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Greenhouse Gases and Climate from a Physical-Chemical Perspective

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Abstract

In our previous publications ¹⁻⁶ we examined the role of carbon dioxide, CO₂, in the greenhouse effect according to Physical Chemistry Principles. This work led to arguments that raised doubts about the human-caused origin of climate change, in opposition to renowned climate scientists. Our results are summarized here as a response as well as a contribution to the current discussion. This specifically concerns the question of what drives the relationship between the concentration of CO₂ and rising temperatures in the Earth's atmosphere. The exchange amounts of CO₂ between the atmosphere and the biosphere as well as between the oceans are considered. The energy flows between space and Earth, as well as on Earth itself, show a negligible impact from human energy production. The criticism also relates to the lack of connection between the history of climate and modern climate research, as well as the overlooked effects of climate protection on the environment.

Kurzfassung

In unseren Arbeiten ¹⁻⁶ überprüften wir nach physikalisch-chemischen Prinzipien die Rolle des Kohlenstoffdioxids im Treibhauseffekt. Das führte zu Argumenten, die Zweifel an der anthropogenen Verursachung des Klimawandels hervorriefen im Widerspruch zu etablierten Klimaforschern. Unsere Ergebnisse und gegensätzlichen Überlegungen werden hier zusammengefasst, sowohl als Reaktion als auch als ein Beitrag zur Diskussion. Dies betrifft speziell die Frage nach der treibenden Kraft zwischen Konzentration von Kohlenstoffdioxid, CO₂, und steigender Temperatur in der Erdatmosphäre. Die Austauschmengen von CO₂ zwischen Atmosphäre und Biosphäre sowie den Ozeanen werden betrachtet. Die Energieflüsse zwischen Weltall und Erde sowie auf der Erde zeigen einen vernachlässigbaren Einfluss menschlicher Energieproduktion. Kritik trifft auch die fehlende Verbindung zwischen der Geschichte des Klimas und der modernen Klimaforschung ^{7,8}, ebenso wie die vernachlässigten Auswirkungen des Klimaschutzes auf die Umwelt.

Keywords: Greenhouse gases, heat capacity, IR-transmitters and -emitters, radiation balance, energy and CO₂ balances, climate and environment protection

Schlüsselwörter: Treibhausgase (TH-Gase), Wärmespeicher, IR-Transmitter und -Sender, Strahlungsausgleich, Energie- und CO₂-Bilanzen, Klimaschutz und Umweltschutz

Introduction

If one compares the specific heat capacities of air (1 kJ/kg K) and water (4,2 kJ/kg K), one finds that a 10-meter-high column of water stores as much energy as a 10 km-high column of air, roughly corresponding to the thickness of the atmosphere. This clearly implies that the ocean, with its high heat storage and its global currents, must play a crucial role in shaping Earth's climate. Over the more than 70% of the Earth's surface covered by oceans, a significant heat exchange with the atmosphere takes place. Since the atmosphere over the land makes heat, cold weather, and climate noticeable for people, the focus is on the climate, especially on changes in the composition of the atmosphere.

Predictions from climate research about climate change are based on the observed correlation between rising CO₂ levels in the Earth's atmosphere and the simultaneous increase in an average “global” temperature. This observation coincides with the start of using fossil fuels during the industrial age. From this, climate researchers conclude that the rising CO₂ emissions from industrial society are responsible for the temperature increase in the atmosphere. By extrapolating this connection to the end of this century, a life-threatening climate change could be predicted. Modern climate research has a big influence on political decisions that affect business and everyday life. This calls for an especially critical analysis.

