

Why CO₂ has nothing to do with temperatures

by
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May 30, 2013

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A comparison of the virtual reality of Greenhouse Theory and the physical reality of the Earth

Or

Why CO₂ has nothing to do with temperatures

By Dr Darko Butina

Scientific literature and most science-based blog sites have been saturated with the hottest topic of them all, the greenhouse theory, GHT, and the greenhouse gases classification, GHGC. This report brings novelty to this discussion in two major ways – it looks at our planet and atmosphere as a space full of molecules and it is written by a retired scientist who worked with molecules all his working life. All molecules are real, they all have very unique physico-chemical properties and all the numbers that you will see in this report are obtained by very accurate measurements.

First we need to establish some basic definitions to avoid any confusion. The most concise description of GHT and GHGC that I found in literature comes from the recent report by John Christy, and I quote: “Earth’s atmosphere includes some gasses which have a distinctive trait: They let sunlight pass through to heat Earth’s surface, but they capture energy that leaves this sun-warmed surface. These are called greenhouse gasses.”

The problem that one has when trying to argue existence and validity of GHT is that *it is impossible to use valid scientific arguments to falsify the greenhouse theory because that theory is not based on science that deals with physical reality of our planet. It is based on a purely theoretical framework that cannot be validated by measurements and therefore cannot be falsified.*

My approach to this problem is to use all the facts that we know about our atmosphere and to explain the differences between Earth, the planet that has the atmosphere, and the Moon which does not, *without the need to evoke GHT or to blame humans or CO₂ for anything.* If I am successful, I will validate this approach and falsify GHT. However, if I *cannot explain* the physical reality that controls our planet without evoking GHT and CO₂, then I will validate GHT and falsify this report.

Before I start with the report, some background to the whole concept of global warming and the origin of GHT is needed.

On June 23, 1988, NASA scientist James Hansen announced the arrival of global warming on our planet to US politicians and the global media. Let’s keep in mind the year 1988 and address the origin of GHT and GHGC by asking three simple questions:

1. Who is the inventor of GHT/GHGC?
2. When was the key paper first published, explaining all the details and experimental evidence about GHT/GHGC?
3. Where was it published?

Let me explain to non-scientists the standard procedure that needs to be followed when publishing ‘the key paper’ informing the rest of scientific community about the new theory or classification. If you are introducing for the first time a new theory or classification labelled ‘greenhouse’ it would be expected that the term ‘greenhouse’ should appear at every part of that paper, in the title, in the abstract, throughout the paper and in the summary and the conclusions. For example, if you try to trace the ‘Theory of Relativity’, you would use a search engine like Google Scholar and you would find its author – the great Einstein quite quickly. However, if you do the same search using the same engine, *but definitely not Wikipedia*, for greenhouse theory/effect/gases all you will find are the papers going back to 1990s, and none of them give any details how the theory was developed and what its purpose is. But you are wrong, I could hear people shouting, that theory goes back to 1900 and its father is the Nobel Prize winner [Svante Arrhenius](#).

The problem with linking GHT to Arrhenius is that any scientist who has been trained in chemistry knows that Arrhenius never published in his working life a paper that uses the term 'greenhouse' and that he would never confuse physico-chemical properties of CO₂ in its pure state with the CO₂'s contribution towards the properties of the mixture called 'air'. No, the truth is that the link between GHT/GHGC and Arrhenius is one of the greatest scams in the history of science and it works in the following way:

Dr Nobody-1 publishes the paper say in 1990, entitled 'greenhouse-something' in some obscure journal that has no recognized peer reviewer system and makes the first link to Arrhenius. Then his best mate, Dr Nobody-2 writes the second paper entitled 'greenhouse-something-else' and references/cites Dr Nobody-1 paper emphasizing the link to Arrhenius made in the first paper. By the time Dr Nobody-3 publishes the third paper, the first line in the introduction section will read 'It is well established fact that the great Arrhenius is the father of GHT and GHGC. Ten years later when you type 'Greenhouse and Arrhenius' you will find that there are, say 100 citations, or references linking Greenhouse and Arrhenius. And why is this scam so foolproof? Because it is almost impossible to get hold of chemistry papers from the late 1800s and early 1900s. If you want to repeat an experiment that is published, say in German chemical journals in 1900, you will find out that there are probably only 4 libraries across the globe that keep those journals. Since those journals are all paper bound and since Arrhenius never published a paper with the title containing word 'greenhouse' it is impossible to check those artificially created links.

