

Csaba Muzsnay^[a]

Keywords: global warming, greenhouse effect, atmospheric water vapor (AWV), greenhouse gases, carbon-dioxide, human activities originated water vapor generators, absorption of long wave radiation, precipitate formation and transport

It has long been known that the absorption of terrestrial energy by water molecules is the largest one (60-75 %), comparing with the lower value (20-24 %) of carbon dioxide molecules. The other gases with greenhouse effect absorb this energy in much smaller extent (8-12 %). In the last 360 years, considering from the industrial revolution, the amount of water vapor resulting on the basis of eight types of major processes, by direct and indirect human activities, and getting into the atmosphere was continuously growing. These are determined, by the appearance of very numerous human activities originated water-vapor/steam generators, the continuous increase of the greenhouse effect and the climate change. The following levels of special and extraordinary behavior of the atmospheric water vapor can be distinguished: 1) molecular, 2) associative (cluster) level, 3) condensation level which can be joined to phase transformations - mainly in the clouds, 4) the level of precipitate formation followed by intense moisture transport, 5) the level of firm difference existing between the atmospheric relations of the Northern and the Southern Hemisphere, mainly due to human activities. The atmosphere near the Earth's surface (in the troposphere) has such a well delimited temperature and pressure domain, in which water with its unique property occurs in all three phases. Water vapors condense easily. The triple point of the other atmospheric components is not achieved. This unique and extraordinary feature of the water plays a determining role in the meteorological processes of the Earth and the development of the climatic relations. All this warming, among other things, is manifested in the melting of the ice of the North Pole and the elevation of the snow altitude line. The primary task is the stopping of the warming of the North Pole Region and the promotion of its cooling. Global solutions appear as mandatory needs, which are very costly to start because extensive investments are required.

* Corresponding Authors

E-Mail: <u>cmuzsnay@chem.ubbcluj.ro</u>

INTRODUCTION

The global warming of the Earth's surface and that of the atmosphere already has a solid experimental basis. There are fierce discussions about the time variability of the weather and strange interpretations of the average global temperatures drop in the second half of the twentieth century. It should be mentioned that the author of this paper was able to interpret the phenomenon of global cooling during 1945-1980.¹

The increased greenhouse effect caused by constantly rising carbon dioxide content of the atmosphere is almost universally accepted, although there is no direct evidence for this. Among the triatomic molecules of atmosphere, the asymmetric water molecules, - because of their polar character, and their highest average concentration, absorb much more strongly the long-wave (terrestrial) radiation, than the symmetric, non polar molecules of carbon dioxide. The absorption of terrestrial energy by atmospheric water molecules is the largest one (60-75 %), comparing to the lower value (20-24 %) of carbon dioxide molecules. The other gases with greenhouse effect absorb this energy in a much smaller extent (8-12 %).

Considering from the industrial revolution, in the last 360 years by direct and indirect human activities, increasing amount of water vapor are getting into the atmosphere on the basis of eight types of major chemical processes.^{2a,3} These determined the continuous increase of the greenhouse

effect and the climate changes, through the appearance of very numerous human activities originated water-vapor generators. The spheres and the climatic systems of the Earth in the last two centuries clearly show noticeable changes. In connection with the global warming and climate change differences of opinion took shape.^{2, 4-8}

Within the framework of this paper we turn our attention to the water vapors resulted directly and indirectly from human activity, that causes weather variability and global warming which is demonstrated on the basis of a five levels theory recently published partially.^{2,3}

Because of the special and extraordinary behavior of atmospheric water vapor the following five levels, with some energetic aspects, can be distinguished: 1) molecular, 2) associative (cluster) level, 3) condensation level which can be joined to phase transformations - mainly in the clouds, 4) the level of precipitate formation followed by intense moisture transport, 5) the level of firm difference existing between the atmospheric relations of the Northern and the Southern Hemisphere, mainly due to human activities.^{2, 9, 10}

DISCUSSION

The levels are constituted by molecular structures, energy states, phase transitions, human agglomerations, and activities, as well as differences in geographical location.