1. Physical-chemical Properties of Atmospheric Gases

Heat storage: Heat is the kinetic energy, E_{kin} , stored in the atmosphere, i.e., the kinetic energy of gas molecules. Each molecule stores heat according to the degrees of freedom available for energy uptake in translational, rotational, and vibrational energy:

$$E_{kin} = E_{trans} + E_{rot} + E_{swing}. \quad (1)$$

The values of the specific molar heat capacities of gases in the atmosphere¹⁻³ confirm the following findings: The triatomic gases, CO₂, and other trace greenhouse gases have about 20% higher molar heat capacity than the main diatomic components of the atmosphere, nitrogen and oxygen, N₂ and O₂. But due to their low concentration, they do not make a significant contribution to heat storage in the atmosphere. Water vapour, at concentrations of a few percents along with its phase changes, is the main carrier of heat storage in the atmosphere. Cloud formation, rainfall, and snowfall reduce the concentration of gaseous water in the atmosphere but leave its heat of transformation in the atmosphere. Thus, the water cycle undoubtedly makes by far the largest contribution to weather and climate in the atmosphere.

Greenhouse Gases as Energy Converters: In climate research, the role of greenhouse gases as converters for the entry of solar radiation as heat into the atmosphere, as well as for trapping IR radiation from the Earth's surface, is emphasized. Among the atmospheric gases, only greenhouse gases have bond strengths that resonate with the electromagnetic radiation energy of IR photons and can absorb it as vibrational energy. This applies to both sunlight and IR radiation from the Earth's surface. The vibrational energy can be transferred as

translational energy to all gas molecules in the atmosphere or emitted again as IR photons in all directions:

$$E_{trans} \leftrightarrow E_{swing} \leftrightarrow E_{phot}. \quad (2)$$

The greenhouse gases are also necessary as converters of the heat bound to the gas molecules in the Earth's atmosphere into infrared radiation to balance out in the radiation exchange with space ².

A point of debate is whether the influx and outflow of energy balance each other and what role the increase in concentration of the greenhouse gases, which are still trace gases, plays in this transfer. One argument against the assumption that Earth's radiation couldn't escape into space is the decrease in CO₂ concentration with increasing altitude according to the Barometric height formula. Additionally, the concentration of water vapour decreases due to condensation. As a result, the assumed 'mean free path' of IR photons increases with altitude.

Absorption of Electromagnetic Radiation in Gases: For the absorption of electromagnetic radiation by absorbing gas molecules, the validity of a logarithmic relationship similar to the *Lambert-Beer* law is assumed. The ratio of the incident intensity I_0 to the transmitted intensity I_l decreases roughly logarithmically with increasing layer thickness d or with rising concentration c . The absorbed portion of the intensity is a measure of the generated heat and, therefore, also of the temperature rise in the gas space:

$$\log (I_0/I_l) = \varepsilon \cdot c \cdot d \quad (3)$$

with the meanings of ε as the extinction coefficient, c as the molar concentration, and d as the layer thickness. Equation (3) applies to incoming sunlight as well as to Earth's radiation. Wavelengths with high absorption, i.e., with a large value of I_0/I_l , are largely absorbed even through a thinner layer, so they contribute a lot of heat. Wavelengths with low absorption, i.e., with a small value of I_0/I_l , mean less heat input. They penetrate a thicker layer. As the concentration increases, the energy input also rises, but only logarithmically. The same then applies to the temperature increase.

2. Balances of CO₂ and Energy at the Earth's Surface

CO₂ Emissions and Exchange Processes: CO₂ is exchanged between the atmosphere, the hydrosphere, and the living as well as the decaying biosphere. On top of that, there are human-caused emissions. Extensive studies and models ⁹ show the challenges in quantifying

the contributions of individual sources and sinks. Table 1 contains a compilation of estimates from various authors, which specifically apply to exchange processes for the year 2021.

Table 1. Comparison of CO₂ exchange amounts.

(1 ton of Carbon, C, equals to 3,67 tons of CO₂.)

