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Climate Physics: Classical Thermodynamics Applied to Greenhouse Gas and Climate Change Hypotheses

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Abstract

Using the Gibbs concept of state functions to define the first and second laws of thermodynamics, we analyse the effects of changes in atmospheric average temperatures and pressures arising from anthropogenic emissions of enthalpy and water, besides CO_2, into the atmosphere. An application of the Hess-Gibbs 1st law of thermodynamic equilibrium (H is a state function) shows that the enthalpy (H) output from fossil fuel consumption is seven times greater than the H-increase of the mean global warming index (GWI), presently 0.0175 K/year, that has given rise to the greenhouse gas hypothesis (GGH). The Joule-Mayer 1st law of irreversible thermodynamics (conservation of energy) shows there is a level of inherent uncertainty, in any multivariate computer model of the global energy budget, which is more than 1000 times the experimental enthalpy flux associated with the GGH. The Carnot-Gibbs 2nd law of thermodynamic equilibrium: entropy and Gibbs energy of water are state functions if its concentration is a well-defined state variable. Here, this concept is used to assess the effect of water vapour output from fossil fuels on climate-change hypotheses (CCH): we report that an anthropogenic global wetting effect of fossil fuels is not negligible. We assess the global effects of endothermic photosynthesis processes in the biospheres land and ocean sinks which, in accord with Le Chatellier principle of Gibbs chemical equilibrium, are enhanced by the anthropogenic increases in both [CO_2] and [H_2O] in the atmosphere. Whereas the long-term effect of the ocean sink may be negligible due to its massive heat capacity, we report evidence of an endothermic effect upon biosphere land areas, which offsets the enthalpy output from the energy industry to a significant extent.

Keywords

Atmospheric Thermodynamics, Fossil Fuel Emissions; Global Warming, Global Wetting, Le Chatellier Principle, Land-Sink Photosynthesis, Ocean-Sink Photosynthesis

1. Introduction

1.1. Alternative Hypotheses

The greenhouse gas hypothesis (GGH) of global warming is based upon computer-model conjectures [1] [2] regarding the spectroscopic properties of the increasing atmospheric carbon dioxide concentration [CO_2]. The widely used expression "greenhouse effect" is misleading. That simply means heat loss, mainly by convection, is blocked by the window glass, hence warming effect. There is no such greenhouse closed-window effect in the Earth's atmosphere. The GGH analogy has arisen from a theory that transducer gases, such as CO_2, that are known to convert photons into enthalpy, absorb IR radiation from the Earth's surface by an amount that increases with the total [CO_2] in the atmosphere.

There exist alternative hypotheses that should also be considered and investigated to test the GGH in accord with scientific method protocol. One such hypothesis, for example, proposed recently by Lightfoot and Orvil [3], is based upon the interacting radiation physics of both CO_2 and H_2O. They reach the conclusion that thermodynamic laws, which we apply in the following sections, are not included in climate models on which the IPCC climate change hypothesis atmospheric temperature is predicted to increase with [CO_2]. Emitting comparable amounts of water from fossil fuel to the atmosphere could also contribute to climate change [4]. We will return to the effect of increasing [H_2O] concentrations produced by the energy industry, in a later section.

The Earth loses heat from its surfaces by Stephan-Boltzmann law of radiation physics depending upon temperature. The total amount of photonic energy, at the same singular frequencies that CO_2 has capacity to absorb, is much less than the absorption capacity of the total concentration [CO_2] in the troposphere [5] [6]. In the IR spectra of CO_2, the lines in the rotational-vibrational bands efficiently absorb about 10% of all IR in the specific IR bands where these lines appear, letting through the remaining 90%, and evidently absorbing absolutely nothing at all other IR wavelengths. Therefore, CO_2 can affect no more than a small fraction of the surface-emitted IR radiation, and photons in this IR-active energy band become fully transduced into enthalpy at a relatively low level. The absorption length does not exceed 300 meters for the relevant lines considered, whereas the troposphere that determines climates extends to a height of around 10 km.

It should be emphasized, however, that these analyses [3]-[6], and indeed also the GGH, are based upon the literature data that the shortest wavelength a CO_2 molecule can transiently absorb and emit is at wavenumber 2349 cm^{-1}. That is a near-IR wavelength. For shorter wavelengths, CO_2 is said to be transparent. That is a central GGH assumption, *i.e.*, based upon the spectroscopic properties of the CO_2 molecule. An isolated CO_2 molecule does not absorb in UV-VIS range, because the first excited electronic state is too high: and absorbs mainly in a single band in IR. These spectroscopic data, however, are obtained for low-pressure pure CO_2 in an otherwise empty bottle, and do not directly apply to atmospheric conditions. For a review on recent research on cluster physics of molecular gases, including H_2O and CO_2, see Sedunov [7].

A central assumption in climate computer models that support GGH is the neglect of clusters of H_2O and CO_2 molecular complexes in air and clouds. The monomer fraction density of both H_2O and CO_2 in ambient air could be as low as 10% as it will decrease with T at height. The radiation absorption and emission properties of atmospheric CO_2, for example CO_2 dimers or H_2CO_3, will have different molecular orbital energy levels, weaker bonds with lower excited states and different vibrational-rotational absorption spectra. The relevant spectroscopy of various CO_2-H_2O complexes are different to those of a rarified gas of isolated CO_2 molecules.

Satellite measurements [8], moreover, show that a reduction of IR emissions in CO_2 bands at some latitudes and heights is partially compensated by increased emissions in CO_2 and H_2O bands at other latitudes and heights. The topmost "single-unit-absorbance" layer where IR radiation detaches from the atmospheric gases and goes directly out, is a height that varies with different absorption wavelengths. For water it can hardly exceed 10 km as water condenses to cloud in the tropopause. For CO_2 it is higher, as CO_2 is homogeneous even at higher altitudes. Because of all these effects, future research should at least consider sound scientific alternatives to GGH to explain global warming since around 1970.

1.2. Geography of Global Warming

A fundamental shortcoming with the IPCC-GGH [1] [2] is that the increased concentration of CO_2 in the atmosphere does not vary significantly with geographic locations in the biosphere where the global warming index (GWI) air temperatures are sampled at land and ocean monitoring stations, with surveillance by satellite [8]. There is a heterogeneous distribution of the mean increase in the biosphere GWI that is used by the IPCC to define global warming. These observations suggest alternative reasons for the heterogeneous land hotspots seen in **Figure 1**.

When the GWI is resolved geographically the greater increase in temperature is patchy with a significant fraction over land areas correlating with the regions of the most intensive shale gas industries. **Figure 1** shows that not just the combustion but also indicates the intensive regions of actual exploration and production of natural gas. This implies that a fraction of the electricity-consumption enthalpy output, is associated, not so much with oil and gas combustion or CO_2 output, but also with the exploration and production operations [9] [10].