The first three levels possess mainly energetic characteristics, at which are determining the changes in energy of molecular structures or physical state of material. The presentation of all levels will happen in separate subsections

[[]a] Babeş-Bolyai University, Chair of Analytical Chemistry, Cluj-Napoca, Romania

Molecular level of electromagnetic energy absorption

The small sized and simple structured molecules have the determining role in properties of the Earth's, atmosphere. The larger molecules with a more complicated structure can be found only in trace amounts, and they do not get a determining role in the energy relations of the atmosphere. According to quantum-chemical calculations and on the basis of molecular spectroscopy measurements, the monatomic noble gases and the most abundant components, like nitrogen and oxygen, with symmetrical diatomic molecules - N_2 and O_2 – are capable of significant interaction only with the electromagnetic radiation of high energy - of the order of electron excitation energy.

These atoms have a spherical electron distribution, and the diatomic molecules have a non-polar character. As a result of this, they interact very limitedly with the solar radiation and their absorption of the low energy Earth radiation is completely negligible.¹¹

The special role of water vapors in the greenhouse effect is due primarily to the V- or triangle- shaped, respectively flattened (distorted) tetrahedron of asymmetric water molecules with permanent dipole moment¹², Thus, it can interact with all the visible, the microwave and the infrared components of the electromagnetic radiation, absorbing the long-wave (terrestrial) radiation. The non-symmetrical water molecule with relatively high concentrations presents big reservoirs (e.g., the oceans, seas, lakes, rivers), and is able to change the thermodynamic states in the atmosphere. Although the linear carbon dioxide molecule is non-polar in ground-state, in the course of vibrations it becomes polar and capable of interaction with radiation. Primarily it absorbs energies radiated from the surface of Earth. Both the quite large and the ever-increasing concentrations produce important greenhouse effect. At the sun's surface there's a high temperature $(5250 \text{ }^{\circ}\text{C})$ with a blackbody radiation spectrum (Fig. 1.) This light passing through the gas components of the atmosphere is absorbed in many frequencies/wavelengths obtaining the absorption bands of greenhouse (GH) gases presented.

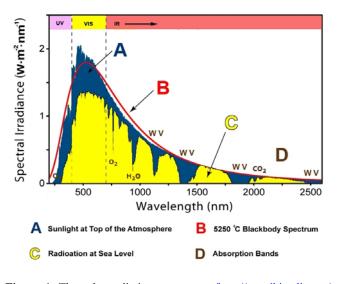


Figure 1. The solar radiation spectrum /<u>http://en.wikipedia.org/</u> wiki/File:Solar_Spectrum.png

The ozone appears mainly in the upper layers of air, in the middle part of the stratosphere (20-35 km altitude) attains its largest concentration, in the so called ozone shield. As a triangle shaped molecule it easy interacts with different energies of photons from sunlight. It absorbs ultraviolet radiation and thus protects the biosphere from the harmful components of sunlight. By means of his greenhouse effect a part of heat radiations is retained from the surface of the Earth. As an oxidant it is decomposed by gases with reductive character (e.g. NO), the Cl atom and the halogenated hydrocarbons catalyze the ozone disintegration. All these threaten the existence of the O_3 -layer, or diminish its thickness.

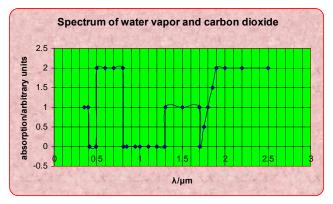


Figure 2. Schematic spectrum of water vapor and carbon dioxide. Arbitrarily, both for easier representation and better transparency of figure the maximum absorption of carbon dioxide (1) is considered as half of the value for water (2). The range of "atmospheric window" is well discernible on the figure (range between $0.8-1.3 \mu m$).

Fig. 2. represents the 2-2 main absorption bands of atmospheric water vapors and carbon dioxide in the range of 0.1-3.0 μ m .The CO₂ has between 1.3-1.7 μ m a very strong absorption band and between 0.35-0.40 μ m a weaker one. In addition, there are smaller absorption bands also in the range of 0.11-0.27 μ m, which are not shown on the graph.^{13, 14} Between 0.5-0.8 μ m the strong water vapors absorption corresponds to rotational-vibration band, while at wavelengths bigger than 2.0 μ m an excessively strong absorption as a rotational band of water vapors is noticeable. At wavelength smaller than 0.5 microns, more precisely in the 0.072-0.49 microns wavelength range water vapors excel in absorbing capability.