<u>Emission and exchange of CO₂^{10,11}</u>	<u>in t C/a</u>
Atmosphere → Biosphere	- 142 x 10 ⁹
Biosphere → Atmosphere	137 x 10 ⁹
Atmosphere → Oceans	- 80 x 10 ⁹
Oceans → Atmosphere	78 x 10 ⁹
Anthropogene Emissions	11 x 10 ⁹
<u>Emissions by Vulcanos</u>	<u>> 0,1 x 10⁹</u>
<u>CO₂-Inventory of Spheres^{12, 13}</u>	<u>in t C</u>
Hydrosphere	37 000 x 10 ⁹
Atmosphere	870 x 10 ⁹

All quantities vary from year to year, similar to fluctuating harvest yields. The oceans, with their huge inventory of CO₂, play an important role in the exchange, since about 70% of the Earth's surface is covered with water. Mixing processes between the air and the moving water surface are important for balancing the partial pressure of CO₂ in the atmosphere with its saturation solubility in the surface layer of the ocean. The exchange of CO₂ with deeper water layers takes a long time. CO₂ transport in the oceans is linked to heat transport. In study ¹², the difficulties of modeling these transport processes are pointed out. The contribution of volcanoes varies a lot and is probably underestimated.

The most reliable data on CO₂ emissions comes from human contributions like energy production, cement manufacturing, and land reclamation. The scale of the exchange processes and their sources of error, in our view, don't provide evidence that the anthropogenic CO₂, which makes up only a fraction of the CO₂ increase, could permanently build up a significant surplus in the atmosphere. Long-term, the concentration of CO₂ in the atmosphere is at a historically low level ¹⁴, not at the optimal growth level for plant life.

Radiation Balance and Climate: Table 2 compares the energy flows from different sources. The human contribution is four orders of magnitude smaller than the solar one, and it is comparable to the energy flow from the Earth's interior through radioactivity and reaction heat.

Table 2. Comparison of natural and human-made energy flows.

<u>Energy flow</u>	<u>Joule</u>	<u>Source</u>
Daily sun exposure	1,06 × 10 ²²	¹¹
Human energy consumption, 2022, daily	1,6 × 10 ¹⁸	¹⁵
<u>Daily heat flow from the Earth's interior</u>	<u>3,8 × 10¹⁸</u>	¹⁶

Radiation balance means that the amounts of energy flowing in from space and back are equal. The balance between solar radiation and Earth's radiation is seen as a so-called steady flow balance. An equilibrium within days or years is not to be expected. There are just too many periodic events (solar activity, cloud formation, pole shifts, ocean currents, etc.) or random events (volcanism, particle radiation, etc.). Climate changes over longer periods in limited regions, including those with significant stress factors for the ecosphere, are therefore to be expected. Because of the large number of influences, climate is considered a chaotic process that cannot be predicted or extrapolated.

3. Modern Climate Research and Climate History

The CO₂-Temperature Correlation: From the perspective of exact natural sciences, the determination by modern climate research that CO₂ is the driving force behind the temperature increase is initially an assumption. Extrapolations about anthropogenic climate change are based on this assumption. The justification of this assumption as a causal connection with results from exact natural sciences is still pending.

The definition of the metric 'global average temperature of the Earth's surface' and details of measurement standards, such as the distribution of measuring stations, are missing. The vast majority of measuring stations are located on inhabited land. In the physical sense, specifying a global temperature average with an accuracy of ± 0.1 degrees is questionable, considering the huge regional and temporal temperature differences on the planet. The timeline of land and sea surface temperatures from 1880 to 2020 shows a faster rise in atmospheric temperature and delayed changes in sea surface temperatures ¹⁷.

History of the Climate: Modern climate research is limited to 200 years of the past and a hundred years into the future. If the period under consideration were extended back by one to two hundred years, the end of the Little Ice Age would be included, and a temperature rise could thus be explained.

The analysis of ice cores from Antarctica ¹⁸ and Greenland ¹⁹ provided results on temperatures and gas composition going back 800 000 and 500 000 years, respectively.

Alternations between ice ages and warm periods with a cycle of about a hundred thousand years were observed. These are explained by changing gravitational forces as regulatory mechanisms that alter the eccentricity of Earth's orbit and the tilt of its axis. Assuming these regulatory mechanisms according to *Milanković* ²⁰ continued, then the climate would have reached the peak of the current warm period about 8 000 years ago. In the long run, we would be on the way to the next ice age. Deviations from the average curve upwards and downwards - climate changes with temperature variations of several degrees over decades to centuries - have been analyzed, for example the Little Ice Age in the Middle Ages or the periods of the “Green Sahara” during the last warm period ²¹, so they are not uncommon.