In the following sections we will apply basic principles of Gibbs' classical

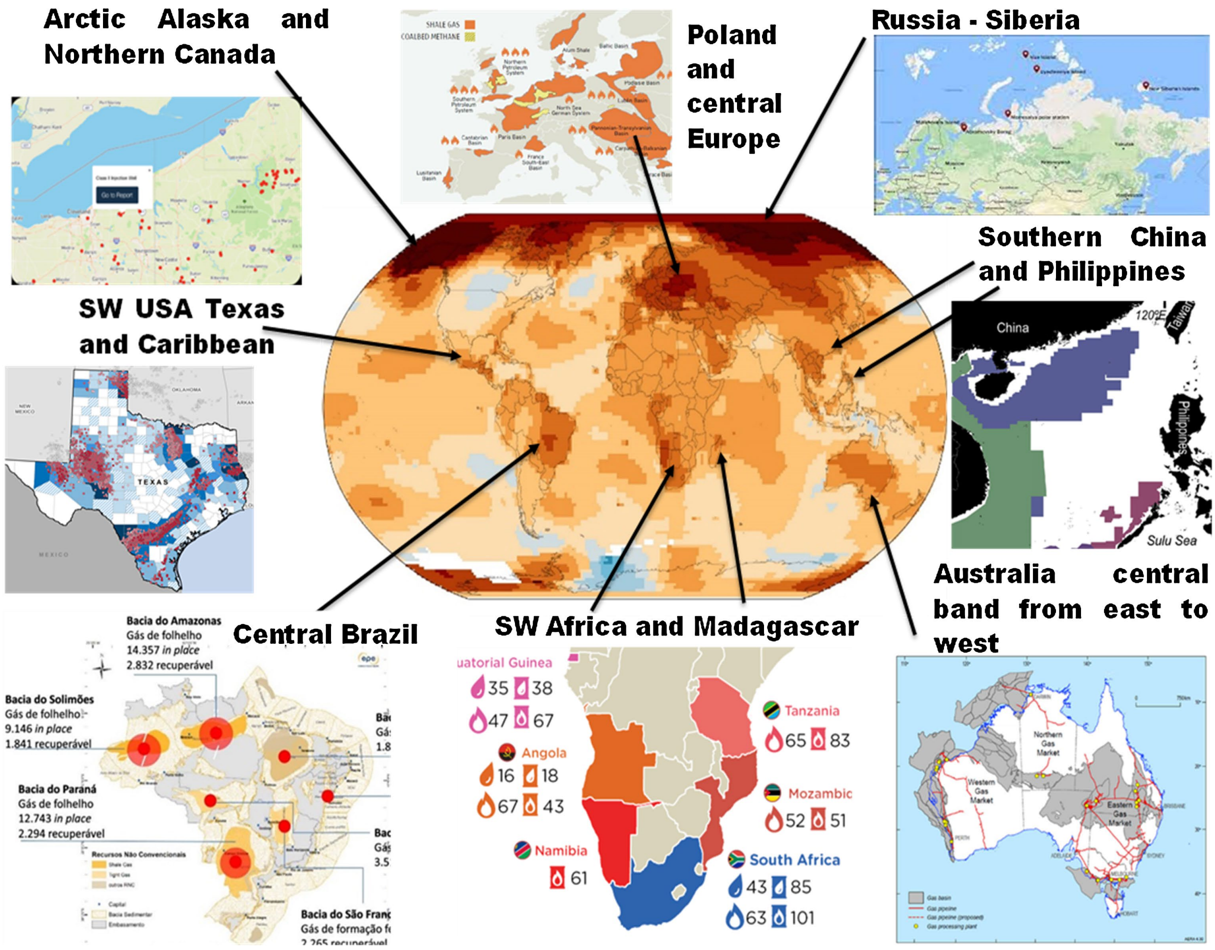

Figure 1. New York Times 15-01-2020: Global warming map of change in average temperature, from 1949 to 2019, at ground and sea levels: the color-coding changes are ΔT (K = ˚Centigrade) -2 -1 0 +1 +2 +3 regions shown as dark brown (+2K or greater) coincide with the regions of the most intense natural gas fracking exploration and recovery operations; for full-size geographical hotspot maps see reference [10]; a list of the original websites is given in APPENDIX to references.

thermodynamics to test the validity of both the greenhouse-gas hypothesis (GGH) of the global warming (0.0175 K/year) and the climate-change hypothesis (CCH) of its consequences. We must emphasize the distinction between these two hypotheses. The GGH is that the GWI from ca. 1950-2025 is caused by increase in CO_2 (presently 2 ppm/year), whereas the CCH is the theory that the GWI index increase (0.085 K over last 50 years) is causing extremes of weather as evidenced by floods or record temperatures, for example.

2. Atmospheric Enthalpy (ΔH) Changes

2.1. Fuel Combustion Emissions

The anthropogenic primary energy consumption amounted to 595 EJ in 2021. This is an experimental result that is generally accepted as being sufficiently accurate. The data from the BP report [11] is shown in **Figure 2**. An application of the

1st law of thermodynamics shows that 595 exa (10^{-18})-Joules emitted into the atmosphere every year is not negligible when we view it alongside the current global warming index (GWI), resolved geographically in **Figure 1**, averages 0.0175 K/year (1970-2021).

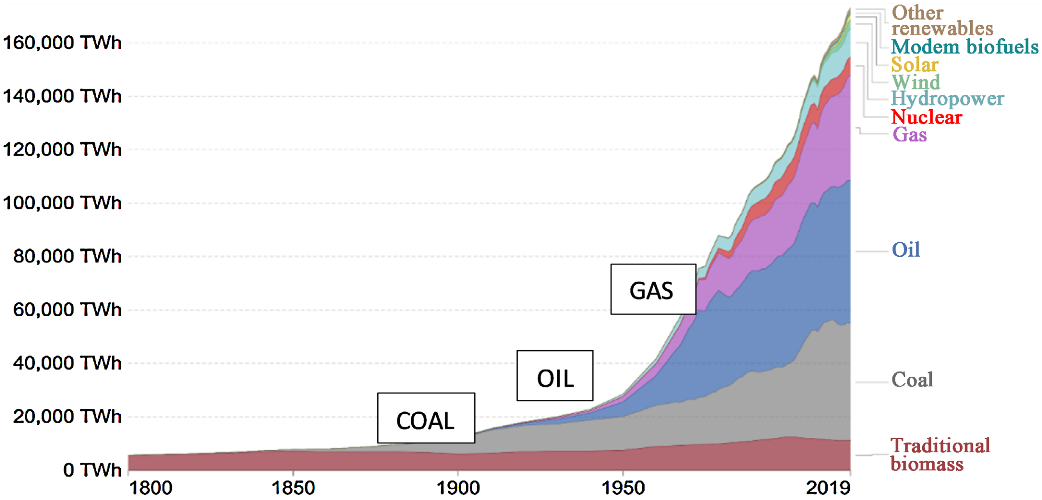

Figure 2. Annual enthalpy output from all fuel sources from 1850 to 2019; industrial carbon dioxide emissions began around 1900 with the use of coal, increased around 1950 with use of oil, and further increased in 1970 with the advent of the natural gas industry as seen in **Figure 3** below.