The fact of the matter is, that the whole religion of man-blamed science started in 1988, and since then, the same group of scientists have declared alarming global warming without publishing a single paper about the temperature trends in thermometer data, the same group of scientist have invented global temperature as a 'proxy-thermometer' without publishing a single paper about that invention and letting the scientific community know who the inventor is, the same scientists have invented the thermometer-hockey stick and then the CO₂-hockey stick without letting the scientific community know where the data is coming from. The same group of scientists have invented GHT and GHGC and yet again never published the details of that great discovery. I guess that we should be describing the period between 1988 to the present time as the **great enlightenment** era in the climate sciences since so many inventions in such a short period of time is unheard of in the history of frontline sciences.

But let us go back now, to the real science and declare the working NULL hypothesis of this paper: ***The same molecules that prevent the earth overheating during daytime are also preventing the earth overcooling during night time.*** BTW, the same NULL hypothesis existed long before invention of GHG and has never been falsified or proven wrong by instrumental data!

Part 1: Atom/elements, Molecules and Mixtures

The key part of this report is to explain the difference between the physico-chemical properties of molecules and the physico-chemical properties of mixtures. Once that difference is understood, it will become very clear why any physico-chemical property of CO₂ in its pure state has absolutely nothing to do with the physico-chemical properties of the mixture called atmosphere or air.

If we describe a universal language called Chemistry as the language based on an alphabet called the 'periodic table', i.e. atoms/elements, then each word in that language is called a 'molecule'. What is so unique about that language is that you cannot have two different words having the same meaning, since each word or molecule has a unique set of properties that are absolute and unequivocally differentiate one molecule from any other molecule. For example, the molecule CO₂ has the same properties during daytime and during night time; whether it is detected on our planet, a planet in another galaxy or an asteroid aimlessly floating in outer-space for the last billions of years. One of the key assumptions of GHT is that during daytime we have 'normal-CO₂' that allows heat energy from the sun to pass through our atmosphere 'free-of-charge' and without the need to do any work, i.e. heating the molecules in our atmosphere, while during night time, it changes to the 'werewolf-CO₂' which plays the role of the 'night time-Sun' and 'back-heats' the Earth completely free of charge and again, all that heat energy gets back to the Earth surface without doing any work.

So what about mixtures? The terms ‘atmosphere’ or ‘air’ are abstract terms that can be described as a “**mixture of different molecules in their gas phase that are NOT connected by any type of chemical bond and they do not interact with each other**”. That mixture, i.e. atmosphere or air, does NOT have **any** physico-chemical property itself but it reflects properties of individual molecules that are part of that ‘collection’. Therefore, the property of any mixture can be calculated or derived from the contribution of each molecule towards that mixture:

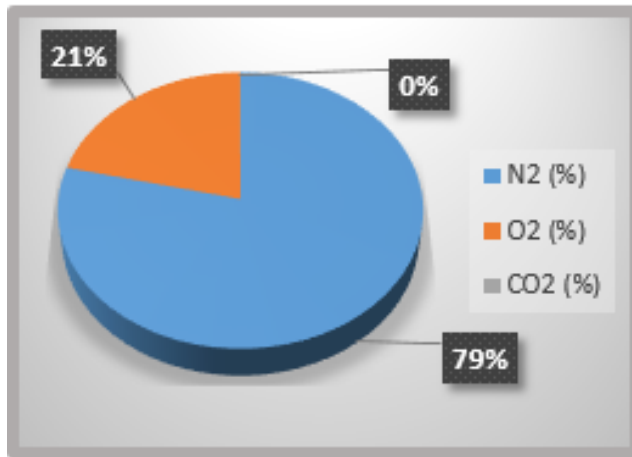


Figure 1. Contribution Index for molecules making-up the mixture called ‘air’: **N2=0.79, O2=0.21, CO2=0.0004**

