The Carbon Cycle
and
Royal Society Math

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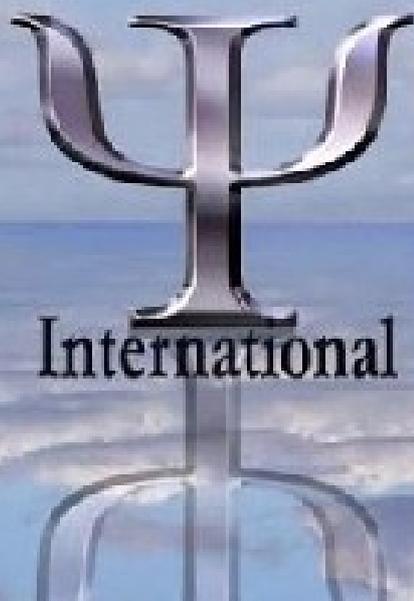
The Carbon Cycle and Royal Society Math

By Dr Klaus L.E. Kaiser*, 3 March 2014

THE CARBON CYCLE

I would like to provide my thoughts on two aspects, namely (i) the carbon cycle and atmospheric carbon dioxide, and (ii) the Royal Society's claim of longevity of atmospheric carbon dioxide (CO_2).

In both issues, I am using order-of-magnitude approaches to calculate some critical numbers. That kind of approach is very useful when trying to get an overview of an issue, without getting lost in burdensome details.

Amount of Carbon in Air

Using a simple approximation of the atmosphere's height as 10 km, but entirely at 1 atmosphere pressure (which should account roughly for the lower density both below and above 10 km height), the volume of air in our atmosphere calculates to:

$$4/3 \times (6.510^6 \ [m])^3 - (6.500^6 \ [m])^3 \times pi \ = \ 5 \times 10^{18} \ [m^3]$$

At a concentration of ~400 ppm, or ~0.04% by volume, of CO_2 in the air, and the mass of air being ~1 kg/m^3 times a weight/volume factor [8] of 1.5, there is or 0.06% by weight, or 0.0006 kg of CO_2 in one m^3 of air.

With the atomic mass of carbon being 12 and oxygen 16, hence the molecular weight of CO_2 being 44, the mass of carbon in CO_2 comes to approximately one quarter of that, or ~25%, or 0.00015 kg C [as CO_2] per m^3 of air. Therefore, the amount of **carbon in the air** (in the form of CO_2) calculates to:

$$5 \times 10^{18} \ [m^3 \ (air)] \times 0.00015 \ kg \ [C]/[m^3 \ (air)] \ = \ \textbf{7.5} \times \textbf{10}^{\textbf{14}} \ \textbf{(kg [C])} \ \textbf{in the air \{Value A\}}$$

Carbon Emissions from Fossil Fuels

Now let's look at the amount of carbon (dioxide) produced by the combustion of fossil fuels. There are four major sources. Values for three of those are easy to obtain, namely oil, coal, and natural gas.

(i) Oil

The world consumes approximately 85 million barrels of crude oil per day. The extraction or recovery processes themselves require energy, so, for simplicity, let's round the 85 to 100 million, or 10^8 barrels/day. One barrel of oil is close to 159 liters. The density of crude oil varies with the source and ranges from ~0.8 to ~1.0. So, let's approximate one barrel to be 150 kg oil. As oil, chemically is essentially [CH_2], i.e. ~85% carbon, let's further approximate one barrel of oil to be ~150 kg carbon. Therefore, the global amount of carbon (as carbon dioxide) emitted from the combustion of crude oil is:

$$10^8 \times 150 \ (kg \ [C]) = 1.5 \times 10^{10} \ (kg \ [C])/day, \ times \ 350 \ days/year = \textbf{5} \times \textbf{10}^{\textbf{12}} \ \textbf{(kg [C])/year}$$

Not all of the crude oil produced is (eventually) combusted, as a significant proportion of the distillate residues is used for road building, etc. However, there also is a significant amount of CO2 produced in the production of crude oil and its distillates. Most of that CO2 is not normally accounted for in the CO2 equation. In addition, significant amounts of methane are being produced alongside the oil in many areas and mostly disposed of by flaring it off. Therefore, I think that my estimate is rather at the low end of the possible range of estimates by disregarding the large amounts of CO2 produced in the oil production and refining processes.

