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Chemistry of the atmosphere and the climate

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ABSTRACT. The influence of the chemical composition of the atmosphere on the greenhouse effect and climate is analysed, and the major role of the biosphere in regulating this composition is discussed. Evidence of the observed variation trends of concentrations of small admixtures of optically active atmospheric components is presented, and the attendant possible changes in climate are outlined. A brief characterisation of the main properties of the atmospheric aerosol is given, and its role in shaping climate assessed.

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I. Introduction

The climate and its changes are governed by the complex interaction between the components of a system composed of the atmosphere, the hydrosphere, the lithosphere, the cryosphere, and the biosphere. This system functions under conditions where solar radiation is practically the only source of energy. The atmosphere plays an important part in the development of the greenhouse effect because it contains a large number of optically active trace gaseous and aerosol components (TGAC).[1–13] Clouds are the most essential climate-forming component of the atmosphere. Their formation is associated with TGAC.[14] This fact determines the key role of chemical and photochemical processes as shapers of climate.

Information concerning the direct influence of various atmospheric chemical components on its absorption of UV radiation, the greenhouse effect, the photochemical formation of oxidants, the acidity of precipitation, and the corrosion of materials is presented in Table 1.[15] The choice of the key atmospheric phenomena is of course arbitrary and may vary according to the specific features of the problem under investigation.

It is also important to consider the large number of indirect influences (e.g. the effect of halocarbons on the ozone content, etc.). The synergism resulting from the interaction between various chemical processes in the atmosphere and biosphere should likewise be taken into account.

Table 2 shows the effect of diverse factors on the development of the chemical composition of the atmosphere.[15]

II. Chemistry of the atmosphere and the greenhouse effect

Table 3 lists the trace gas components (TGC) that exert a significant influence on the development of the greenhouse effect and related chemical processes in the atmosphere. Sixteen different characteristics of these components are presented.[12,13] The degree of reliability of available data on the sources of these components, their concentration and the variation trends for the latter, their lifetime in the atmosphere, their chemical activity, and their contribution to the greenhouse effect, has been assessed. There are still many gaps in our knowledge of the cycle of such important TGC as CH_4, CO, N_2O, and NO_x. The fact that our data on the contribution of processes connected with fossil fuel combustion (for the generation of energy) are not completely reliable, is a matter for great concern, because these contributions may account for 75% of the total anthropogenic emissions. For a clearer picture of the impact of the greenhouse effect on climate, studies of climatic chemical phenomena should be continued.

The reliability of estimates of anthropogenic influences on the chemical composition of the atmosphere, and of the environmental changes they cause is greatly limited by our inadequate knowledge of the relevant physical, chemical, and biological processes. Within a time scale of about a decade, the atmosphere, the continents and the seas represent a single system. The physical and chemical processes in the atmosphere which are subjected to increasing anthropogenic loads play a vital part in the development of biogeochemical cycles. Life on our planet depends on these cycles.

The main feature of the atmosphere is its heterogeneity. A fundamental feature of the atmosphere is its heterogeneous nature. Water in all its states plays a major role in the chemistry of the atmosphere. In particular, it is a source of hydroxyl OH (the main participant in gas-phase reactions), and of peroxide H_2O_2 (a critical oxidising agent in reactions between liquid components). Water in its liquid form (clouds and rain) has a significant effect on the chemical transformations of various compounds as well as on the tropospheric cycles of sulphur, nitrogen, carbon, halogens, and other elements. It is impossible to give an adequate description of these cycles without a detailed investigation of the processes of transformation of gas into particles and the part played by clouds and rain in these events.

Studies of the heterogeneous chemical processes in the atmosphere are of crucial importance for an understanding of the special features of the development of biogeochemical cycles. Such studies are expected to: (1) establish the relationship between homogeneous and heterogeneous processes and the rates of the gas-phase reactions; (2) establish the role of heterogeneous processes in transport phenomena, physical and chemical transformations, and washout mechanisms—all of which govern the spatiotemporal variability of the key components of the biogeochemical cycles (rain clouds,

rainless clouds, aerosols etc.); and (3) reveal the contribution of heterogeneous processes as factors responsible for changes in weather and climate.