What we are seeing in Figure 1 is that **every single property** of our atmosphere can be explained by its two major contributors, the **molecules of N2 and O2**. It follows that CO2’s contribution cannot be detected by any standard instruments since every property of CO2 in its pure state has to be multiplied by 0.0004 to reflect its own contribution to the resulting property of that mixture! The set of measured properties, heat capacity Cp and Cv plus density, for molecules N2, O2 and CO2, and also for air, are listed in Table 1:

Gas	Formula	%in Air	Cp (kJ/kg K)	Cv (kJ/kg K)	Density (kg/m ³)
Nitrogen	N2	78.00	1.04	0.74	1.17
Oxygen	O2	21.00	0.92	0.66	1.33
Carbon Dioxide	CO2	0.04	0.84	0.66	1.84
Air			1.01	0.72	1.21
Derived from N2+O2			1.00 (99.45%)	0.716 (99.42%)	1.192 (98.50%)

Table 1. Measured properties for N2, O2, CO2 and Air. Source: <http://www.engineeringtoolbox.com/>

The definition of heat capacity is ‘**the amount of heat energy in kJ needed to warm 1kg of gas by 1^o K**’ and since its importance in experimental sciences, very accurate measurements have been done for the most common molecules. *Please note that contrary to the GHT, every molecule has a heat capacity with molecules N2 and O2 in their pure state absorbing more heat than CO2 in its pure state.* If the law of mixtures works we should be able to derive the heat capacity for air from the measured heat capacity of its two major contributors, N2 and O2. Please note: Cp represents heat capacity at constant pressure while Cv is at constant volume.

Exercise 1: Deriving the heat capacity of air at a constant pressure, Cp, from the measured heat capacities of N2+O2 alone:

Contribution for N2: $(78.0/100) \cdot 1.04(C_p) = 0.81 \text{ kJ/kg}$

Contribution for O2: $(21.0/100) \cdot 0.92(C_p) = 0.19 \text{ kJ/kg}$

Total contribution (calculated) N2 +O2 = 1.00 kJ/kg Measured (air): 1.01 kJ/kg per 1K

Exercise 2: The heat capacity of air at constant volume, Cv:

Contribution for N2: $(78.0/100) \cdot 0.74(C_v) = 0.58 \text{ kJ/kg}$

Contribution for O2: $(21.0/100) \cdot 0.66(C_v) = 0.14 \text{ kJ/kg}$

Total contribution (calculated) N₂ +O₂ = 0.72 kJ/kg Measured (air): 0.72 kJ/kg per 1K

If we want to calculate the contribution of CO₂ (used as 0.04% or 400 ppm for simplicity) towards any property of air all that is needed is to multiply that property with the ‘CO₂-contribution index’ (0.04/100) which is **0.0004**:

The contribution of CO₂ towards the heat capacity of air: (0.04/100)*0.84 (C_p) = **0.00034 kJ/kg**, or in terms of CO₂ contribution towards 1^oK of warming, 0.0004*1 = **0.0004^oK**.

Therefore, for air to warm by 1^oK, CO₂ contributes exactly **0.0004^oK**, or if we double the concentration of CO₂, that amounts to massive **0.0008^oK** of warming! *I think that there is a quite clear message here – don’t estimate the contribution of CO₂ towards warming, look it up.*

If we now look at the air mixture from N₂+O₂ vs. CO₂ ratios:

- **999600** ppm of air belong to N₂+O₂ molecules, while **400** ppm to CO₂ molecules (**2500 : 1** ratio)
- From a single CO₂’s molecule point of view, **1 molecule of CO₂** is surrounded by **2500 molecules of N₂+O₂**

The explanation that GHT offers, is that this mysterious blanket does not exist during daytime, but is acting as the ‘proxy-Sun’ during night time. The ‘texture’ of the blanket consists of 2500 parts of ‘nothing’ and 1 part of ‘everything’ and while 1 part of ‘everything’ is extra-warming the whole of the Earth, 2500 parts of ‘nothing’ are just sitting there and doing nothing. A good analogy would be buying Swiss cheese where the ‘cheese bit’ is CO₂ while the ‘holes bits’ are N₂+O₂. If you believe in GHT, you would buy an empty pack of Swiss cheese which would taste really great **but only during night time** when the ‘cheese-bit’ miraculously appears out of nothing. However if you are the person who uses his/her brain you would see that as a great scam.