In the range of 0.8-1.3 microns neither CO_2 nor water vapors get absorbed and through this well known "atmospheric window" the long-wave radiation from Earth's surface escapes into the space. The energy of the sun-ray, with its variety of color and wavelength, reaches the earth's surface, illuminates and warms it. IR emission from the Earth's radiation can get back into the space, but mostly it's absorbed by water vaposr and carbon dioxide in the atmosphere - these substances become almost opaque for the radiation in IR. If other gases are present (e. g. CH_4 , N_2O), they also absorb, the "atmospheric window" closes more and more, all together it's warming the air layer near the Earth very effectively - in form of long wave ray - 240 W.m⁻² of energy radiated out into space directly.^{13, 3}

The level of molecular association, of cluster and aerosol formation

Water molecules establish hydrogen bonds with almost all atmospheric components forming clusters. The following clusters are more frequent:

- water-water (7>n>1), where n is the total number of water molecules),
- sulfuric acid-water
- nitric acid-hydrochloric acid-water: HNO₃-HCl-H₂O (see Fig. 3),
- inert gas-water
- and many others.

The stability of the above association compounds decreases with temperature increase.

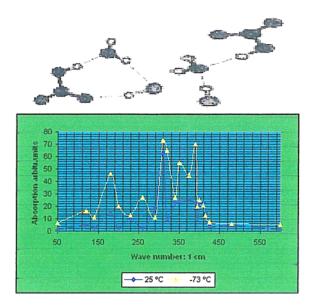


Figure 3. A spectral detail referring to HNO_3 -HCl-H₂O cluster at two temperatures. At -73 °C the cluster is stable and ring-shaped, at 25 °C the cluster is less stable, by ring opening there is a chain formation.

The pronounced aggregation under certain conditions leads to aerosol formation. All types of these aggregations absorb terrestrial radiant energy. Aerosols absorb directly the radiant energy of the sun too.¹⁵

The level of condensation, which is connected with the phase transformation of water

Both the temperature and pressure of the atmosphere near the Earth's surface (troposphere, stratosphere) varies in a limited area in which the three phases (vapor /gas, liquid, ice /solid) of water with their special properties can be present simultaneously - at temperatures corresponding to the triple point (T: 0006 °C = 273.156 K and P_{vap}: 6.11 mb).¹⁶ This interphasic equilibrium (See: p = f (T) diagram - Fig. 4.) is established quickly especially between liquid and gaseous phases with fast evaporation of liquid water and easy condensation of vapors at greater temperatures than 0 °C along the blue curve. At lower temperatures than 0 °C along the blue curve the water vapors are in equilibrium with the ice (solidified water). The nearly vertical brown line separates water (liquid) from the solid water (ice) Parallelogram delimited by coordinates: p=0 to 1.0 bar and T = -100 to 100 °C (the green colored area on the reduced form of Fig. 4.) represents the boundary conditions of the earth's atmosphere and the existence of water in the 1-3 states of aggregation. In this parallelogram between -80 °C (p=1 b) and -100 °C (p=0.1 b) the CO₂ can be condensed but only at greater pressures than the partial pressure of carbon dioxide in atmosphere. Thus, the atmosphere near the Earth's surface has such a well delimited temperature and pressure domain, in which water with its unique property occurs in all three phases.

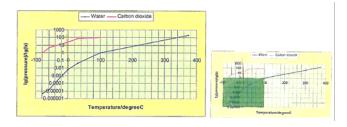


Figure 4. Pressure-temperature dependence (p=f(T)) for two components of air: water vapors and carbon dioxide. The pressure axis is logarithmic.

It must be emphasized that the triple point of water is objectively determinable and reproducible, but this doesn't happen in the atmosphere for the other nine basic components. The triple points of the rest of the atmospheric components – other that water - (especially of carbon dioxide) are not achieved. This unique and extraordinary feature of the water plays a determining role in the meteorological processes of the Earth and the development of the climatic relations.

The formation of precipitation, and the intense transport of humidity

The fact that only water condenses (by liquefaction or solidification) among the ten basic components of the atmosphere having a real triple point in the troposphere, is a unique and extraordinary property, that plays a decisive role in meteorological processes of the world. In the atmosphere, due to local differences in temperature and pressure it's generating either vertical transport (convection) or horizontal transport (advection) of moisture able to have three states of aggregation.¹⁷ The occurrence of storm cells involves a starting pulse: e.g. - among other things - the introduction of water vapors in the atmosphere by human contribution.