The anthropogenic influences on climate are multiple and diverse. Without going into the subject of micro- and mesoclimate, let us discuss the global processes resulting from changes in the amount of optically active trace gas and aerosol atmospheric components that have an impact on the greenhouse effect. In this connection the problem of increasing concentrations of atmospheric CO_2 becomes important, as well as the assessment of its effect on climate.[16]

Such an estimate is necessary for: (1) predicting industrial development and its effect on the biosphere in the coming 50–100 years; (2) establishing the regularities of the global carbon cycle; (3) developing a reliable climatic theory. However, at present there are too many uncertainties for us to be able to solve these three problems. By way of example, let us consider the current state of knowledge of the carbon cycle. There are conflicting estimates of the contribution of marine and continental biota to this cycle. Research over the last 10–15 years has clearly established that there is a large number of TGAC and that their contribution to the greenhouse effect is considerable.[4] Hence it is hard to get sufficiently reliable predictions for the next 50–100 years of climatic changes due to anthropogenic factors, though there is no question of the urgent need for these.

Table 1. Effect of the chemical components of the atmosphere on its most important phenomena.[15]

Constituents	Absorption of UV radiation	Greenhouse effect	Photochemical formation of oxidants	Acidity of precipitation	Decreased visibility	Corrosion of materials
C (soot)		+			+	
CO_2		+				
CO						
CH_4		+				
C_xH_y			+		+	
NO_x			+	+	+	
N_2O		+				
NH_3/NH_4^+				+		
SO_x		+		+	+	+
H_2S						+
COS						
Organic sulphur						
Halocarbons		+				+
Other halides						
Trace constituents						+
O_3	+	+	+			+

Note. + shows that this component affects the respective phenomenon.

Atmospheric composition is largley determined by the processes occurring in the biosphere. This is why the anthropogenic influences on the biosphere that change the cycles of its various components exert a considerable influence on the climate.[17,19]

Continuous synthesis and degradation of organic matter take place in the biosphere. The chemical composition of the environment is maintained in a stable state by virtue of the closed cycles of substances in the biosphere. In the pre-industrial period with its slight anthropogenic disturbances of biospheric processes, balance of the flow of substances reached a level of ~0.01% as a result of synthesis and breakdown in the biosphere.[17] This happened because there were naturally selected correlated communities of living organisms involving a huge number of species. The anthropogenic effect resulting from the synthesis and breakdown of organic matter and industrial products causes an imbalance in the fluxes of substances. This fact calls for the immediate solution of the following fundamental ecological problems: (1) ascertaining to what extent the cycles of substances in an undisturbed atmosphere are closed; (2) determining the maximum disturbances that do not cause irreversible biospheric and environmental changes; (3) obtaining data on the current state of the biosphere and environment, particularly on the extent of closure of the cycles of substances.

Table 2. Main factors affecting the chemical composition of the amtosphere.

Constituents	Oceans and estuaries	Marshland	Crops	Wild vegetation	Domestic animals	Wild animals	Biomass combustion	Petrol combustion	Coal combustion	Industrial processes
C							+	+	+	
CO_2	+		+	+			+	+	+	
CO	+			+			+	+	+	+
CH_4		+	+	+	+	+	+			
C_xH_y	+		+	+			+			
NO_x	+		+				+	+	+	+
N_2O	+		+	+			+	+	+	
NH_3/NH_4^+		+	+	+	+	+	+		+	
SO_x								+	+	+
H_2S	+	+	+	+						
COS	+	+		+						
Organic compounds	+	+		+						
Halocarbons										+
Other halides								+	+	+
Trace constituents							+	+	+	+

Note: x means that this factor affects the content of the respective component.

