POSSIBLE GREEN HOUSE GASES AND GLOBAL CLIMATE CHANGE

PETR ZÁMOSTNÝ[a], PAVEL KUKULA[a], and JOHN S. YOUNG[b]

[a]Department of Organic Technology, Institute of Chemical Technology, Technická 5, 166 28 Prague 6, [b]Hampshire Research Institute, Cameron 1600, Alexandria VA, USA

Received April 17, 1998

Key words: greenhouse gases, global climate change, greenhouse effect, global warming, radiative forcing

Introduction

Global climate change, or more specifically global warming, is one of the most serious environmental problems, which starts to attract the mankind attention lately. Nevertheless, the public awareness of global warming as serious problem is still negligible in comparison with other environmental threats (e.g. ozone depletion and toxic pollution). Predominantly countries with "traditionally ecological" policy, e.g. Scandinavian countries, and these feeling most threatened by possible effects of global temperature rise pay an increased effort to investigation of the problem.

The general principles and causes of global warming are well known now qualitatively, but sort of quantitative understanding of relations between reasons and consequences is necessary to develop, in order to provide environmental policymakers with data to support their decisions. It means, that there are need to cut off greenhouse gases emissions (and after the Kyoto summit it is also possible to say there is will to cut them off), but it is also apparent, that it is not possible to stop emitting green house gases completely. Therefore policymakers need to know which gases are the most dangerous in order to optimize the emission policy, and achieve decreasing of overall green house gases emissions effect.

"Greenhouse effect" and global climate change

Solar radiation is the only important income to the Earth energy balance. Wavelength of bulk of the radiation coming to the Earth belongs to visible or ultraviolet part of spectrum. Atmosphere is almost completely transparent for these wavelengths, so that nearly all radiation, which is not reflected by atmosphere, penetrates directly to the surface, where its energy is being absorbed, heating the Earth. Surface subsequently emits energy back to the universe, but as its temperature is substantially lower than the one of Sun, wavelengths of that radiation are much larger, belonging to the infrared part of spectrum.

Surprising fact is that the Earth surface's energy output exceeds its direct input from solar radiation by more than thirty percent. This would make Earth's temperature to decline continually, unless it used some "trick". The matter of that "trick", called greenhouse effect, consists in Earth's atmosphere ability to absorb a significant amount of infrared radiation coming from surface (about 1/3) and to reradiate it back

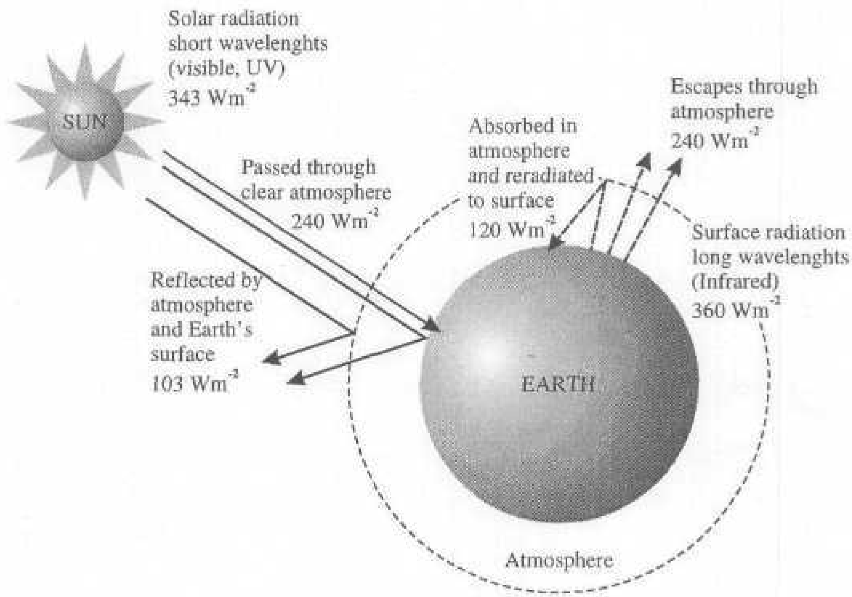

Fig. 1. **Energy balance of the Earth.** Solid arrows represents visible and UV solar radiation dashed ones the infrared radiation from Earth surface

to surface. A major part of absorption takes place at the lowest atmosphere layer - troposphere, and thus the net radiation output from planet, measured at tropopause (thin atmospheric layer above troposphere), is substantially lower than apparent output measured at surface. The energy balance of the Earth is described on Figure 1.