The fulfillment of at least four balance conditions ensures the understanding of the major processes in the atmosphere.^{17, 18}

1) The water balance: excess water vapors do not accumulate, but carrying both atmospheric humidity and precipitations as either to the North Pole or to the drier areas.

2) The heat balance: Most of the radiation deficit observed Earth's surface near the Arctic is compensated by the latent heat of water vapors that is released by its condensation during cooling (Fig. 5.).¹⁹

3) The angular momentum balance of Earth-atmosphere system: Introduced water vapors into the atmosphere by human contribution and pumped through greenhouse energy are not lost, they also contribute to both atmospheric warming and other neighboring areas.

4) The equilibrium distribution of air masses.

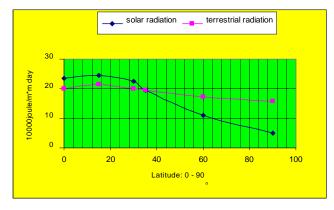


Figure 5. Variation of two types of radiant energy in function of northern latitude. At 35 ° latitude the two radiations are leveling.

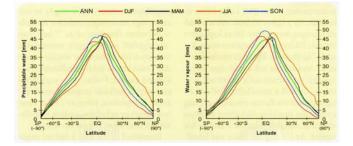


Figure 6. Water vapors column of the atmosphere (in mm) during 4 seasons of year averaged zonal, seasonal and by time, from July 1990 to June 1995 using TOVS Path – B data (right) and from 1991 to 1995 using NVT data (left). On both figures it's noticeable, that much greater quantities of water vapors stream in the direction of the North Pole than in the direction of the South Pole, mainly in summer (JJA), but in the Spring (MAM) and Autumn (SON) period. The blue curve (ANN) is averaged over the year, it also supports the previous commentary.

The distinctive difference level between the atmospheric phenomena of the Northern and the Southern hemisphere

Heating phenomena presented above is manifested in many ways, e.g. by suddenly melting of North Pole ice in the summer, but in a lesser extent ice melts at the South Pole too, and by increased thickness of snow in the mountains - especially in the northern hemisphere, because there is a clear and distinct difference between the two hemispheres of the globe. Thus: - land area is much smaller (1/4-1/3), than that covered by water (2/3-3/4), but the land on the north is more than ~ 2/5 as against 1/5 land area on the south. 90% of the population lives and works in the Northern Hemisphere and 90% of the water vapor resulting from human activities get into these parts of the atmosphere. Comparing the corresponding seasons, the northern

hemisphere has wetter seasons mainly due to human activities. This part of the atmosphere contains more vapors, being wetter than the southern one (see also the Fig. 6).²⁰

Winters are about equally wet, but summers in the Northern Hemisphere are more humid. Thus in August humidity is higher by 20%, and the average temperature is higher by 2.2 °C. Vapor content of the atmosphere in the North are higher than in the South primarily because of more extensive human activities.

The most sensitive sensor of global warming caused by water vapors, is the Arctic, with the North Pole and Greenland (Fig. 6.), and respectively the Antarctic.

Most important global tasks

- Reducing the water vapor content in the atmosphere, not by any means, but respecting a comprehensive and continuous program of permanent reduction of water vapors emitted by mankind. - Gradual restoration of the North Pole to the frozen state it had before the beginning of the industrial revolution.
- 2. Stopping the warming of the Arctic, especially in summer, promoting its gradual cooling is the main task. In this way, we could avoid the further weakening of the Gulf Stream, the rise of the ocean's level and such prevent the flooding of seaside cities and settlements. ^{2b, 3, 9}
- 3. Making serious global investments for both vapor condensation, and reducing the evaporation of water used in industry, agriculture and many other fields to obtain the formulated major goals. It involves the establishment of an overall control system for efficient operation of expected processes and technologies. When an internationally valid political decision has been reached, aiming at the complete and continuous retention from the atmosphere of all water vapors resulting from human activity a decision that is compulsory for every nation detailed action plans have to be developed and implemented while ensuring all reasonable and legitimate secrecy requirements.
- 4. Ensuring the central role of natural sciences especially that of Chemistry and Engineering through increased contribution from scientific institutions and national scientific organizations.

CONCLUSIONS

Global warming is due not only to the increasing carbon dioxide content of atmosphere; it can be attributed to the great quantity of water vapors generated both directly and indirectly by mankind.