An analysis of biospheric energy permitted the establishment of the distribution of energy fluxes and of biogens in organisms, depending on their size.[17] It appears that 99% of the biospherical energy flux can be attributed to organisms less than 1 cm in size. Highly closed biogeochemical cycles become feasible if less than 1% of the energy flux is utilised by organisms larger than 1 cm in size. These conclusions confirm empirical data for natural communities undisturbed by anthropogenic effects.[17]

Studies of the extent of carbon cycle closure, based on the changes in carbon isotope composition of tree growth rings, are of fundamental importance.[18] The redistribution of carbon may occur mainly between four reservoirs: atmosphere, oceans, fossil fuel, and

the biosphere. Carbon "leakage" beyond the confines of these reservoirs can be disregarded. In order to establish the changes in the carbon content of the ocean and the biosphere, it is enough to find them just for one of these two reservoirs. The changes in the second one can be calculated from the equilibrium equation (law of the conservation of matter). Oceanic carbon absorption is described by two constants. The first is determined by the physicochemical absorption resistance to changes in the total carbon content, including bicarbonates and carbonates. The second is governed by the absorption resistance to concentration changes of dissolved gaseous CO_2 alone. This latter constant corresponds to changes in biological activity.

Table 3. Influence of various trace gas components in terms of their effect on the chemical processes in the atmosphere and on global climate.[12,13]

Constituent	Effect on		
	chemical processes	climate	climato-chemical phenomena
Carbon dioxide	0	2	1
Ozone	2	2	2
Methane	2	1	1
Carbon monoxide	2	0	1
Nitrous oxide	2	1	1
NO and NO_2	2	0	1
Hydroxyl	2	0	1
Trichlorofluoromethane	2	1	1
Dichlorodifluoromethane	2	1	1
Bromochlorodifluoromethane	2	0	1
Bromotrifluoromethane	2	0	1
Sulphur dioxide	1	0	1
Carbonyl sulphide	1	0	1

Note. The following notation is used: 2, strong effect; 1, moderate effect; 0, weak effect.

Because of the buffer effect on the absorption of the main ^{12}C isotope and the absence of such an effect on the absorption of the other carbon isotopes (the Bolin–Eriksson effect), these two specific constants appear in different combinations in the balance equation.[19] This allows us to estimate two independent combinations of constants from the changes in ^{14}C and ^{13}C carbon isotopes in the growth rings. In addition, an empirical buffer factor of resistance to CO_2 penetration through the atmosphere–ocean interface is used in the calculations, and corrections are made for the ^{13}C isotope fractionating. In this case no information about processes taking place in the ocean and biosphere or about their structure is required.

According to known estimates[17–19] with a significance level above 70% the emission of carbon from land biota is greater than that caused by the combustion of fossil fuel. The seas absorb the biosphere emissions, changing in the process their biological activity. As a result, the carbon content in the biosphere as a whole, including land and sea, remains essentially unchanged. On the other hand, carbon content changes separately in the land and marine parts of the biosphere, and the atmospheric carbon fluxes that reflect these changes are considerably greater than the emission due to fossil fuel combustion.

No notice has been taken to date of the possible changes in oceanic biological activity. For this reason, it was believed that carbon emissions from land biota were lower than from fossil fuel combustion. If this factor is not taken into account, agreement with the carbon balance equation has a lower than 30% significance level. It is evident that carbon cycle studies demand a new approach to the problem of anthropogenic influences on climate.

In studies of the impact of increasing amounts of atmospheric CO_2 on climate, an effect that should raise the tropospheric and lower the stratospheric temperature, feedback mechanisms have not been sufficiently considered till now. Thus, higher tropospheric temperatures should affect the distribution of water vapour, cloud, wind, rainfall, sea ice, etc. It is by no means clear in advance what the total effect of the respective feedbacks would be: would it lead to a mutual compensation of opposite effects or to an increased CO_2 effect? The same is true for the stratosphere, where changes in temperature conditions may affect photochemical processes and lead to a redistribution of such an optically active component as ozone. We are still very far from a good understanding of the mechanism of the CO_2 effect on climate. Additionally, the atmosphere is subject to the effect of many other optically active trace gas components (e.g. nitrogen oxides, freons, etc.).[3–7] Accordingly, this calls for: (1) reliable parametrisation of the radiative properties of various gases and establishment of their priority in climate models (e.g. the climatic consequences of an increase in tropospheric ozone content should be taken into account); (2) development of atmosphere models that take into account the typical features of fields of concentration of significant low-concentration gas components; (3) long-term observations to define the trends for such components; (4) development of such photochemical blocks of climate models as would permit us to turn the concentrations of optically active trace gas components into internal variables of such models; (5) continuing laboratory investigations to specify the rates of various photochemical reactions and to enlarge the database of fine structure parameters for the absorption spectra of optically active atmospheric compounds; (6) improvement of climatic models for assessing the effect of atmospheric composition on climate by interactive consideration of oceanic processes, also in the presence of ice on the water.