The major gaseous compounds of the atmosphere - nitrogen, oxygen - are quite transparent for infrared radiation. Only the minor compounds, e.g. carbon dioxide, water vapor, and artificial impurities, are capable of capturing infrared photons, due to its energy corresponds to the rotational or vibration energy of given gas bond. These gases are called greenhouse gases (GHG). Although occurring in little amounts, they are able to keep the Earth's temperature at the present level.

According this theory, the surface temperature of the Earth depends significantly on the amount of GHG in atmosphere. As long as mankind had not come to the industrial age, the concentration of natural GHG in atmosphere was maintained at the relatively steady level (if only several last millennia are taken into account) and the sources of GHG were fully compensated by their sinks. The industrial age brought additional manmade emissions of some natural GHG (CO_2, N_2O and CH_4) and emissions of artificial gases with similar effects (e.g. chlorofluorocarbons, sulfur hexafluoride), making the atmosphere slightly harder to penetrate for infrared radiation. This greenhouse effect strengthening had started to increase the average global temperature primarily, and many consequent effects, summarized under the term "Global climate change", occurred or start to occur[1].

The matter of problem is that climate changes started during 20* century have extremely large "inettia" and it is a long-term task to stop them. One reason is the limited ability of the environment to compensate artificial emission sources of GHG by their sinks, second is, that artificial emissions can hardly be expected not only to stop, but even diminish. Figure 2 describes the rise of global average temperature from the end of the 19^{th} century until presence (0.3 °C–0.6 °C) and three possible scenarios of its development in future according the Intergovernmental Panel of Climate Change (IPCC). The "low" scenario assumes that GHG emissions will remain at its present values, "best" scenario assumes the most probable alternative of linear increase of emissions, and the "high" scenario assumes the emissions volume will rise exponentially.

The size of the observed warming is compatible with what climate models suggest should have resulted from past GHG emissions. It is also small enough to have been caused instead by natural variability (although it is also plausible that natural variability has temporarily masked some of the warming caused by GHG emissions). Although serious scientific debate centers on the rate of warming, possible feedback controls at temperatures not yet achieved, and the severity of the consequences of warming, there is little doubt that warming is occurring[2]. Other explanations, such as a link with the solar sunspot cycle, remain tentative suggestions. Among the various possible explanations of the observed trend in recent global temperatures, the GHG hypothesis has the strength that it is both compatible with the available evidence and is supported by a plausible physical mechanism[3].

Greenhouse gases and their global sources

Greenhouse gases can be split into two groups respecting whether there are their natural sources or not - natural and artificial greenhouse gases

Natural greenhouse gases

Carbon dioxide, water vapor, methane, nitrous oxide and ozone have substantial natural sources in addition to manmade production, and there are powerful natural mechanisms for their removal as well. These mechanisms possess certain ability to absorb the sources scale-up due to human activity, but the rising concentration of some GHGs in atmosphere shows they are not sufficient.. The natural and anthro-