(ii) Coal

The world consumes more than double the amount of crude oil in the form of coal. The latest numbers available are for 2008 [1]. No adjustment of any sort is necessary, and that consumption is:

$$7 \times 10^{12} \text{ (kg [C])/year}$$

(iii) Natural Gas

In 2007 the world's natural gas consumption was in the order of 3.2×10^{12} (m^3 [gas]/year) [1]. Natural gas is largely composed of methane, chemically CH4, but also to varying degrees (up to 20%) of the compounds ethane [(CH3)2)], propane and butane. For simplicity then, we use the same approximation as for oil, namely [CH2]. Under normal (atmospheric) pressure, therefore, one cubic meter of gas contains approximately 40 mol of [CH2], and with 12 [g [C]/mol] = 500 g ([C]/m^3) = 0.5 (kg [C])/(m^3 [gas]). Therefore, on an annual basis, the world production of carbon (in the form of CO2) is:

$$3.2 \times 10^{12} \text{ (m^3 [gas])/year} \times 0.5 \text{ (kg [C])/(m^3 [gas])} = \mathbf{1.6 \times 10^{12} \text{ (kg [C])/year}}$$

This value is definitely at the low end of the range of estimates as it does not include the large amounts of natural gas used in the extraction of the gas plus what is used up in compressing and/or cooling to send it to storage or for shipment as liquefied natural gas.

(iv) Wood

Wood and other solid biofuels, such as dung, are used widely around the world, both for cooking and heating. For example in the USA, wood pellets can be purchased in bag quantities to burn for space heating. In northern areas, outdoor burners, heating hot water for consumption and space heating via closed circuits, require a few large logs per day and have automatic air dampers, which open on demand (for more heat). In Europe, wood chip heating systems allow completely automated operation for weeks without the need for a refill.

In many countries, say in the latitude range 30 to 60 degrees (in both hemispheres), wood from abundant trees and bushes is the primary source of energy for cooking and heating. In other areas, not normally requiring home heating but energy for cooking, dried dung from animals is used.

Of course, much wood goes into construction. Some of that is used and later re-used or discarded. Other parts are incorporated into structures, from house frames and beams to furniture. In that form, wood often resides for many decades, or even centuries without change. But eventually it will be disposed of to either rot or be burnt. In either case, the result is conversion to CO2 (in the case of rot via intermediate compounds) which is released to the atmosphere. So, from that perspective alone, only the consumption of wood (including that which is not directly intended for heating purposes) is relevant.

The estimated world harvest of wood for all uses for the year 2007 is ~3.5 10^9 cubic meters, approximately one half of which is used directly for heating. At an estimated carbon content of 50% (the rest is water and minerals), that equates to

$$3.5 \times 10^9 \times 10^3 \times 0.5 = \mathbf{0.75 \times 10^{12}\ (kg\ [C])/year}$$

(v) Total Anthropogenic Carbon Emissions
Simple addition of the numbers of carbon amounts from the different sources provides an estimate of the global annual contribution of anthropogenic (man-made) CO2 to the atmosphere. This number comes then to

14.3 x 10^12 (kg [C])/year, rounded to **14 x 10^12 (kg [C])/year {Value B}**

The US Department of Energy (US DOE) released, on Jan. 31, 2011, its latest estimate for the global anthropogenic (man made) release of CO2. It was **30.5 x 10^12 (kg [CO2])/year,** or **9 x 10^12 (kg [C])/year. As the reader will note, my own estimate, which I believe to be quite conservative, is approximately 1.5 times that of the US DOE.**

Carbon Emissions from Natural Sources
The amount of CO2 released annually by natural sources on the globe is rather difficult to ascertain or even to estimate. However, there are some measurements and data which can shed more light on that. It should be noted, that in this context, no net gain or loss of CO2 from the photosynthesis and respiration by plants will be considered, rather only net additions from non-biological sources.

For example, the Kilauea volcano on the Island of Hawaii alone is estimated to emit 9x10^6 kg [CO2] per day, or (9x10^6 x 12/44 x 350 = ~10^9 kg [C] per year, out of a few vents [2]. Of course, there are thousands of other volcanic vents, all around the globe, that emit CO2 on a continuous basis on land alone. In addition, there are thousands of vents beneath the sea, along the continental plate boundaries, along fault lines and hotspots inside the earth. Altogether, these zones of volcanic activity comprise a stretch of 60,000+ km in length.