III. Trends in changes of content of atmospheric trace gas components and their effect on climate

It is now generally accepted that anomalies of the radiative effect on the atmosphere due to increasing amounts of anthropogenic trace gas components (TGC) may become a dominating factor in climatic changes over several decades or longer, though there is as yet no conclusive cause and effect explanation for the changes in climate in the last 125 years.[20] Climatic changes over several decades can, for instance, be caused by the intrinsic variability of the system "atmosphere–ocean–land–cryosphere", the basis of which is the inconstancy of oceanic, sea ice and glacial heat reserves.

It was important that studies of the greenhouse TGC established that the contribution of several polyatomic TGC per molecule to the greenhouse effect was much greater than that of CO_2.[7] Thus, for instance, the contribution of freons-11 ($CFCl_3$) and -12(CF_2Cl_2) is 10^4 times greater than that of CO_2. This calls for a serious study of the part played by numerous TGC in the development of the greenhouse effect.

The results of studies of the influence of stratospheric ozone disturbances on tropospheric climate effected through the radiative-dynamic stratosphere-troposphere interaction are very important. Recent calculations also show that an increase in tropospheric content promotes development of the greenhouse effect.[7]

Computational modelling has demonstrated that should the concentrations of numerous TGC's retain their rate of increase during several future decades, the resulting rise of ground surface air temperature (GSAT) may exceed the rise in temperature observed in the last 100 years. It can cause an effect comparable to that caused by the rise in CO_2 concentration. Stratospheric changes caused by anthropogenic factors may also considerably exceed natural decennial fluctuations. In particular, calculations have established the dependence of tropical tropopause temperature on concentrations of ozone and freons.[6]

Today, first and foremost, it is necessary to study the interaction between radiative, chemical, and dynamic processes which determine in particular the ozone layer resistance to chemical factors. The "radiative-dynamic" interaction of the tropo- and stratosphere, as well as the exchange of LCGC between them are major aspects of the anthropogenic effects on climate. These problems are connected with the need to take into account stratospheric water vapour and ozone content. Observations on long term trends in the content not only of CO_2 but also of O_3, water, and of such TCGC as methane, nitrous oxide, freons, etc., are becoming increasingly urgent.

Accordingly, various aspects of the TGC effect on climate are discussed in detail.[20] Analysis of data on the greenhouse effect of TGC showed that this had grown in the last few decades at a rate 3 to 10 times higher than in 1850–1960. The cumulative balanced rise in GST due to CO_2 and other TGC after 1850 should by 1960 have reached a level of 0.7 to 2 K, the TGC contribution being about 30% (the indeterminacy being mainly due to the unreliable estimate of climatic sensitivity to radiative disturbances). Approximate calculations within the framework of a nonstationary one-dimensional model (observing diffusion in the ocean) showed that by 1980 the heating was likely to have reached 0.4–0.8 K (with the range of balanced heating equalling 0.7–2.0 K).

Calculations of heating, according to various assumptions on the temporal dynamics of TGC content, led to the conclusion that the possible GSAT rise between 1980 and 2030 will range form 0.8 to 4.1 K. Hence in 180 years (1850–2030) the cumulative heating of the system in equilibrium can reach 1.5–6.1 K. However, because of the huge thermal inertia of the seas, only 40–50% of this heating is likely to take place by 2030.

If the current growth rate for TGC remains unaltered in future decades as well, the climatic system will become increasingly unbalanced. One should keep in mind that, although several freons[10,114,115,14,13B] with a life span of ~100–500 years do not contribute appreciably to the greenhouse effect today (nor will they in the coming 50–100 years), their continued emission at the same rate might lead to considerable climatic changes in the centuries to come.