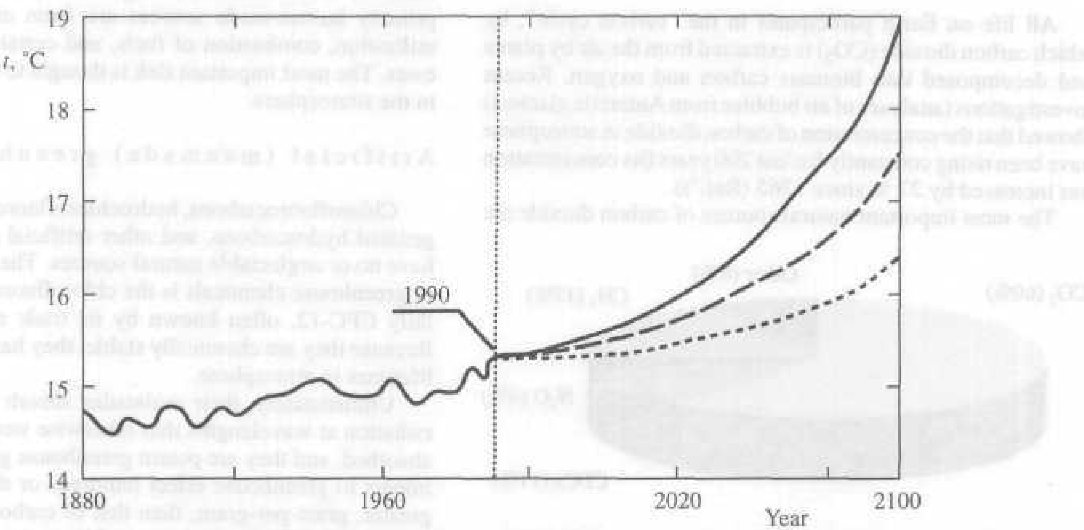

Fig. 2. **Global average temperatures from the end of 19th century to presence, and their predictions to year 2100 according IPCC.** Dotted line is for low, solid for high and dashed for most probable levels of emissions

Table I
Global Natural and Anthropogenic Sources and Absorption of GHGs

Gas	Sources		Absorption	Annual increase in the atmosphere
	Natural	Human		
CO_2 (mil. tons of carbon)	150 000	7 100	154 000	3 100-3 500
CH_4 (mil. tons of gas)	110-210	300-450	460-660	35-40
N_2O (mil. tons of gas)	6-12	4-8	10-17	3-5

pogenic sources of three most important GHGs are illustrated in Table I.

Water vapor

Water vapor is the greenhouse gas occurring in the atmosphere in concentrations about 2 %, and is the most abundant greenhouse gas. It is being emitted into the atmosphere in enormous volumes through natural evaporation from surface water sources and returned to Earth in the form of rain and snow. Water vapor is so plentiful in the atmosphere already that additional emissions are unlikely to absorb any significant amount of infrared radiation. It is also likely that the amount of water vapor held in the atmosphere is generally in equilibrium, and that increasing emissions would not increase atmospheric concentrations. Nevertheless, the water vapor presence in atmosphere is crucial for the natural Earth's greenhouse effect existence.

It is also important to note, that the equilibrium amount of water will change, if the air temperature will be changed due to other causes, and this may be a "feedback" effect acting to accelerate global climate change. According to currently available information, anthropogenic water vapor emissions at the Earth's surface are unlikely to be an important element in climate change.

Carbon dioxide

All life on Earth participates in the "carbon cycle", by which carbon dioxide (CO_2) is extracted from the air by plants and decomposed into biomass carbon and oxygen. Recent investigations (analyses of air bubbles from Antarctic glaciers) showed that the concentration of carbon dioxide in atmosphere have been rising constantly for last 200 years (its concentration has increased by 27 % since 1765 (Ref.[4])).

The most important natural sources of carbon dioxide are releases from the oceans (90 billion tons per year), aerobic decay of vegetation (30 billion tons), and plant and animal respiration (30 billion tons)[6]. Known anthropogenic sources account for 7 billion metric tons of carbon per year. The principal anthropogenic source is the combustion of fossil fuels, which accounts for about three-quarters of total anthropogenic emissions of carbon worldwide. Natural processes (primarily, uptake by the ocean and photosynthesis) absorb all of the naturally produced carbon dioxide and some of the anthropogenic carbon dioxide.

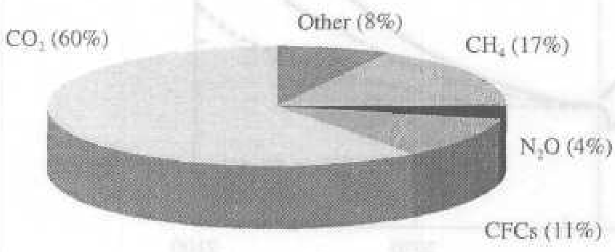

Fig. 3. Subscription of different GHGs to greenhouse effect (percentage of total)

Methane

Methane is released primarily by anaerobicdecay of vegetation, by the digestive tracts of termites in the tropics, and by several other lesser sources. The principal anthropogenic sources are leakages from the production of fossil fuels, human-promoted anaerobic decay in landfills, and the digestive tracts of domestic animals. The main sources of absorption are thought to be decomposition (into carbon dioxide) in the atmosphere and decomposition by bacteria in soil. The anthropogenic sources have increased atmospheric concentration of methane by 100 % since 1765.