The temperature and CO₂ curves showed similar trends over the hundreds of thousands of years. What's interesting is the observation that the CO₂ peaks apparently occur several centuries after the temperature peaks ¹⁷. The delayed adjustment of the ocean's temperature and the CO₂ equilibrium between the ocean and the atmosphere could be reasons for this.

The regulation mechanisms from the past still continue to work today. So even now, temperature could be the driving force for the climate and for the release of CO₂ from the ocean.

4. Climate Protection vs. Environmental Protection

Demands for climate protection from modern climate research are measures to reduce CO₂ emissions, especially by shifting from fossil fuels to solar energy. The low area efficiency and fluctuating availability burden the expansion of wind and solar power plants. This requires, besides building the plants, an extensive network of power lines to “collect” the electricity and a new “smart” distribution grid for quick interventions when supply fluctuates. If renewable energy sources fail, backup power plants are needed. Significant electricity storage will also not be available in the future. Renewable energies are suitable for decentralized consumption, but not as the main energy source for an industrialized country.

Renewable energies, including their additional investments for raw material extraction, require a lot of space. High raw material consumption ²² - e.g., for concrete for wind converters, copper for the power grid, lithium, silver, cobalt, nickel, and rare earths materials for batteries - causes environmental damage. There's no such thing as “green mining.” These side effects are usually downplayed when evaluating energy sources.

Even more far-fetched are attempts to reduce CO₂ concentrations by capturing it from exhaust gases or extracting it from the air and storing it in final repositories (CCS), or to use the separated CO₂ along with 'green' hydrogen to synthesize new hydrocarbon compounds (CCU). These processes come with high energy loss and, thus, increased entropy ^{4, 23}. Efforts to counter unavoidable climate change would be better spent protecting people and the environment from the effects of natural climate change. Human influence on local and regional climates through city design, greenery, or creating suitable water areas could play a positive role here.

Summary

The observed correlation between CO₂ levels and global temperature rise in the Earth's atmosphere since the start of the Industrial Revolution has not yet been confirmed as a causal relationship. Water vapour has the strongest effect on the climate among the greenhouse gases. However, the climate discussion focuses on the small share of human-made CO₂.

The heat in the 'greenhouse Earth' is stored by all gas components according to their molar heat capacities and concentrations in the atmosphere, which means that most of it is in the main components, nitrogen and oxygen. Greenhouse gases act as transmitters and senders between heat energy and photon energy, without which the process of energy exchange between the Earth's atmosphere and the space could not take place in either direction.

The exchange of CO₂ between the atmosphere and plant life, as well as the water world in the form of oceans, is many times greater than human emissions. Oceans and plant life can also temporarily be sources of CO₂. Together with the huge amount of CO₂ in the atmosphere and especially in the oceans, a balance of human emissions can be assumed.

Human energy production is about four orders of magnitude smaller than the energy from daily sunlight. The largest heat reservoir is the water of the oceans, and the biggest heat transport comes from ocean currents. The climate in the 'Earth greenhouse' is a downstream process.

The 'greenhouse' of the Earth's atmosphere is an open system. There is a dynamic equilibrium, which is the cause of climate change. The lack of connection to climate history must be seen as a shortcoming of modern climate research

The separation and storage of CO₂ (CCS) as well as the conversion of CO₂ with hydrogen into synthesis gas (CCU) are energetically associated with large increases in entropy and are therefore to be rejected within climate protection projects. The low density of solar energy and the effort required to 'harvest' it are the reasons for high land and raw material demand. As a result, climate protection often clashes with environmental protection.

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Helmut Ullmann and Martin Bülow: Developing ideas, writing and interpreting data as well as reviewing the manuscript.

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