The interaction of chemical, reactive and dynamic processes in the atmosphere, as well as adequate consideration of the seas and clouds as climate-forming factors, are of special interest. So far even the sign of the cloud feedback has not been reliably established, while the assessed values for the decelerating influence of the seas range from several decades to a hundred years. As the spatial-temporal distribution of TGC is highly heterogeneous, assessment of its effect on climate in 1-dimensional models should be regarded as purely illustrative. Two- and three-dimensional models allow more reliable calculations.

Problems which should be given top priority include the following: (1) establishment of the role of chemical reactions and transport (advection, diffusion) as determinants for ozone concentration fields, as well as of nitrogen oxides and CO; (2) consideration of the temperature feedback affecting water vapour content and chemical reactions in which hydroxyl participates; (3) analysis of the contribution of biogenic sources of methane and nitrous oxide; (4) investigation of the dependence of stratospheric water vapour content on temperature at tropical tropopause level, because water vapour reaches the stratosphere mainly through breaks in the tropical tropopause.

Regular observations of TGC are becoming crucial, because the regularities of the spatiotemporal distribution of such important TGC as CO, O_3 and nitrogen oxides are still poorly understood. Direct measurement of the TGC radiative effect reflected in the special distribution of short and long wave radiation in the free atmosphere (up to the upper boundary of its optically active layer) is also unquestionably an urgent problem. Temperature changes at ground level in the tropo- and stratosphere remain an important field of study. The spectral parameters of TGC call for further investigation. Reliable evaluation of the TGC contribution to the greenhouse effect depends on their correct determination.

In order to obtain more reliable estimates of the effect of CO_2 concentrations on climate, several external climate-forming factors were analysed. These include the concentrations of TGC and tropo- and stratospheric aerosol, the solar constant, the characteristics of the underlying surface, and the volume of industrial heat release (with TGC concentration being the main factor).[11]

Table 4. Concentrations of "greenhouse" TGC and their rate of increase.[7]

Component	Concentration, p.p.m.*	Current rate of increase (%/year)
Carbon dioxide	340	0.4
Stratospheric ozone	(0.1–10)	0–0.3
Tropospheric	(0.02–0.1)	0–0.7
Methane	1.7	1.2
Carbon monoxide	0.12	?
Trichlorofluoromethane	$1.9 \cdot 10^{-4}$	5–8
Dichlorodifluoromethane	$3.5 \cdot 10^{-4}$	5–8
1,1,1-Trichloroethane	$1.3 \cdot 10^{-4}$	5–8
Freon-113	$0.3 \cdot 10^{-4}$	15–20
Carbon tetrachloride	$1.5 \cdot 10^{-4}$	1–3
Ethylene and other carbohydrates	10^{-3}	?
Nitrous oxide	0.3	0.2
Nitrogen oxides	$(3 \cdot 10^{-5}$–$0.015)$	?
Carbon disulphide	$0.3 \cdot 10^{-4}$	?
Carbonyl sulphide	$5 \cdot 10^{-4}$	?
Sulphur dioxide	$1.0 \cdot 10^{-4}$	?
Stratospheric water vapour	3–5	?

*Possible limits of changes in concentrations are shown in parentheses.

Table 4 presents current data on the values of the mixing ratio (weight fraction) for various TGC and the respective rates of increase.[7] The high rate of increase of methane concentration is very important, but the reason for this is not yet clear. It could include intensified anthropogenic emission (due to growing population, the expanding area of paddy fields, burning of vegetation, etc.), and the drop in hydroxyl concentrations (the reaction with OH is the main CH_4 sink in the atmosphere). The factors that determine the rise in nitrous oxide concentrations (combustion of fossil fuels, denitrification of fertilisers, etc.) have also not been sufficiently deeply studied. It seems that fossil fuel combustion and fertiliser denitrification are the major processes increasing the nitrogen oxide content of the lower troposphere.

Table 5. Sensitivity of ground surface air temperature (GSAT) and total ozone content to TGC concentration changes (ppm, parts per million; ppb, parts per billion).