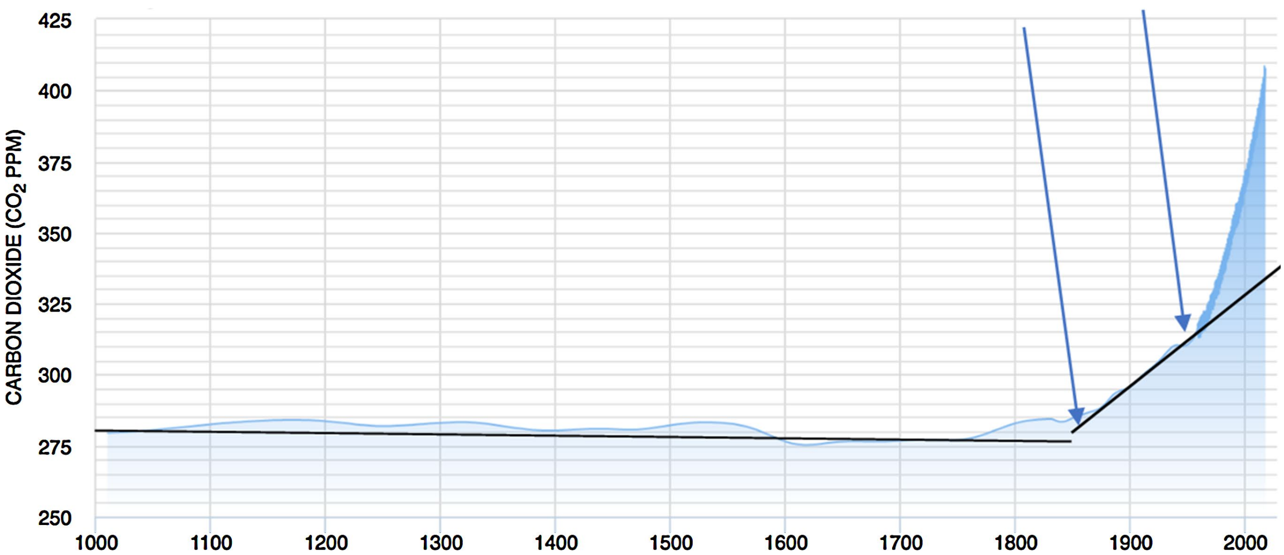

Figure 3. Average concentration of CO_2 in the Earth's atmosphere over last thousand years: until the beginning of the industrial revolution, ca.1850, with the coal and steam engine era, the [CO_2] level remained constant below 285 ppm, then increasing by ~ 1 ppm/annum for 120 years from 1850 to 1970 spanning coal and oil eras: it has been increasing by roughly 2 ppm/annum since 1970 around the same time natural anthropogenic natural gas use as a fuel began.

The experimental rate of heat increase in GWI (**Figure 4**) was previously confirmed by Jin *et al.* [12] and is equivalent to an average rate of fuel enthalpy output of 0.04 W·m^{-2}. The data of Jin *et al.* also disagrees with the greenhouse gas hypothesis. "The globally averaged terrestrial AHFs (anthropogenic heat fluxes) were estimated at 0.05, 0.13, and 0.16 W·m^{-2} in 1970, 2015, and 2050, respectively, but were found to vary greatly among countries and regions. The warming distributions over predominantly populated land areas as reported by Jin *et al.*, are inconsistent with the greenhouse-gas hypothesis. This article confirms that the temperature increases contradict the greenhouse gas hypothesis, since CO_2 increases (**Figure 3**) would lead to uniformly distributed anthropogenic enthalpy increases.

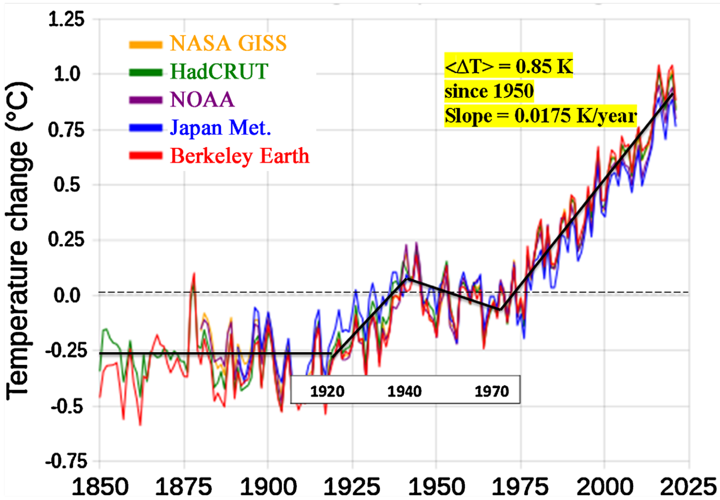

Figure 4. Global warming index (GWI) from 5 different sources, from 1850 to 2025: the present annual rate of increase average temperature <ΔT> (GWI) per year is 0.0175 ± 0.0005 K; the smoothed fluctuations with a periodicity of 4 - 5 years arise from solar system planetary insolation effects; the total mean GWI increase, linear since zero in 1970, is 0.875 K https://data.giss.nasa.gov/gistemp/.

Figure 4 shows that before the beginning of the present rise in the GWI around 1950, for many decades even before industrial revolution from 1850 to 1920, the GWI was 0.00 ± 0.1 K, *i.e.*, zero, by the definition of "global warming", to within the accuracy that mean air temperature can be measured at monitoring stations. Using the accurate approximation of ideal-gas heat capacity of the atmosphere, C_p = (7/2)nR where R is the molar gas constant (8.3145 J/K·mol) and n = 1778 × 10^{18} mol is total atmosphere mass converted to moles, we obtain C_p = 5174.1 eJ/K independent of temperature (T) and pressure (p). The mean concentric heat transfer emission rate corresponding to the current GWI, 0.0175 K/year, gives the enthalpy change $\Delta H = C_p \Delta T$ and the time-dependent surface heat flux $H(t)$ is

$$H(t) = C_p \Delta T / (s \times A) = 0.0061 \text{ W/m}^2 \quad (1)$$

where W is power in Watts, s is the time of 1 year in seconds and A is the surface area of the Earth. The result of average power to heat the atmosphere by GWI present rate is approximately 7 times smaller than anthropogenic fossil fuel heat production (~0.04 W/m^2)

2.2. Global Warming Hotspots

The geographical distribution of 2K+ hotspots (**Figure 1**) is direct experimental evidence that a substantial fraction of the global warming index (1950-2020) of ~1 K may be accounted for by enthalpy emissions from fracking operations in the shale gas industry. These contributions to the GWI, that are used to define the atmospheric greenhouse global warming effect, are not included in any of the computer models reported by IPCC [1] [2] nor in the standard textbooks on climate modelling [13] [14]. These operations increase the lapse rate slightly in the Earth's lithosphere, or solid land surfaces. The lithosphere surfaces are in steady-state thermal coexistence with the atmosphere at sea and ground levels at a global average ground temperature of 285 K (**Figure 5**).