Nitrous oxide

The principal source of nitrous oxide is thought to be bacterial breakdown of nitrogen compounds in soils. The primary human-made sources are from nitrogen fertilizers utilization, combustion of fuels, and certain industrial processes. The most important sink is thought to be decomposition in the stratosphere.

Artificial (manmade) greenhouse gases

Chlorofluorocarbons, hydrochlorofluorocarbons, perhalogenated hydrocarbons, and other artificial greenhouse gases have no or neglectable natural sources. The best-known class of greenhouse chemicals is the chlorofluorocarbons, particularly CFC-12, often known by its trade name, "freon-12". Because they are chemically stable, they have extremely long lifetimes in atmosphere.

Unfortunately, their molecules absorb reflected infrared radiation at wavelengths that otherwise would be largely unabsorbed, and they are potent greenhouse gases, with a direct *impact* to greenhouse effect hundreds or thousands of *times* greater, gram-per-gram, than that of carbon dioxide. On the other hand if CFCs are destroyed in stratosphere by sunlight, they release chlorine radicals causing ozone decomposition, and thus having an indirect effect on global warming. This indirect effect is significant and may cause complications in GWP estimation as it will be discussed in following section.

Figure 3 provides comparison of various greenhouse gases contributions to greenhouse effect.

Radiative forcing and Global Warming Potential

A good quantity to assess the instant effect of certain GHG emission is radiative forcing. It can be defined by following equation

$$a(m_{GHG}) = \frac{\Delta R(m_{GHG})}{\Delta m_{GHG}} \qquad (1)$$

where a is the specific radiative forcing, R net average radiating flux through tropopause from the Earth surface, m_{GHG} the amount of greenhouse gas in atmosphere. Amount of GHG in atmosphere can be expressed in any of mass, volume or concentration units and subsequently a is related to that type of unit. The tracking of changes in radiation flux through tropopause respective to the changes of GHGs concentration in atmosphere is a difficult task complicated by many approximations and uncertainties. Thus, the computation of radiative forcing requires rigorous models and extensive atmospheric and geochemical data[5].

According to equation (*1*) radiative forcing for the change of greenhouse gas amount depends on the total amount of that gas being already in atmosphere. Each gas absorbs radiation in a particular set of wavelengths, or "window", in the spectrum. In cases, where concentrations of the gas are low and no other gases block radiation in the same window, small emissions of the gas will have a disproportionate absorptive effect. However, if concentrations of the gas rise over time, a larger and larger portion of the total light passing through the "window" will already have been captured, and the marginal effects of additional emissions will not be as large. Therefore, the effect of an additional unit of emission of a gas that is relati vely plentiful in the atmosphere, such as water vapor or carbon dioxide, tends to be less than that of a rare gas, such as sulfur hexafluoride. This "diminishing return" effect implies that increasing the concentration of a particular gas reduces the impact of additional quantities of that gas. Thus, the relative impacts of various gases will change as their relative concentrations in the atmosphere change. Additionally the specific radiative forcing of a particular gas is also reduced by increasing concentration of any other gas sharing whole or part of its window.

The exact computation of specific radiative forcing of greenhouse gas requires rigorous models and extensive amount of experimental data. Since the computation is result of system with many variables and approximations, the average error of estimated radiative forcing is about 30 %. In order to get more understandable form of results, radiative forcing of a particular GHG is often related to that of carbon dioxide.

As long as only instant (or short time) effect is subject of our interest, radiative forcing fits well to our needs. However, different greenhouse gases differs also in their atmospheric lifetimes, qualifying the period of time it would take for natural processes to remove a unit of emissions from the atmosphere. Some gases, such as chlorofluorocarbons, have very long atmospheric lifetimes, in the hundreds of years, while others, such as carbon monoxide, have lives measured in hours or days. Methane, which decays into carbon dioxide over a period of a few years, has a much larger short-run effect on global warming than does an equivalent amount of carbon dioxide. Global warming potential (GWP) was introduced to conclude overall impact of GHG emission within specified time horizon into one quantity. It can be computed from known radiative forcing of a greenhouse gas and information about its life cycle according following equation

$$GWP = \int_0^{TH} [ax(\tau)] d\tau \qquad (2)$$

where TH is specified time horizon (usually 20, 100, 500 years), x time, and x the fraction of originally emitted amount, that is active in atmosphere in time x. Relative global warming potentials of selected GHGs are provided in Table II (Ref.[6]).