Since everything in this report is connected with reality and measurements using ‘real’ instruments, let us look at NASA’s depiction of how the thermometer works:

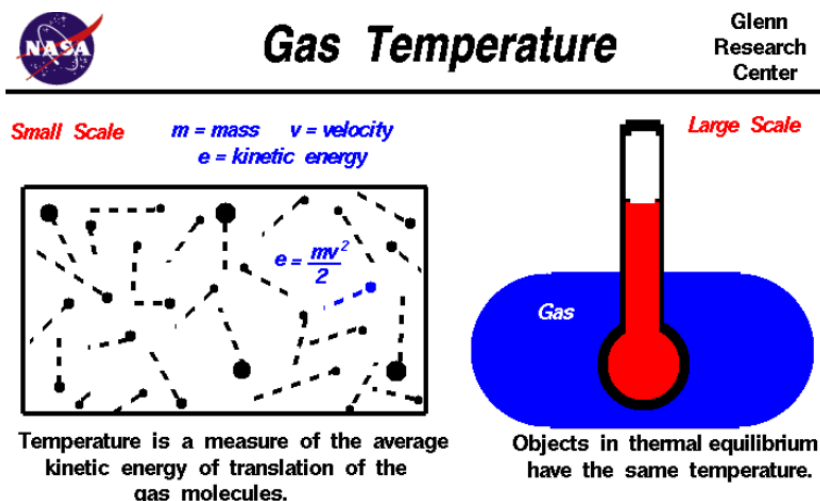


Figure 3. Thermometer in thermal equilibrium with the molecules surrounding it

What the figure above is telling us is that the number recorded by the thermometer is not just ‘another’ number, but the number that has physical meaning – it reflects the kinetic energy of the molecules that are surrounding that thermometer. If we connect Figure 3 with the ratio of N₂+O₂

molecules to CO₂ molecule of **2500:1** in the mixture called ‘air’, and if thermometer has an accuracy of +/- 0.5 C it becomes obvious that CO₂ with its contribution index of 0.0004 will not influence the thermometer.

Any experiment that involves air and standard thermometer will be detecting properties of only two molecules, N₂ and O₂.

It is the same with a standard IR-spectrometer – if we put, say 1g of air in spectrometer, all we will get is a flat line at 0% absorption indicating that no molecule in air is absorbing in IR. But how does that fit with IR-based CO₂ detectors? They are specialised instruments that are not calibrated on the total mass that enters the detector but only take into account the amount of CO₂ that can be detected, i.e. 99.99% of molecules in the air sample are being ignored.

Part2: Atmosphere and Water Mass

The amount of overheating and overcooling could be seen in the table below:

	Max Temp (in C)	Min Temp (in C)
Moon (Z=0)	123.0	-233.0
Earth (Z=0)	58.0	-89.0

What makes our planet so unique is the fact that it retained water in its liquid state for millions of years and without that molecule we would not be discussing GHT today. What is important to realize is that everything on our planet is local and nothing is global, including temperatures.

To estimate the number of molecules that make-up our atmosphere and the oceans, we need some accurate coordinate system where X-Y plane at Z=0 represents sea-levels, Z= +100km represents the top of the atmosphere and Z= -4km represents the average depth of oceans:

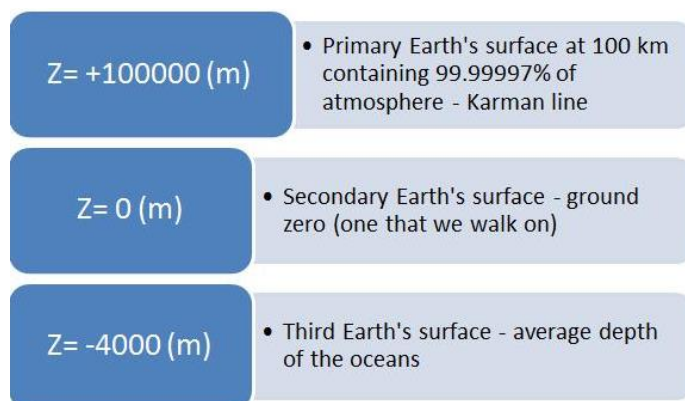


Figure 2. Boundaries that define atmosphere and water heat capacity

The total volume of our atmosphere is between **Z=0** and **Z = +100km**, while the total volume of our main heat storage, i.e. the oceans, is between **Z=0** and **Z = -4km**. In contrast, the Moon’s atmosphere is between Z=0 and Z=0, while the Moon’s water heat storage does not exist.

Estimating the number of molecules in atmosphere and the oceans

1 mol of any molecule contains 6×10^{23} molecules, known as Avogadro number. **1 mol of any gas molecule** occupies volume of **22.4 litres**; therefore **1 litre of any gas molecule contains 0.04 mols per litre** ($1/22.4 = 0.04$). To estimate the total number of molecules contained within our atmosphere we need to multiply the total number of litres in atmosphere by 0.04 mols and **by 6×10^{23} molecules**.

On the other hand, **water in its liquid state contains** 1000g of H₂O per 1 litre, and having a molecular weight of 18 grams it means $1000/18 = 55.6$ **mols per litre**. Therefore, 1 litre of liquid water, i.e. the oceans, have $55.6/0.04 = 1390$ more molecules per litre than 1 litre of our atmosphere.

It is estimated that our **atmosphere contains 4.2 billion cubic kilometres of air**, while our **oceans hold 1.3 billion cubic kilometres of water** in its liquid state. Since every molecule has heat capacity, a huge amount of the sun's heat energy will be used during the daytime to keep warming this incomprehensibly large number of molecules that occupy the space between $Z = +100\text{km}$ to $Z = -4\text{km}$.

The heat capacity of Air and the Oceans

The heat capacity of air (C_p) is 1.01 kJ per 1kg, Table 1, and for simplicity of calculations I will approximate it to be 1.0 kJ/kg. The sun will use **1kJ** of its energy to warm **each kg** of air by **1°C**. There are quite a few estimates of the mass of our atmosphere but all of them come up with the same number, **10^{18} kg**. To put that in perspective – once the heat energy from the sun enters our atmosphere and by the time it reached $Z=0$ level it had to use **1.0×10^{18} kJ to warm-up air molecules by just 1°C!** And then, the water that covers 70% of our secondary surface at $Z=0$ comes into the equation! The heat capacity of water is 4.2 kJ/kg with the best estimates that our 'hydro-mass' is around **10^{21} kg** which means **4.2×10^{21} kJ would be needed to warm-up our hydro mass by just 1°C!** Bearing in mind that water's heat capacity is 4 times larger than the heat capacity of our atmosphere and that 1 litre of water has 1390 times more molecules than 1 litre of air, it is estimated that the top 8 meters of oceans can store the same amount of heat as the whole of the atmosphere.

Let me remind the reader that the **two main assumptions** that the GHT is built upon are:

- That the heat energy from the sun simply 'deposits' itself at the $Z=0$ level during daytime without doing any work and all the work that GHG are doing is during night time
- That we should be able to balance all that energy along the lines – that what comes in must come out, i.e. that the heat energy does not do any work and that it cannot be stored in our oceans for long periods of time

However the physical reality that is controlling our planet tells us a completely different story. There are the same number of molecules in total, between our atmosphere and hydro mass and **all** of them have heat capacity and therefore will absorb the heat energy whether it is coming from the sun down or from $Z=0$ going up. There are **only two types of molecules** that count when it comes to **atmosphere, N₂ and O₂** with **total heat capacity** at around **10^{18} kJ**. There is **only one molecule** that counts when it comes to our **oceans**, and that is H₂O with the **heat capacity** of **10^{21} kJ**.