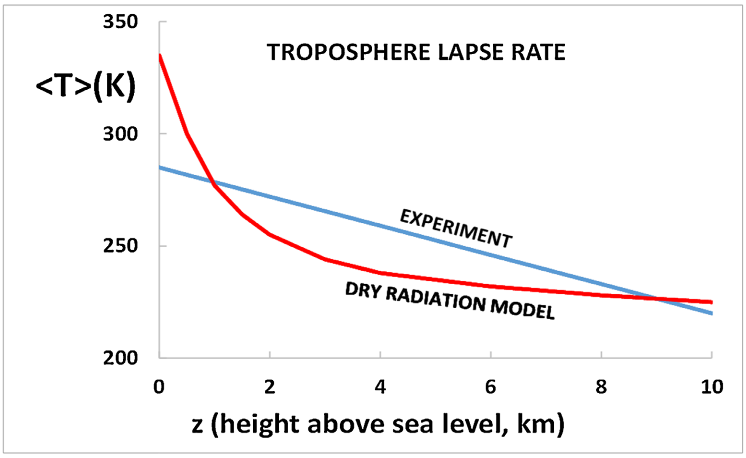

Figure 5. Average temperature (<*T*>) profile (lapse rate) in the Earth's troposphere up to 10 km; blue line is experimental observed mean T-profile showing a constant lapse rate of −6.5 K/km; red line is a minimalist computer model [14] [15] effect of radiation balance of dry air without H_2O or CO_2: the predominant effect of humidity and clouds, is to reduce the GWI baseline, sea level, average temperature <*T*> by around 50 K from 335 to 285 K.

At ground- and sea-levels, both the mean GWI temperature <*T*> and the gradient of temperature (lapse rate) d<*T*>/d*z* coincide with values in the earth's lithosphere up to the tropopause at 10 km around the height of the highest mountains. This steady-state equilibrium has been disturbed, since around 1970, to some extent that is difficult to quantify, in the areas of anthropogenic seismic and earthquake activity in the lithosphere [9] [10].

According to an analysis in the journal Science, by Supran *et al.* [16], evidence suggests company reports on GGH are a distraction from the real global warming effects. There are compelling enthalpy output analyses that disparage GGH as established science and confirm just the opposite. Block *et al.*, in 2004 [17], focused research into enthalpy increases in some industrial regions of Europe. They concluded 20 years ago, from minimalist computer models, that the direct effect discussed in their paper is smaller than the expected warming caused by increasing greenhouse gas concentrations predicted by computer climate modelling. They concluded that anthropogenic heat will become more important in the future, because of the steady increase in world energy consumption and the growth of population in urban areas.

Further experimental evidence against the proclamations, based upon IPCC assumptions, that anthropogenic heat is negligible [18], has been reported in the article by Flanner [19] who concluded that "nearly all energy used for human purposes is dissipated within the Earth's land-atmosphere system. Thermal energy released from non-renewable sources is therefore a climate forcing term. Averaged globally, this forcing is only +0.028 $W·m^{-2}$, but over the continental United States and Western Europe, it is +0.39 and +0.68 W/m^{-2} respectively". These figures cannot be construed as negligible considering that 0.04 $W·m^{-2}$ is an accurate estimate of the present experimental global average heating from fossil fuels, and that 0.0061 $W·m^{-2}$ is the present global warming rate of GWI increase.

3. Conservation of Energy Models of GGH

3.1. Radiation Balances

Overwhelming evidence against the "anthropogenic heat is negligible" claim [18] can be gleaned from the 2012 global radiation balance by Flanner's analysis [19], and by Stephens *et al.* [20], whence the entire Earth is treated as a closed isolated thermodynamic system, open only to electromagnetic radiation transfer. Computer models of all these processes are based upon the Joule-Mayer 1st law of irreversible thermodynamics [21]. Stephens *et al.* concluded that the global balance of energy fluxes within the atmosphere or at the Earth's surface cannot be derived directly from measured fluxes and is therefore uncertain. This lack of knowledge of surface energy fluxes profoundly affects our ability to understand how Earth's climate responds to increasing concentrations of greenhouse gases.

In other words, computer modelling [13]-[15] of all the contributions to the concentric mean energy budget at the Earth's biosphere surfaces. Balancing the budget cannot tell us anything about the reason for the biosphere GWI of 0.0061 ± 0.0001 $W·m^{-2}$ from the radiation balance at the Earth's surface where the biosphere GWI $<\Delta T>$ is recorded. Stephens *et al.* report (**Figure 6**) a net Earth's surface radiation balance of 0.6 ± 17 $W·m^{-2}$, with a level of uncertainty far exceeding the calculated imbalance by orders of magnitude. Far from supporting the GGH, these results, summarized in **Figure 6**, confirm the absurd claim of IPCC climate modelling conclusions [1] [2] *i.e.* that multivariate computer modelling establishes GGH as scientific truth. In the IPCC computer models [1] [2], the entire Earth is a closed system that can exchange heat only by radiation to and from space. The total energy-flux balance includes many sources and exceedingly complex terms with large uncertainties, as explained below.

Stephens *et al.* modified the original, which was published in an IPCC report [1] https://judithcurry.com/2012/11/05/uncertainty-in-observations-of-the-earths-energy-balance/.

3.2. Earth's Energy Balance

One of the smallest terms within the Earth's energy budget is the greenhouse-gas (CO_2) hypothesis energy flux. We can define this hypothetical positive quantity

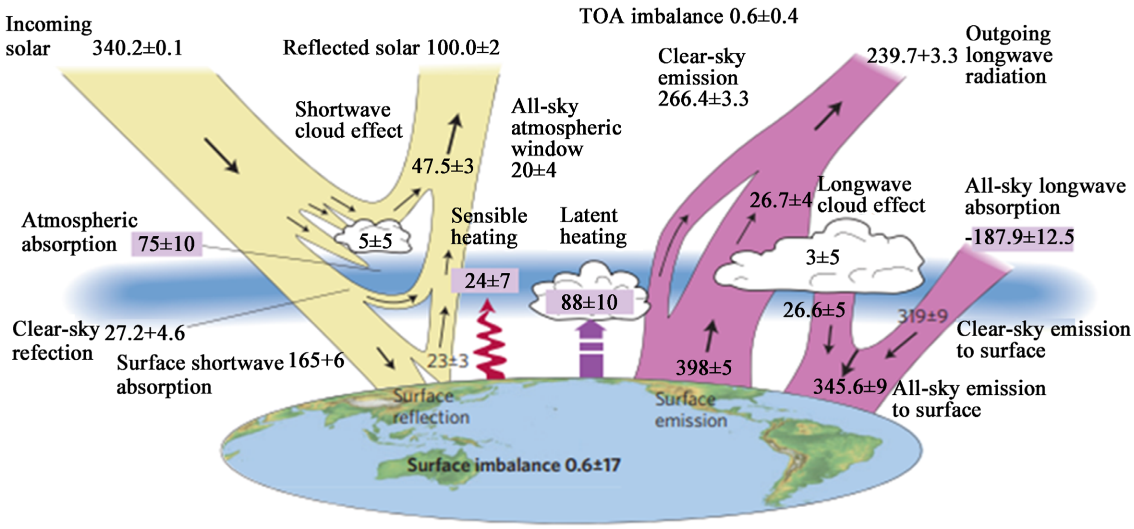

Figure 6. Radiation balance terms in the GGH master equation (2) shown from Stephens *et al.* [20]: all values of the energy fluxes quoted here with estimated uncertainties are in Wm^{-2}.

as an excess energy flux arising from 40% increase in [CO_2]: $\Delta E_{ggh} = E[CO_2\text{: 400 ppm}] - E[CO_2\text{: 285 ppm}]$.