Table II
Numerical Estimates of Global Warming Potentials Compared with CO_2 Direct Effects (kg of gas per kg of Carbon Dioxide)

Gas	Lifetime [Years]	Direct Effects for Time Horizons of		
		20 years	100 years	500 years
Carbon Dioxide	variable	1	1	1
Methane	12±3	56	21	7
Nitrous Oxide	120	280	310	170
HFC-23	264	9 200	12 100	9 900
HFC-125	33	4 800	3 200	11
HFC-134a	15	3 300	1 300	420
HFC-152a	2	460	140	42
HFC-227ea	37	4 300	2 900	950
Perfluoromethane	50 000	4 400	9 500	10 000
Perfluoroethane	10 000	6 200	9 200	14 000
Sulfur Hexafluoride	3 200	16 300	23 900	34 900

Although the global warming potentials for direct effects of greenhouse gas emissions (Table II) are valuable results, the whole problem is more complex. Many gases are chemically active, and they may react in the atmosphere in ways that have an influence on formation or decomposition of other greenhouse gases. For example, nitrogen oxides and carbon monoxide combine to promote the formation of ozone, which is a potent greenhouse gas, while chlorofluorocarbons boost atmospheric ozone decomposition, thus promoting global cooling. These indirect effects have sometimes proved impossible to summarize in terms of global warming potentials. Indirect effects also imply that changes in relative concentrations of various greenhouse gases would tend to change their relative effects. IPCC paid an effort to investigation of indirect effects of chlorofluorocarbons (CFCs), hydrochlorofluorocar-

Table III
Numerical Estimates of Global Warming Potentials Compared with CO_2 Direct and Indirect Effects (kg of gas per kg of Carbon Dioxide)

Gas	Magnitude of Effects							
	20-year Time Horizon				100-year Time: Horizon			
	Direct Effects	Direct and Indirect Effects			Direct Effects	Direct and Indirect Effects		
Chlorofluorocarbons								
CFC[a]-11	4 900	1 200	to	2 900	3 800	540	to	2 100
CFC[a]-12	7 800	6 000	to	6 800	8 100	6 000	to	7 100
CFC[a]-113	4 900	2 800	to	3 800	4 800	2 600	to	3 600
HFCs[a], PFCs[b] and others								
HCFC-22	4 000	3 500	to	3 700	1 500	1 300	to	1 400
HCFC-123	300	60	to	70	90	20	to	50
HCFC-124	1 500	1 300	to	1 400	470	390	to	430
HCFC-141b	1 800	660	to	1 200	600	170	to	370
HCFC-142b	4 100	3 600	to	3 800	1 800	1 600	to	1 700
Halon-1301	6 100	-14 100	to	-97 600	5 400	-14 000	to	-84 000
Tetrachlormethane	1 900	-500	to	-2 600	1 400	-650	to	-2 400
1,1,1-Trichlorethane	300	-400	to	-1 000	100	-130	to	-320

[a] HFC - hydrochlorofluorocarbons, [b] PFC - perfluorocarbons

bons (HFCs), and other halogenated compounds in ozone layer[7]. Table III presents estimates of direct and indirect effects magnitudes, according IPCC. It is believed that some gases exert a net cooling effect (Halon 1301) (Ref. [8]).

Conclusions

Signs of global climate change have been revealed during the last century, most significantly in average global temperature, sea level, precipitation trends, and polar ice volume. Although the question, whether this change is result of human activity, is still alive, most of environmental studies indicate answer is "yes". Therefore, it appears to be reasonable to pay an effort to reduce further increasing of GHGs concentration.

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P. Zámostný[a], P. Kukula[a], and J. S. Young[b] *("Department of Organic Technology, Institute of Chemical Technology, Prague, [b]Hampshire Research Institute, Cameron, Alexandria VA, USA):* **Possible Green House** Gases **and Global Climate Change**

The article concerns in greenhouse gases emissions and their effect on global climate change. It provides illustration of the greenhouse effect mechanism based on the Earth energy balance. It deals with the most important natural and artificial greenhouse gases, identifies their possible sources and sinks, and provides information about ways of assessment of their relative impact on environment. The radiative forcing and the global warming potential and their values according to the IPCC are discussed.