Furthermore, there are a number of active volcanoes on the earth. Most do not erupt in continuous fashion, but in spurts of massive events, where many cubic miles of material, lava, ash and gas, are emitted over a short period of time. For example, the Eyjafjallajokull volcano on Iceland, which erupted in April, 2010, Mt Sinabung on Java, Indonesia, which erupted in 2010, 2013 and 2014, Mount Kirishima Shinmoe volcano in Japan, which erupted in February, 2011, Mount Kelud on Java, Indonesia which erupted on 15 February 2014 are examples of such volcanoes. All had been dormant for many years. The Bezymianny volcano, Kamchatka, Russia, is one of the world's most active volcanoes, erupting explosively approximately once per year. Erupting volcanoes exist somewhere on earth almost all the time. In fact, according to the Global Volcanism Program of the Smithsonian's National Museum of Natural History [3], there are 20 volcanoes that are erupting each day. This number does not include active volcanoes in the deep oceans.

The composition of volcanic gases varies considerably. Apart from water vapor constituents include CO2 and SO2 (sulfur dioxide), H2S, COS, CH4, H2, CO, Ar, N2, HCl, and HF. Together, these gases typically comprise between 90 and 99% of the dry gas of which CO2 and SO2 commonly make up the bulk.

While certainly not the only gas emitted by most volcanic eruptions, CO2 is most commonly also the main component in that mixture. Changes in the CO2/SO2 molar ratio of pre-eruption gases have been used to predict eruptions. That ratio though varies considerably between different volcanoes, namely from ~1:1 to ~100:1. But for many eruptions, it is in the neighborhood of 50:1. Using that estimate mean ratio (50:1), and estimated values for SO2 emitted from the Krakatoa eruption (in 1883) of 100 x 10^9 (kg [SO2]), and the Pinatubo eruption (in 1991) of 20 x 10^9 (kg [SO2]), one can estimate the corresponding amounts of CO2 emitted to 1.25 x 10^12 (kg [C]), (or 5 x 10^12 (kg [CO2]), and 0.25 x 10^12 (kg [C]), respectively.

Using a value of only one **1/100** of the (total) Pinatubo eruption, i.e. 0.0025 x 10^12 (kg [C]), on a per day basis and multiplying with the minimum number of volcanoes that are erupting daily (see above), multiplied by the number of days per annum, the result is probably a big surprise to many readers:

0.0025 x 10^12 (kg [C])/ day x 20 [volcanoes] x 365 [days/year] = **17 x 10^12 (kg [C])/year**

That value, of course, is only considering land-based active volcanoes. As the surface area of the oceans is approximately four times that of the land mass on earth, and assuming a similar distribution of volcanoes beneath the sea as on land, four times the amount of CO2 from land-based volcanoes could be contributed by sea-based volcanoes. However, not all of the CO2 from undersea volcanoes and vents will actually make it to the surface of the ocean and then to the atmosphere. Much of the gas is likely being intercepted and dissolved within the deep water column from where it will be precipitated as carbonate salts. Therefore, for the mass balance calculations here, let's assume that only one half of the sub-sea gas emissions will reach the ocean surface, to be added to the atmosphere as CO2. As a result, an additional amount of 35 x 10^12 kg [C] per year gets so added by natural emissions beneath the sea.

In total, the amount of CO2 from natural sources added to the atmosphere is then:

52 x 10^12 (kg [C])/year {Value C}

This amount equals approximately 1/10th of the total amount of carbon in the earth atmosphere (as CO2) and is approximately four times the total anthropogenic CO2 emissions from all natural carbon fuels per annum at this time.

THE ROYAL SOCIETY'S MATH

The recent "rebellion" by senior members of the *Royal Society* (RS) forced it to revise their guide "Climate change: a summary of the science". The new guide [5], published on September 30, 2010, has a single paragraph under the heading *The Carbon Cycle and Climate*. In that, it says:

*"Current understanding indicates that even if there was a complete cessation of emissions of CO2 today from human activity, **it would take several millennia for CO2 concentrations to return to preindustrial concentrations"** [emphasis added].*

Can that be true?