Then, we can collect all the terms in an energy balance equation to be solved for ΔE_{ggh} in any Joule-Mayer energy conservation multivariate computer model. There are no less than 20 resolved terms in the incoming and out-going radiation balance ($E_{sun} - E_{earth}$) listed in the review of Stephens *et al.* [20] (**Figure 5**). A GGH "master equation" can thus be summarized (see Wikipedia: "Earths Energy Budget" for list of terms with self-evident subscripts):

$$\begin{aligned}\Delta E_{ggh} &= \left(E_{sun} - E_{earth}\right) + E_{gg} + E_{elec} + E_{ff} + E_{alb} - E_{ref} + E_{insol} \cdots E_n \cdots \\ &= 0.0061\ \mathrm{W/m^2}\end{aligned} \tag{2}$$

(n = unknown number of all non-negligible E_{flux} source terms in the equation: a full list is unlimited!) Using conservation of all energy sources in accord with Joule-Mayer law, in conjunction with the radiation balance for the total energy flux, as derived by the IPCC climate modelling community, it is widely claimed [13]-[15], however, that a multivariate computer-model, based upon this global energy balance of known energy flux sources, can lead to the confirmation of current GWI surface flux is $\Delta E_{ggh} = 0.0061\ \mathrm{W/m^2}$, as an established science truth. However, the uncertainty in just the biosphere surface radiation balance is ± 17 $W\cdot m^{-2}$ [20], which is ~3000 times greater than the GWI experimental result for ΔE_{ggh}.

A common misrepresentation of the IPCC greenhouse-gas hypothesis is that the 40% increase in CO_2 can explain the increase in mean global surface temperature of 1 K since preindustrial times. **Figure 3** shows that the concentration [CO_2] increase above the baseline 285 ppm disagrees with the theory. The [CO_2] increase began with the use of coal at the start of the industrial revolution around 1850, whereas the global warming index from 1850 to 1920 was zero, *i.e.*, in disagreement with the GGH. The absence of climate-change events before 1950 may be explained by coal combustion, as unlike hydrocarbon fuels, coal does not emit H_2O into the atmosphere (Table 1).

Table 1. Fossil fuel emission reactions (i) carbon from coal (~1850-2020), (ii) octane from crude oil (~1920-2070) and (iii) methane from natural shale gas reservoirs.

Reaction	carbon oxygen	carbon dioxide	water	enthalpy (= ΔH)
i	$C + O_2$	$\rightarrow CO_2 +$	none	+394.0 kJ/mol
ii	$(1/8)\ C_8H_{18} + (25/16)\ O_2$	$\rightarrow CO_2 +$	$(9/8)\ H_2O$	+678.8 kJ/mol
iii	$CH_4 + 2O_2$	$\rightarrow CO_2 +$	$2\ H_2O$	+890.3 kJ/mol

4. Gibbs' 1st and 2nd Laws: State Functions

4.1. 1st Law

The beauty of Gibbs' classical thermodynamics is that for all real irreversible processes, however many, however complex, whatever may be our ignorance of mechanisms and time scales, reversible heat defines heat capacity at constant pressure ($C_p dT = dQ_{rev}$) defines the state functions [21], enthalpy (1st law Hess-Gibbs) $\Delta H = Q_{rev}$, and entropy (2nd law, Carnot-Gibbs) entropy $\Delta S = Q_{rev}/T$. No matter what the irreversible-path complexity of the cycle of intermediate processes, no matter how great our ignorance of kinetic mechanisms of these processes, at a constant thermodynamic equilibrium state of air, at a fixed recording station, at constant composition, the state is defined only by its temperature (T) and pressure (p). Then, with T and p fixed, the heat change $Q_{rev} = \Delta H = T\Delta S = 0$, for all cyclic processes if the GWI is zero, as seen in Figure 4 from 1850 to 1950.

To apply this basic tenet of thermodynamics to a non-zero GWI, we don't need to know any of the detail of mechanisms or sources of heat transfer. In order to discover possible reasons for global warming, we only need to look at what has changed since the Earth was at near steady-state equilibrium in the pre-industrial global warming era. Notwithstanding the plethora of complex heat transfer processes and mechanisms involved, many of which are inextricably related, and some unknown, the Earth approaches a steady state whence the net radiation balance at the top of the atmosphere is exactly zero, if the GWI $<\Delta T>$ atmosphere is zero.

The heat flux $0.6 \pm 0.4\ W \cdot m^{-2}$ at the top of the atmosphere is just a small fraction of the sum of the uncertainties in Figure 5, as calculated from satellite data by Stephens *et al.* [20]; they estimate the mean heat transfer rate uncertainty to be of the order $\pm 17\ W \cdot m^{-2}$ at the Earth's surface. For comparison, heat forcing of GWI by GGH at the Earth's surface is presently calculated to be $0.0061 \pm 0.001\ W \cdot m^{-2}$, *i.e.* around 3000 times smaller.

From Figure 4, given C_p atmosphere, we calculate that between 1850 and 1950 the mean GWI/decade is $0.000 \pm 0.001\ W \cdot m^{-2}$. That is the margin of error, given that modern monitoring stations define and measure air temperatures to an accuracy within ±0.01 K. Since enthalpy is a state function, if ΔT changes, what are possible reasons for the corresponding enthalpy flux change? The greenhouse-gas hypothesis and computer models, that can parameterise it, neglect the experimental result: the fossil fuel discharges an amount of heat, globally, that is several times greater, than is assumed in the greenhouse-gas hypothesis, to explain the present GWI. This result begs the question, not "what causes global warming (1950-2023)?", but "what counteracting effects cause global cooling of the anthropogenic heating that presently prevails?"

4.2. 2nd Law

Likewise, we can apply the 2nd law of equilibrium thermodynamics [21] "Entropy (or Gibbs energy) is a state function" to the question: can a change in GWI of 1 K over 70 years change the climate. The Earth's climates are principally determined by atmospheric pressure fluctuations leading to cloud formation that occurs when moist air cools and saturation pressure drops (p_s) with cloud formation. When the climate change is zero, there is no change in either of the state functions enthalpy or entropy, hence also Gibbs energies that determine the cloud condensation equilibria. The Clapeyron Equation (3), derived from Gibbs 2nd law, relates the change in p_s that would occur due to global warming, *i.e.*, $\Delta T > 0$:

$$\Delta\left(p_s\right) = p_s S_{vap} \Delta T / \left(RT\right) \tag{3}$$

If T is ~ 280 K, and $\Delta T = 1$ K *i.e.* GWI, S_{vap} ~ 150 J/(mol·K), R is the molar gas constant, we obtain a change in Δp_s of 0.5 mb, if p_s is 10 mb. A more accurate estimate will be reduced by lower value of S_{vap} due to entropy of cloud formation. This simple result tells us that the main property that determines climates has changed by only a small amount because of a GWI rise of 1 K over a 70-year period. This may not be of significant consequences compared to much larger natural geographical and seasonal fluctuations around the mean temperatures and pressures, $\langle T\rangle(z)$ and $\langle p_s\rangle(T)$, that determine the Earth's climates.