What complicates the thermodynamics of **top-water-layer-to-air** exchange and **top-water-to-bottom-water** exchange is that the temperature at the bottom of the oceans is just above 0°C so there is this great competition during night time between the surface water warming-up air above it, and warming the cold water below. The scientists who study the oceans tell us that to 'up-well' the cold waters from the oceans' floor to the surface might take up to 1000 years meaning that the sun's heat energy has to work very hard, very slowly and for long, long time to bring all those water molecules from the oceans' floor back to the surface.

Let us summarise the facts presented so far and compare the assumptions used to postulate greenhouse theory and greenhouse gases classification against the well-known and well understood physico-chemical properties of molecules that make up our atmosphere and the oceans:

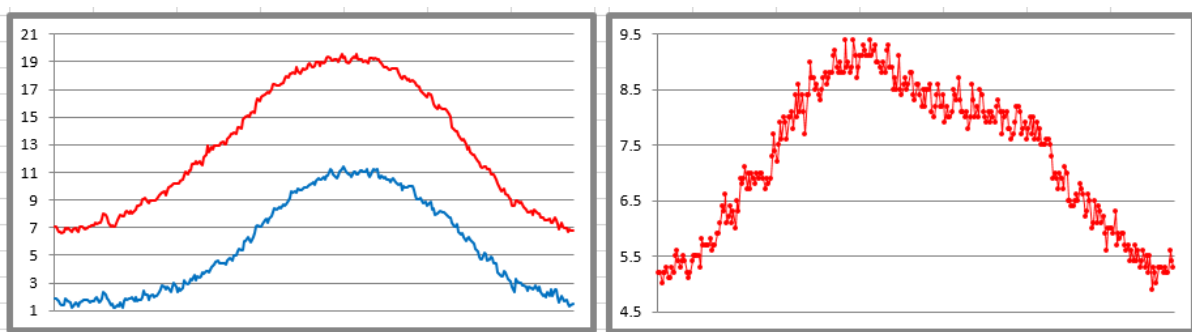
1. It assumes that the surface of the earth starts at $Z=0$ while in reality it starts at $Z= +100$ km. Error=100km and **4.2 billion cubic kilometres of air**
2. It assumes that the oceans do not have any depth. Error=4km and **1.3 billion cubic kilometres of water**
3. It assumes that the atmosphere does not have heat capacity during day time. Error= **10^{18} kJ**
4. It assumes that the oceans do not have heat capacity during daytime. Error= **10^{21} kJ**
5. Same assumptions as in 3. and 4. have been made for night time, with the same errors
6. It assumes that N_2 and O_2 do not have heat capacity. Error: 99% of **10^{18} kJ**
7. It assumes that molecules have different properties depending whether it is daytime or night time. This is not an error but either ignorance or fraudulent science
8. It assumes that the properties of molecules in their pure state is the same thing as their properties when part of a mixture. This is not an error but either ignorance fraudulent science
9. It assumes that the CO_2 molecule functions as the 'night-time-sun'. Error: **10^{18} kJ + 10^{21} kJ**
10. It assumes that 1,000,000ppm=400ppm. Error: 2500

The above list could be also called '**10 reasons for mankind to be cheerful**', since whatever is happening with the temperature patterns on our planet, it has nothing to do with burning fossil fuels, with CO_2 or us. We are all protected by 3 molecules, N_2 and O_2 in the atmosphere and H_2O in our oceans.