The global and international actions should provide concomittant reduction of the huge amounts of water vapors and carbon dioxide originated from human sources of any kind. The amount of atmospheric water vapors resulted directly or indirectly by human activities must be condensed and stored very wisely and efficiently.

REFERENCES

- ¹Muzsnay, Cs., 17th Internat. Conf. on Chem., Cluj-Napoca, November 3-6, **2011**, 62.
- ²Muzsnay, Cs. Magy. Kém. Lapja, **2011**, 64(9), 265-272; Magy. Kém. Lapja, **2011**, 64(10), 301-306.
- ³a) Muzsnay, Cs., 15th Int. Conf. Chem., Târgu-Mureş November 14, 2009, 59, b) Muzsnay, Cs., and Muzsnay, Cs. jun., 15th Int. Conf. Chem., Târgu-Mureş, November 14, 2009, 77.
- ⁴Muzsnay, Cs., Int. Conf. "The contexts of sustainable development, environmental protection and nature conservation in Carpathian Basin", Pécs, 15-th September, 2010.
- ⁵Pentagon Report, in *"Magyar Szó" Online*, (In Hungarian) Iss. 21, 22 February, **2004**.
- ⁶Miskolczi, F. M., a) *Időjárás* **2007**, *111(1)*, 1., b) *Energy Environ*. 2010, 21(4), 243.
- ⁷Berényi, D., Term. Tud. Közl. (Budapest), 2011, 142(3), 101.
- ⁸Czelnai, R., Term. Tud. Közl. (Budapest), 2011, 142(4), 148.
- ⁹Muzsnay, Cs., 16th Int.. Conf. Chem., Cluj-Napoca, November 11, 2010, 63.
- ¹⁰Muzsnay, Cs., Int. Conf. Environ. Progress, Cluj-Napoca, 11th November, 2011, 56.
- ¹¹a) Császár, A., *Term. Tud. Közl.* 2009, 140(2), **2009**, 60-64; b) Császár, A., Furtenbach, T. and Czakó, G., *Magy. Kém. Foly.* **2006**, 112(4), 123-8.

- ¹²a) Chaplin, M., "Water Structure and Behavior"; http://www.lsbu.ac.uk/water/molecule.html, (http://www.Isbu.ac.uk/water/chaplin.html) - with regularly and frequently renewed chapters. b) Muzsnay, Cs., 1) Stud. Univ. Babeş-Bolyai, Ser. Chem., V., **1984**, 29, 49. 2) Magy. Kém. Foly. 1987, 93(2), 54.
- ¹³Uherek, E., Environmental Science Published for Everybody Round the Earth Educational Network on Climate, ESPERE Climate Encyclopedia, 2004, Mainz, Max Planck Institute for Chemistry; (http://www.atmosphere.mpg.de/enid/2640).
- ¹⁴Borşan, D., "Fizica atmosferei" (in Romanian) 1981, Univ. Bucureşti, Bucureşti, 125.
- ¹⁵Gómez, P., C., Gálvez, O., Mosteo, R., G., Puzzarini, Cr., Escribano, R., *PCCP*, **2010**, *12*, 4617.
- ¹⁶Atkins, P., W., "*Physical Chemistry*", **1992**, V. I. Capitols: 1 and 6 (in Hungarian), Tankönyvkiadó, Budapest.
- ¹⁷Czelnai, R., Introduction to Meteorology I. Fundamentals of Atmospheric Science (in Hungarian), 1993, Nemzeti Tankönyvkiadó, a) 93-95, b) 110, c) 125, d) 122, 130, and e) 115-118.
- ¹⁸Czelnai, R., Götz, G. and Iványi Zs., Introduction to meteorology II., The atmosphere in motion and oceans (in Hungarian), Nemzeti Tankönyvkiadó, Budapest 1998, a) 346-347, b) 11-14, c) 56-61, 303-307.
- ¹⁹Rákóczi, F., "The atmosphere our living space" (in Hungarian), **1998,** Mundus Magyar Egyetemi Kiadó, Budapest, 32-38, 40, 41, 50.
- ²⁰Hantel, M., volume editor, Observed Global Climate in Landolt-Börnstein, New Series, Group V. Geophysics, Vol. 6, 2005, Springer Verlag, Berlin, a) 5-4, b) 5-12.

Received: 24.02.2013. Accepted: 13.03.2013.