5. Climate-Change Hypothesis

5.1. Weather Pattern Fluctuations

The IPCC reports that claim GGH and CCH [1] [2] to be established scientific truth, equate the greenhouse-gas hypothesis to their climate-change hypothesis. GGH and CCH are certainly not synonymous, and probably not even related as a corollary. They are quite distinct concepts, however. Global warming is not a hypothesis: the current GWI of 0.0175 K/year since 1970 is an experimental result of independent verifiable sources. The unanswered question is: "could this slight warming effect cause significant changes in the Earth's land climates equivalent to the predictions of CCH?"

The Earth's climates, or weather patterns have been changing for countless different known and unknown reasons, including galactic and insolation events, and lithosphere geothermal activity since its surface solidified 4,000,000,000 years ago. Eventually, water began to collect in, and evaporate from, its basin bottoms. It is still changing, over the surface spatially, and on all time scales. It is possible that the climate changes we are witnessing in recent decades (e.g., more floods) are related to the GWI index, but that is a different hypothesis. The climate-change hypothesis (CCH) remains to be tested against experimental results by the scientific method. The IPCC-CCH can be summarised: "the increase in GWI from zero in 1950 to ~ 1 K in 2020 is the cause of changes in the Earth's land climates, as evidenced by record temperatures (since records began only 200 years ago) and increased flood frequency on the land surfaces since around 1980. The CCH hypothesis of IPCC [1] [2] assumes the increase in land surface flooding is caused by enhanced evaporation rate from sea surface, and increase in water in the troposphere, caused by the increase in GWI (~1 K since 1920: **Figure 4**).

Therefore, whilst the CCH remains an unsubstantiated hypothesis, we should consider alternative hypotheses provided they are based upon sound science. The Earth's various weather patterns that determine the climates are driven mainly by the pressure gradients depicted as contours of isobars that we see daily on TV weather forecasts. A corollary of the greenhouse gas CO_2 hypothesis of global warming, is that if the GWI index returned to a sustainable zero GWI = 0, by eliminating further emissions of CO_2 (C-net zero IPCC policy), then the Earth's climates would stop changing. Is this hypothesis now a scientific truth?

Whereas a heat enthalpy output corresponding to 0.85 K over 70 years, in a typical land surface climate, with seasonal fluctuations in temperatures varying by an average of ± 50 K between winter and summer, seems an unlikely cause of fundamental changes other than extending summer by a day, and or shortening winter by a day, perhaps? The global weather patterns are determined, not by fluctuations in temperatures at the Earth's surface, but by fluctuations in pressure around the global mean annual surface air pressure 1013.5 mb. By contrast with the wide fluctuations in temperature between the extremes of winter and summer, weather patterns, such as rainfall statistics, and extreme events, such as flooding, are determined by extremely small fluctuations between high pressure clear skies (>1020 mb) and low-pressure cloudy skies (<1005 mb). It is the cloud formation that causes the surface temperature extremes from winter to summer. Pressure fluctuations are determined by the amount of water in the atmosphere that can be regarded as a 2-phase equilibrium, between condensed cloud colloid, and steam at a partial pressure (humidity) of the order of 0.01 atmosphere pressure.

5.2. Van't Hoff Equation

The Earth's climates are therefore mainly determined by atmospheric pressure fluctuations that depend on the equilibrium constant for water mole fraction in air $[H_2O]_{air}$. The van't Hoff equation derived from Gibbs 2nd law (entropy is a state function) tells us roughly what the annual increase in the equilibrium constant concentration $[H_2O]_{air}$ if the mean temperature of the air increase ($<\Delta T>$) is present GWI 0.0175 K/year (from **Figure 4**). H_{vap} is the latent heat of evaporation of water in a cloud. Assuming Dalton's ideal gas law, then:

$$\Delta \log_e \left\{ \left[H_2O \right]_{air} \right\} = \Delta H_{vap} \left\langle \Delta T \right\rangle / RT^2 \sim 0.001 \quad (4)$$

The equilibrium additional state variable water concentration $[H_2O]_{air}$ that determines weather patterns, and also the climate rate processes, is changing, on average, only by a small degree due to GWI compared to natural geographical and seasonal fluctuations around $<T>(z)$ and $<p>(z)$ that determine the Earth's climates (**Figure 7**). The total change in the mean concentration <◎$[H_2O]_{air}$> however, caused by the output from the fossil fuel industry, may not be negligible, by comparison.

Besides CO_2, and enthalpy (*H*) the fossil fuel industry emits large quantities of water into the atmosphere; just as with the *H*-effect, the effect of water emission in fuel combustion is generally considered negligible in computer modelling, and IPCC-GGH reports compared to total pre-climate-change $[H_2O]$ effects in the Earth's energy budget. Since before the GGH hypothesis fashionable by political consensus in the 1980's, it has been known that the GGH hypothesis alone, is a very unlikely scenario. **Table 1** shows that burning (gasoline or diesel) fuel emits slightly more H_2O than CO_2, whereas natural gas (CH_4) emits twice as much water as petrol, diesel or kerosene, per mole of carbon.

The atmospheric pressure (*p*) can be simply related to the temperature (*T*) by the barometric formula [22], in the first approximation of treating air as an ideal gas (*R* is molar gas constant, m is molar mass, *g* is gravitational constant, *z* is height, and p_0 is the global atmosphere mean sea level pressure).

Then,

$$p = p_0 \exp\left[gmz/(RT) \right] \quad (5)$$

since *T* is an absolute temperature, we note that changes in *T* of less than 1 K will result in changes in pressure, p/p_0 that are so small, less than 1 mb (= 100 Pa), to be insufficient to change seasonal weather patterns, as seen in **Figure 7** for illustration, or any associated climate changes. The same argument applies to other thermodynamic processes, such as evaporation of sea water, the rates of which vary exponentially with changes in absolute *T*(K).

Typical average monthly pressures for the extreme seasons January and July are shown in **Figure 7**. there are very large average temperature differences between January and July but the two patterns look much the same, temperature fluctuations do not affect the climate so much as small variations in pressure: up to ±10 mb (1% of $<p_0>$) cause climate changes depending on water concentration $[H_2O]$, or humidity.

