Troposphere/Lower Stratosphere						
AIR	wt%		419.000			
O ₂	23.24			7.0906E+17	91.4	6.4838E+19
N ₂	76.76			2.3419E+18	104.8	2.4539E+20
H ₂ O _(v)	0.00	(No moisture above 6.4 km elevation)				
total	100.00	MW = 28.939		=====		=====
TOTAL				3.0508E+18		3.1023E+20
OUTPUT: (1998)						
Upper Troposphere/Lower Stratosphere in 1998 cooler by 1.37 C or 2.412 F						
AIR	wt%		421.412			
O ₂	23.24			7.0906E+17	91.9	6.5191E+19
N ₂	76.76			2.3419E+18	105.4	2.4673E+20
H ₂ O _(v)	0.00	(No moisture above 6.4 km elevation)				
total	100.00	MW = 28.939		-----		-----
Subtotal				3.0509E+18		3.1192E+20
UV energy not absorbed as shown by 1.37°C (2.412 °F) cooling						-1.6898E+18
TOTAL				3.0509E+18		3.1023E+20
				Mass Balance =	100.00%	Energy Balance = 100.00%

These are straightforward balances based on real temperature measurements at two different points in time. It is similar to this. Say you have one million pounds of water. You measure the temperature of the water, and then you add one million Btus of energy into it and measure the temperature again to find it has raised 1 °F. The mass and energy balance in Table 2 shows the effect of the additional energy being absorbed by the troposphere/earth (surface to 8 km above sea level) in 1998 compared to 1966.

**TABLE 2. HEAT ABSORBED IN LOWER TROPOSPHERE AND EARTH SURFACE
Atmosphere from 0 km to 8 km above Sea level
Mass and Energy Balance for 1998**

Basis: 0°R & H2O(l)

INPUT: (1966)

Lower Troposphere + Earth's Surface

		<u>TEMP. °R</u>	<u>LB</u>	<u>BTU/LB</u>	<u>BTU</u>
AIR	wt%	484.000			
O ₂	23.22		1.4491E+18	105.0	1.5220E+20
N ₂	76.67		4.7862E+18	120.3	5.7571E+20
H ₂ O _(v)	0.11		6.8664E+15	1273.1	8.7417E+18
total	100.00		-----	-----	-----
Subtotal			6.2422E+18		7.3665E+20
	MW = 28.925				
EARTH (8-34")	Assumed specific heat @ 1 Btu/lb/°F		4.9773E+17	484.0	2.409E+20
	Additional UV energy to Lower Troposphere (1998)				1.6898E+18
			=====		=====
TOTAL			6.7399E+18		9.7924E+20

OUTPUT: (1998)

Lower Troposphere + Earth Surface due to 0.48° C warming (+ 0.864 °F)

AIR	wt%	484.864			
O ₂	23.22		1.4491E+18	105.2	1.5247E+20
N ₂	76.67		4.7862E+18	120.5	5.7670E+20
H ₂ O _(v)	0.11		6.8664E+15	1273.5	8.7443E+18
total	100.00		-----	-----	-----
Subtotal			6.2422E+18		7.3791E+20
	MW = 28.925				
EARTH (8-3/4")	Assumed specific heat @ 1 Btu/lb/°F	484.864	4.9773E+17	484.9	2.4133E+20
			=====		=====
TOTAL			6.7400E+18		9.7924E+20

Mass Balance = 100.00% Energy Balance = 100.00%

The additional UV-B radiation passing through the upper atmosphere is sufficient to heat the lower troposphere and the top 8-3/4 inches of the earth by 0.48 °C. The temperature of the lower troposphere and 8-3/4" of earth (land and water) in 1996 had an average heat content of 2.109 x 10²⁰ Btu and in 1998, it had a heat content of 2.4133 x 10²⁰ Btu.

The extreme northern clime (60 to 90° N latitude) surface temperatures¹² increased more than twice the average increase (1.15 °C vs. 0.48 °C) for the whole earth from 1966 to 1998. This is caused by less ozone in the stratosphere in polar climes where ozone destruction is exacerbated. There is an anomaly in Antarctica. Whereas, the Signey Island landmass that is in Northern Antarctica has warmed, south at Vostok, there has been a cooling effect. Although the cooling at Vostok needs to be analyzed in some detail, because of the large ozone hole in Antarctica, it seems likely that black body radiation from Vostok (some 11,400 feet above sea level) to outer space is most likely the cause, especially since this phenomenon occurred over the same time span that stratospheric ozone destruction took place.

Besides carbon dioxide increases in the atmosphere, methane concentrations have seen a doubling in the last 200 years¹³. A recent study¹⁴ showed that permafrost melting in North Siberia is releasing methane sequestered there since the Pleistocene era (10,000 to one million years ago) from the surface of thawing lakes. Further, methane is being emitted at a rate much greater than previously thought. The methane being released is estimated to be 100 times the rate of carbon dioxide released from the burning of fossil fuels. Methane (CH₄) slowly converts to CO₂ in the atmosphere.

Conclusion

Recent global warming is not from CO₂ but rather from chlorofluorocarbons that have destroyed stratospheric ozone. One can completely account for the recent 0.48°C rise in earth's temperature with the additional UV-B light that is hitting the earth due to ozone destruction.

Ozone destruction has also indirectly created an increase in CO₂ concentrations due to the melting of the permafrost in Siberia that has warmed over twice the average earth temperature. With the melting of the permafrost, there has been a significant release of methane. Methane slowly reacts with oxygen to convert to CO₂ in the atmosphere. Unless we remove the CFCs from the atmosphere, the whole earth will continue to be warmer than normal and higher concentrations of CO₂ will most likely exist until the CFCs in the stratosphere slowly disappear naturally over the next 50-100 years. The exceptions that could alter this in the future are large volcanic eruptions or weather modification as originally proposed by physicist Freeman Dyson, wherein fine particulate is sprayed into the stratosphere to simulate a volcanic eruption.

China and other developing countries are to phase out CFC production in 2010. Some CFC production plants have already been shutdown ahead of schedule in these developing countries, which is very beneficial. However, it would not be that difficult to remove CFCs from the atmosphere to bring earth's temperature back to normal much quicker. Although the atmosphere is intricate in the way it acts and reacts, it is clear that CFCs are the dominant cause of greater than normal earth warming over the past four decades.

Acknowledgements

I would like to thank Christopher Monckton for his support and guidance concerning the publishing of this paper. I would also like to pay tribute to three gentlemen; Paul Crutzen, Sherwood Rowland, and Mario Molina, who in my opinion saved this earth through their work on the CFC effect on the environment. If they had not worked to stop CFC production, what we are seeing now with global warming would be nothing compared to how bad it would have been without their efforts to stop its production.

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