Let's try to figure it out. We know already some important numbers:

(i) CO2 in Air, Amounts and Rates of Addition, Calculated from Emissions

As described in the paragraphs above, the following values can be calculated with reasonable certainty:

Total CO2 in the atmosphere **{Value A}**:	**750 x 10^12 (kg [C])**
Total CO2 emissions from anthropogenic sources **{Value B}**:	**14 x 10^12 (kg [C])/year**
Total CO2 emissions from natural sources **{Value C}**:	**52 x 10^12 (kg [C])/year**
Total CO2 emissions from all sources {**Values B+C= Value D**}:	**66 x 10^12 (kg [C])/year**

(ii) CO2 Increase, Calculated from Change in Air Concentrations

Knowing both the total amount of CO2 in the air and the change of CO2 concentration, using the average concentration and annual change over the last twenty years of ~1.8 ppm/year [4], we can calculate the **net increase (from all sources) to the atmosphere as follows**:

750 x 10^12 (kg [C]) x 1.8 [ppm/year] / 400 [ppm] = 3.4 x 10^12 (kg [C])/year {Value E}

(iii) Rate of Removal of CO2

(a) Removal of Anthropogenic CO2

As we have already calculated the total anthropogenic production of CO2 {Value B} as 14 x 10^12 (kg [C])/year, if there were no removal at all, the concentration in air would rise by {Value A}/{Value B} = 2% or 8 ppm per year. As the observed rate of increase is only a 1.8 ppm per year it is obvious that there is a strong natural removal process in place.

Just for argument's sake, if we were to assume that all net addition of CO2 to the atmosphere was solely from anthropogenic sources, the net amount of (anthropogenic) addition minus increase in the air, gives the (**minimum**) rate of removal of anthropogenic CO2 from the air, namely {Values B-E= Value F}:

(14-3.4) x 10^12 (kg [C])/year = **11 x 10^12 (kg [C])/year {Value F}**

In other words, only ~20% of the anthropogenic CO2 would remain in the atmosphere after one year.

However, the removal **{Value F} of 11 x 10^12 (kg [C])/year must be considered as a maximum value for anthropogenic CO2 as it would imply the concurrent, additional 100% removal of the entire net additions of CO2 from natural sources.**

Nature cannot different between anthropogenic and natural CO2. Therefore, CO2 from both sources will be removed at equal rates.

(b) Removal of Natural CO2

Prior to mankind's large scale burning of fossils fuels, beginning, say, 200 years ago, the concentration of CO2 in the atmosphere was approximately 300 ppm. The anthropogenic addition of CO2 at that time was negligible. However, the natural processes of CO2 addition and removal were already in place for many millions of years. Therefore, the subsequent addition of anthropogenic CO2 would not have changed those natural rates to any large extent.

So, if the rate of removal, as calculated above as 11 x 10^12 (kg [C])/year, would not have been balanced by equal additions from natural sources, the earth's atmosphere would have become depleted of any CO2 in a very short time, namely (500/11) = 45 years. Obviously, that never happened.

In fact, the earth's atmosphere never had much less than 200 ppm CO2 but was rather at much higher concentrations in prehistoric times. Because the natural carbon sinks cannot differentiate between anthropogenic and natural CO2, the natural removal processes apply equally to both. That means that the minimum rate of carbon removal must be greater than the **{Value F}** below:

Total CO2 removal by natural processes (**minimum), {Value F}**:   11 x 10^12 (kg [C])/year

If there were no natural CO2 removal processes at all, the CO2 concentration in the atmosphere should then double at a rate of (750/14) or approximately every ~50 years. However, as shown above, the total emissions are much larger and the CO2 increase even less. Therefore, the actual rate of CO2 removal must be much larger, at least in the order of 10(+)^13 kg [C]/year.

This number is calculated from the total amount present in the air divided by the sum of annual additions from both natural and anthropogenic sources. However, over the last 100 years, at most it has increased by only 1/3, i.e., from approximately from 300 to 400 ppm (parts per million by volume).

This much lower than expected increase (based solely on fossil fuel and biomass consumption) in the atmospheric CO2 can only be explained by strong natural removal processes.

The total CO2 removal cannot be any less than the sum of additions (from all sources) less any observed increase in the atmosphere. Therefore, assuming that the calculated additions from natural sources {Value C} are correct, hence the sum of all additions being **66 x 10^12 (kg [C])/year**, the total removal (of all CO2) by natural sinks must be several times larger, namely below or near {Value G} as shown below:

Total CO2 removal by natural processes (**maximum), {Value G}**:   54 x 10^12 (kg [C])/year

If the CO2 were to stay in the atmosphere for millennia (practically meaning having a negligible rate of removal), why has its level in the atmosphere not doubled in the last 8 to 10 years, or increased tenfold-plus over the last 100 hundred years? Even if there were no natural sources whatsoever (and no removal), the CO2 in atmosphere from anthropogenic sources alone would have had to have doubled (to 600 ppm [v/v]) over the last 35 years alone. Obviously, that has not been the case.