Fossil fuel water emissions, summarised by fuel type, for example in **Table 1**, may not support GGH, they may be are neglected in computer models of the global energy-budget Equation (2). We note that the steep increase in $[H_2O]$ on replacement of coal by natural gas, that besides a 25% higher enthalpy output per mole of CO_2, burning natural gas results in twice as much water emission per mole of CO_2 than hydrocarbons. This may not be a negligible contribution to a global effect of reducing the mean barometric pressures that would then cause "climate change" by global wetting, rather than global warming.

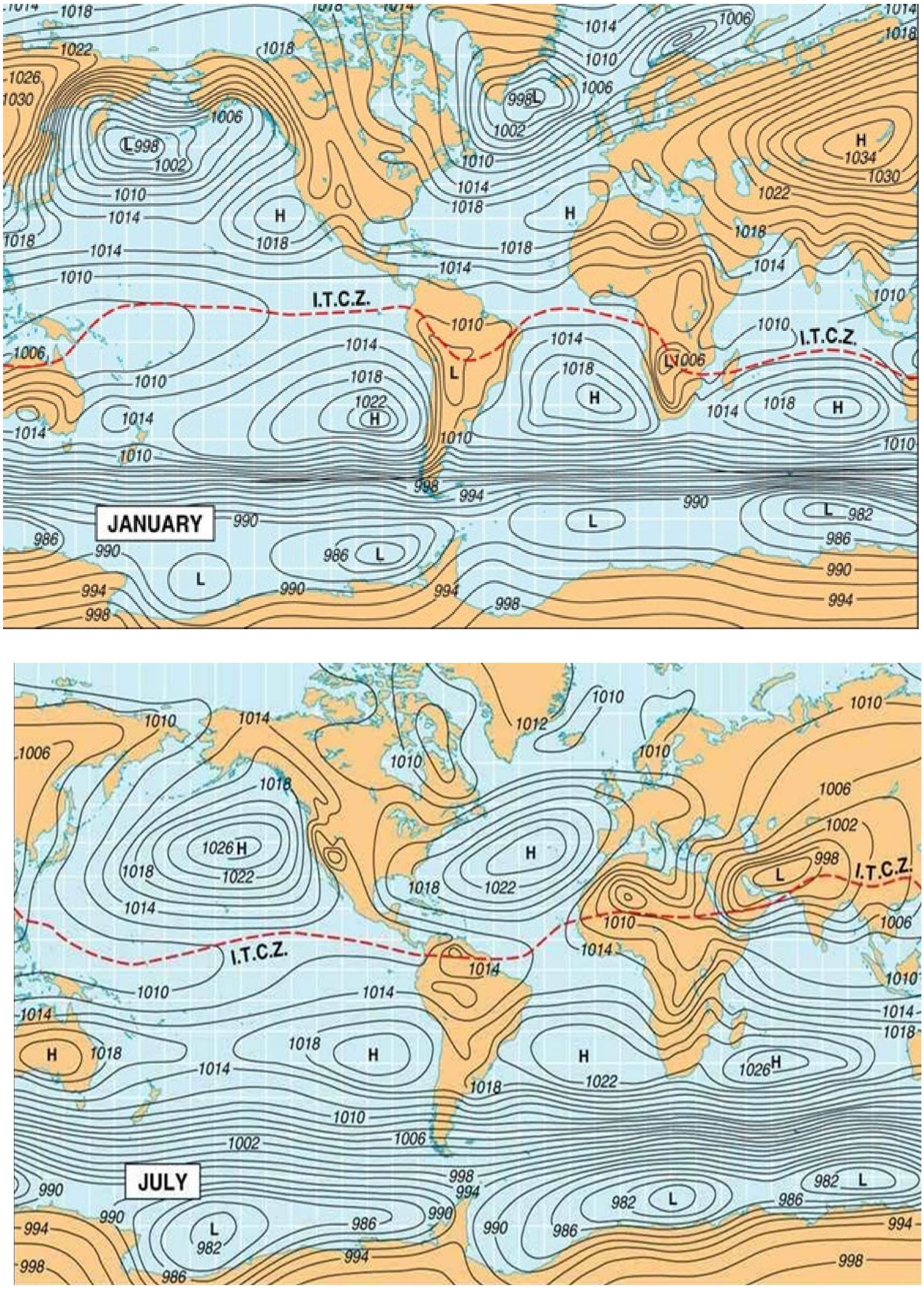

Figure 7. Global atmospheric pressure isobaric contours that determine weather patterns and Earths climates (millibar units): are mid-winter month averages (January 2022) and midsummer month averages (July 2022). The Intertropical Convergence Zone (ITCZ) is a low-pressure belt near the equator where trade winds from the Northern and Southern Hemispheres pressure gradients converge causing increased rainfall.

Accordingly, we need to consider alternative hypotheses. For example, we note that the present annual total water in the atmosphere [23] is approximately 700 × 10^{15} mol, and increasing by 1.5% per decade, giving an annual rate of increase as 1.05 × 10^{15} mol/year. From present 2022 output of H_2O from the oil and gas industries using the BP fossil fuel combustion data [11], and mole balances in **Table 1** we obtain a figure close to 1.0 × 10^{15} mol/year of anthropogenic water vapour. Is this a coincidence? Probably not: the observation could perhaps help to explain the conclusion of physicists Lightfoot and Orvil [3] that water vapour combined with CO_2 are the global coolants that counteract the anthropogenic enthalpy increase from fossil fuels in **Figure 2** and **Table 1**.

6. Endothermic Photosynthesis Processes

6.1. Global Coolants

Endothermic processes that convert H_2O and CO_2 into vegetation and plankton biomasses, by photosynthesis on land and in ocean—are atmospheric open sinks, which may counteract the energy industry's H_2O, CO_2 and ΔH enthalpy emissions, to some extent. As with all chemical reactions, photosynthesis can be reversible in both directions, but in nature, the reaction is catalysed by radiation from sun in daylight and the reverse reaction, dissociation of carbohydrate (using glucose reaction for example) by the Earths IR radiation by night, *in vivo*, with the presence of a catalytic enzyme.

photosynthesis by day $6CO_2 + 6H_2O + \text{UV-radiation} \rightarrow C_6H_{12}O_6 + 6O_2 - 2814\ \text{kJ}$

dissociation by night $C_6H_{12}O_6 + 6O_2 + \text{IR-radiation} \rightarrow 6CO_2 + 6H_2O + 2814\ \text{kJ}$

Judging from the respiration equation above, the amount of the heat absorbed during photosynthesis is equal to the energy released at night when respiration continues. The net effect of a continuous bio-reaction process over all time is photosynthetic production of vegetation with a net cooling effect.

6.2. Le Chatellier Principle

Photosynthesis chemical reactions are driven by the Gibbs energy difference between reactants and products that is related via the 2nd law, "Gibbs energy is a state function", to the equilibrium constant at ambient pressure of the variable gas concentrations.

$$K_p = \left[C_6H_{12}O_6\right]^{1/6}\left[O_2\right] \big/ \left[CO_2\right]\left[H_2O\right] \qquad (6)$$

As glucose is solid, its concentration in the equilibrium is effectively a constant since the reaction rate depends only on the radiation photon intensity, all photosynthesis reaction rates are determined by photon catalyst intensity and hence are of zero order. We can immediately conclude that increasing [CO_2] by a factor of 2, say, will promote the equilibrium in the direction of more photosynthesis product, and enthalpy absorption, by a factor of 2 without changing the rate in a continuous steady-state process. This is in accord with Le Chatellier's principle of reaction equilibria that predicts the effect of changing T or p, or concentration of any reactants or products on the equilibrium extent of reaction. CO_2, therefore, is a biosphere GWI coolant by this, and also various energy transfer processes. The associated photosynthesis endothermic effect can be roughly estimated if we can quantify the land and ocean sinks biomass production by photosynthesis.