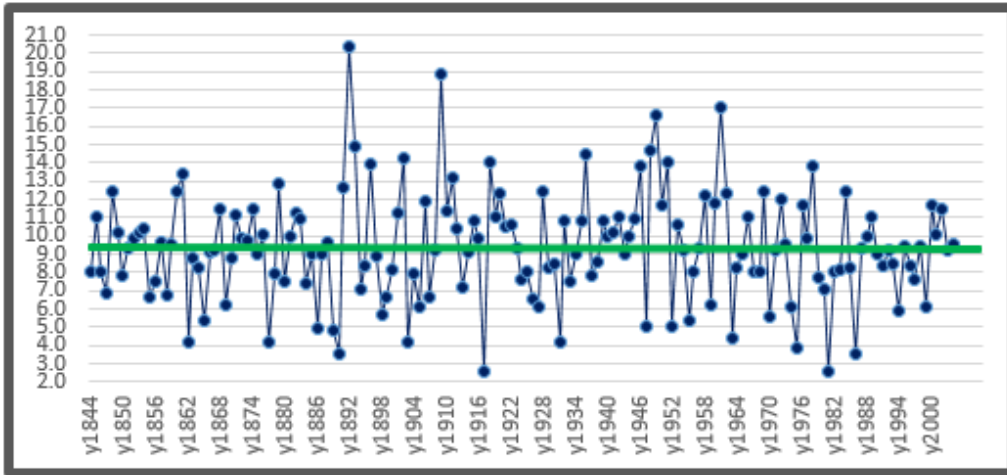
Numbers: Virtual Reality vs. Reality

The IPCC's report in 2007 quotes the increase of 'global temperature' by $0.7^\circ C$ in the last 100 years which translates to $0.007^\circ C$ per year.

So let us come back to real Earth, look at some real numbers and see how 'sensitive', in terms of temperatures our planet really is. But to appreciate this part we must view the earth as a very dynamic system without any equilibrium and where each 'fixed-to-ground' thermometer has its own and unique history. The dataset comes from one of the oldest archive of daily thermometer data that is in the public domain, the Armagh Observatory, UK, and covers the years between 1844 and 2004. All the details about this dataset can be found in my recent publication at www.l4patterns.com.



The graph on the left compares daily T_{min} averages against the corresponding T_{max} averages for each of 365 days over 161 years (1844 to 2004). The graph on the right represents a difference between T_{min} and T_{max} for each day. So, the average difference between T_{max} and T_{min} (January 1) is around $5^\circ C$, while the largest difference of $9.4^\circ C$ were observed on May 10, May 18 and June 3. So let us look at one of those days, May 10, and see what information in terms of heat energy from the sun we can extract from the daily data:



Since we are now looking at a single day, the X-axis represent the year when the difference between Tmax130 and Tmin130 (May 10) was observed. Four largest differences were observed in 1892(20.4C), 1909(18.9C), 1949(16.6C) and 1961(17.0), while the lowest differences observed in 1917(2.6C) and 1981(2.6C). The importance of the above graph cannot be overstated, since it gives us the key information about the **maximum amount of the heat energy from the sun that is available to molecules surrounding the Armagh's thermometer** on each day and in each year. For example, the largest amount of energy, 20.4 kJ/kg (remember that the heat capacity of air is 1kJ per 1C, i.e. 1kJ=1C), was available on May 10 in 1892 enabling temperature increase of 20.4C from the night time temperature, Tmin, to the Tmax on May 10, 1892. In order for us to understand Tmax temperatures we must understand the corresponding Tmin temperature. When we take the difference between Tmax and Tmin on any given day and on any given year, we are detecting the maximum amount of heat energy available to the molecules (N₂+O₂) surrounding that thermometer and it follows that in order to understand the trends in Tmax space, we must first understand the trends in Tmin space, since the former is the result of the energy available to the latter. And to understand those trends we need the right type of data, yes, that 'must-not-be-mentioned', the daily thermometer data. Also note that the variations in daily energy/temperature ranges are in tens of °C in the real world of our planet, while in tenths of 1C in the virtual world of some single point in the space called 'global temperatures'.

When it comes to temperatures or CO₂, the future research should be to treat the two as a completely different and not connected topics. If one wants to understand the temperature patterns on our planet, then the answer can be found in the understanding of the source of that heat, the sun, and the movements of the physical objects that make-up our atmosphere and stand between the sun and the thermometer at Z=0, i.e. the molecules of N₂ and O₂ at different weather stations.

If however, one wants to understand different observed concentrations of CO₂ at the ground level, one has to look at the water-to-air dynamics, driven solely by solubility of CO₂ in water and therefore by temperature, and at the biomass-to-air dynamics driven solely by photosynthesis and therefore by CO₂, water and sunlight. A report dedicated to CO₂ along the lines: 'Everything you wanted to know about CO₂ but afraid to ask' will appear on the CO₂-page by the end of this month, May 2013.