It is also obvious then that the statement by the Royal Society that it would take "millennia" for atmospheric CO2 to return to levels at preindustrial times upon a (theoretical) complete and sudden cessation of all manmade CO2 release to the atmosphere cannot be true. As mentioned already, nature cannot differentiate between a CO2 molecule from natural and one from anthropogenic sources (disregarding variations between carbon isotopes). It is also evident that the natural sources of CO2 are far greater than those from the combustion of fossil fuels.

Furthermore, there are several peer-reviewed papers reporting the residence time (RT) of the average molecule of CO2 in the atmosphere to be between 5 and 10 years.

For example Essenhigh [6], who reviewed these figures, concluded that the RT of CO2 in the atmosphere is somewhere between 5 (for ^{12}CO2) and 16 years (for ^{14}CO2). In a similar review, Segalstad [7] also concluded the RT of CO2 to be close to 5 years. A variety of other indirect methods, using carbon isotope ratios and the like, all came to similar conclusions.

The meaning of the term "residence time" is similar to that of the term "half life", though the latter is mostly used in conjunction with radioactive decay. A half-life of, say 5 years, means that more than 98% of a substance will disappear in a time span of 30 years. In terms of a lake, for example, "residence time" (RT) is commonly defined as "the average time a particular molecule of water will remain in a body of water", when considering its volume and the volumes of all inflows and outflows per time. Hence, a RT of, say, 5 years, would mean that - if there were a 100% exchange of resident with non-resident molecules - the entire mass of water would be replaced in 5 years. In practice, of course, that is not the case, as there is always mixing of old and new water. This is not any different in the atmosphere. Also, there is no way to differentiate between two molecules of the same isotopic make-up, whether they have existed for millions of years or are brand new, they are simply identical and cannot be distinguished. Hence, the natural carbon sinks cannot differentiate between anthropogenic and natural CO2.

Therefore, even if the RT of CO2 in the atmosphere were only, say, one year, it can be demonstrated that, statistically, there would still be millions of CO2 molecules residing in today's atmosphere that had been emitted by small fires lit in caves by the Neanderthals, some 100,000 years ago. Of course, such a conclusion is entirely meaningless in the context of anthropogenic CO2 concentrations in the atmosphere. The residence time of some individual molecules does not constitute any knowledge on residence time of the average molecule, or the annual turnover rate of the total in that environment.

Returning then to the original question, namely: Can it be true that "*it would take several millennia for CO2 concentrations to return to preindustrial concentrations?*" One can easily conclude that the answer must be: **No.** Furthermore, it is simply a follow-up conclusion that **The Royal Society's statement is wrong.**

But, what else does it mean? Again, that is easy to answer:

1. First, it means that the turnover rate (addition to and removal from the air) of CO2 is orders of magnitude faster than implied by the RS statement.

2. It means that CO2 in the atmosphere is rapidly being taken up by the plants on land and even more so by the oceans. In the oceans, CO2 gets converted to organic matter through photosynthesis. That is the process from which essentially all life on earth is derived. If the statement by the RS about the longevity of CO2 in the atmosphere were true, CO2 levels in the air would have increased – from both mankind's influence and natural sources - not just by a few percent, but by a factor of 2 or so *over the last decades alone*. Clearly, that is not the case.

3. Last but not least, it means that the whole CO2-climate-change scenario, as portrayed by the RS (and many others for that matter) is in shambles. As the CO2 from mankind's burning of fossil fuels and the much larger emissions from natural sources are consumed by organisms on land and in the water at a rate nearly identical to that of its total addition, it could not possibly take "several millennia" to return to a pre-industrial level upon a (theoretical) cessation of all of mankind's CO2 emissions.

In summary

The Royal Society's claim that it would take millennia for CO2 from human activity to dissipate from the atmosphere is clearly untenable. However, it would also appear inconceivable to think that the RS would not have done a few of such simple order-of-magnitude calculations, as shown above, to confirm the veracity of their claims. Therefore, even though it took months to prepare the revision to their previous document on that subject, it appears **the Royal Society's math is still wrong.**

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