We have performed simple calculations of significant effects based upon the assumption that the ocean plankton photosynthesis takes all its energy from the sunlight that would otherwise heat up the oceans, and that the land sink takes all its energy from the sunlight that would otherwise heat up the atmosphere. Preliminary results of an analysis for this minimalist 2-sink model of the atmosphere system, land surface, and ocean volume have been obtained and summarised in **Table 2**. Our simple calculations to estimate the effects are based upon a knowledge of the entire ocean and atmosphere heat capacities, and total enthalpy absorbed in biosynthesis, from both the atmosphere by land sink, and ocean sink. The ocean sink is deemed to be in steady-state open coexistence for heat and mass transfer of CO_2 and H_2O. The heat capacity of the entire oceans is estimated from the specific heat of water at 288 K and then multiplying by the ocean mass. The heat capacity of the atmosphere is accurately estimated by the diatomic ideal gas value $(7/2)R$, where R is the universal gas constant. The biosynthesis land sink enthalpy is equilibrated within the atmosphere. The results a in **Table 2**.

Table 2. Endothermic photosynthesis cooling process summary.

	Heat capacity C_p kJ/K	Enthalpy absorbed $<\Delta H>$ kJ/year	Annual ΔT cooling degrees K
Land sink	5.6×10^{18}	0.42×10^{18}	−0.075
Ocean sink	8.0×10^{21}	0.68×10^{18}	−0.000085

If the land sink cooling effect of 0.42×10^{18} kJ/year estimated from all photosynthesis processes on land surfaces is applied uniformly to the atmosphere, we obtain the cooling rate $(\Delta H/C_p)$ - 0.42/5.6 = −0.075 K/year. The endothermic cooling effect of the ocean sink is 6.8×10^{17} kJ/ year is applied uniformly to the oceans we obtain a cooling rate is $(\Delta H/C_p) - 0.68/8.0 = -0.000085$ K/year for ocean is negligible by comparison. The net land-sink cooling effect is 4-times greater than the GWI (0.0175 k/year). If this were to double with $[CO_2]$, it would counteract the annual increase in T from all fuels (in **Figure 2**) by around 65%. Just as with the heating effects of fossil fuel combustion, the land biosphere cooling effect of photosynthesis is far from negligible. Land photosynthesis is a significant contributor to the global atmospheric energy balance. Moreover, according to the principle of Le Chatellier applied to the land photosynthesis processes, the net effect of increasing $[CO_2]$ in the atmosphere is to significantly increase its capacity as a biosphere global coolant contribution to the GW.

7. Conclusions

In summary, there are several independent experimental observations to test the

GGH using principles of thermodynamics that do not accord with its basic assumptions. First, we can conclude that the 1st law of thermodynamics applied to the atmosphere's enthalpy change corresponding to a GWI of 0.0175 K/year confirms anthropogenic enthalpy output from the energy industry is several times greater than the GGH requisite output. A corollary of this result is that GGH must remain an unsubstantiated hypothesis.

Another corollary of the conclusion is that "global warming", and "climate-change", are not necessarily synonymous as commonly presumed. The GWI averages are experimental thermophysical property data that are now widely accepted as the experimental data, which a hypothesis must explain. The climate-change hypothesis (CCH), *i.e.*, that the GWI increase of 0.85 K (1970-2020) has caused, *inter alia,* floods, and heat waves, increasingly witnessed, since ca. 1970, is quite a different hypothesis that could be explained by other warming effects. The evidence we have suggests flooding is enhanced by global wetting from water vapour output from the energy industry. Global warming is associated with reduced average humidity. The fact that the increase in CO_2 began with the industrial revolution in 1850, whereas the GWI only began to increase at first in 1920, and by its present rate in 1970, with a mid-period of cooling 1940-1970 are experimental observations that disagree with the GGH.

Computer modelling can be educational, but it cannot be used as a research tool to test and verify the GGH as a scientifically established truth. The multivariate computer modelling of atmospheric energy balance processes, based upon the Joule-Mayer conservation law of all irreversible thermodynamic contains many unknown terms. Uncertainties in the many known variables involved, moreover, far outweigh the hypothetical GGH enthalpy output. For example, sufficiently accurate computer models require various input parameters that describe phenomenological absorption and emission properties requiring a quantifiable knowledge of spectroscopic and transducer properties of atmospheric CO_2 complexes, besides isolated monomers *in vitro*, that does not presently exist.

Finally, the 2nd law of thermodynamics applied to cloud condensation, suggests that global wetting from the energy industry, rather than global warming by an amount 0.3% of total $\langle T \rangle$ (Kelvin) GWI in 50 years, is a more plausible explanation of climate change than the GGH hypothesis. The Earth's weather patterns are determined by small fluctuations in pressure that depend, not so much upon small variations in mean temperatures, but on humidity, or concentrations of atmospheric water. The total amount of $[H_2O]$ in the atmosphere is increasing by 1.5% a decade, *i.e.*, roughly the same rate that water is globally being emitted by combustion of fossil fuels. Therefore, there are more clouds, hence the Earth's average biosphere GWI will also increase, very slightly with the atmospheric $[H_2O]$ concentration. Global wetting from natural gas combustion (mainly methane) is a far more plausible scientific explanation of the GWI increase since 1970, rather than coincidence, than the IPCC hypothetical greenhouse gas emission effect.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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Appendix

Further referenced websites to accompany the caption to Figure 1 (visited 25 March 2025)

1) https://www.nytimes.com/interactive/2020/01/15/climate/hottest-year-2019.html

2) https://ballotpedia.org/Fracking_in_Alaskahttps://ballotpedia.org/Fracking_in_Alaska/

3) https://thenarwhal.ca/what-is-fracking-in-canada/

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6) https://www.drillingcontractor.org/the-arctic-confronting-the-cold-hard-truths-about-the-last-frontier-13206

7) https://www.fractracker.org/map/us/texas/

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11) https://cen.acs.org/articles/93/i3/China-Backpedals-Shale-Gas.html

12) https://geoexpro.com/oil-and-gas-exploration-in-the-philippines/

13) https://www.ga.gov.au/scientific-topics/energy/resources/petroleum-resources/gas

14) https://rightnow.org.au/opinion/what-the-frack-is-coal-seam-gas/

15) https://warsawinstitute.org/russian-drilling-antarctic/

16) https://www.spglobal.com/commodityinsights/en/market-insights/latest-news/oil/022120-russia-stokes-political-tensions-with-hunt-for-antarctic-oil