Component	Change in TGC concentration	Change in GSAT, °C	Change in total ozone, %
CO_2	330→600 p.p.m.	1.5–4.5	3.1
Methane	1.7→3.4 p.p.m.	0.2–0.4	2.1–3.3
Chlorocarbons	0→1.0 p.p.b. ($CFCl_3$)*	0.5	−3.3 to −5.5
	0→2.7 p.p.b. (CF_2Cl_2)*		
	0→1.8 p.p.b. ($CFCl_3$)**	1.0	−15.7
	0→5.0 p.p.b. (CF_2Cl_2)**		
	0→1.5 p.p.b. (CH_3CCl_3)**		
Nitrous oxide	0.3→0.6 p.p.m.	0.3–0.4	−8.7 to −10.7
Ozone	doubling of tropospheric concentration	0.9	
Water	3–6 p.p.m. in stratosphere	0.6	

*Steady emissions at 1977 level.
**Doubled steady emissions at 1983 level.

The TCG effect on climate has three known mechanisms: (1) direct radiative action; (2) climatochemical interaction (TCG-created changes in atmospheric chemical composition); (3) dynamics-dependent feedback. Table 5 contains data on the effect of rises in concentration of various TGC on globally averaged values for ground surface air temperatures (GSAT) and on ozone concentration. This evidence was obtained on one-dimensional models.[7] In computer climate modelling, the influence of the tropospheric aerosol is not as a rule considered. However, it should be remembered that it could increase the amount of solar radiation reaching the Earth by 5 W m^{-2}. This is comparable to the effect of doubled CO_2 concentrations. The considerable uncertainty seen in the evaluation of anthropogenic effects on climate is due to the absence of reliable data on the parameters of cloud formation.

Table 6 shows how high the GSAT may rise under the influence of CO_2 and other TGS.[11] Calculations were carried out at predetermined values for relative humidity, the height of the top cloud edge, and the ice cover albedo. A similar study is described in Ref. 2.

Table 6. Possible rise in ground surface air temperature (GSAT) due to CO_2 and other TGC.[11]

Component	GSAT rise, °C	
	1950–1980	1980–2010
CO_2	0.25	0.39
$CO_2+NO_x+CH_4+NO_2+O_3+$ chlorocarbons	0.50	0.80

IV. Aerosol and climate

The atmospheric aerosol is a product of a complicated set of chemical and physical processes. Because these processes are so complex, and the life of the aerosol is relatively short, the chemical and physical characteristics of the latter are highly variable.[4] This variability is so great and the observational data are so fragmentary, that so far it has proved impossible to make a sufficiently reliable estimate of the total balance of different types of aerosol. The available estimates of the strength of the global sources of natural and anthropogenic aerosol are purely tentative.

However, there is no doubt that the estimates for anthropogenic aerosol are the more reliable (it is especially difficult to assess natural aerosol concentrations over inaccessible parts of the ocean and the continents). This is the reason for the low reliability of data on natural/anthropogenic aerosol ratios, though on a global scale the effect of man's economic activity on the sulphur and nitrogen cycles can be clearly seen.

Depending on composition and sources, one can classify natural aerosols as follows: (1) products of sea spray evaporation; (2) mineral dust carried into the atmosphere by wind; (3) volcanic aerosols (both directly emitted into the atmosphere and resulting from gas-phase reactions); (4) particles of biogenic origin (again, both directly emitted or the product of gas-phase reactions); (5) smoke from biota combustion on land; (6) products of natural gas-phase reactions (e.g. sulphates formed by the oxidation of sulphur derived from the ocean surface).

Similarly, there are several types of anthropogenic aerosols: (1) direct industrial emissions (e.g. particles of soot, smoke, and road dust, etc.); (2) products of gas-phase reactions. Besides that, we should distinguish tropospheric and stratospheric (mainly volcanic) aerosols. Aerosols may be formed in gas-phase reactions as a result of the following processes: (1) homogeneous homomolecular nucleation (formation of tiny new liquid or solid stable particles in the gas phase in the presence of only one gaseous component); (2) homogeneous heteromolecular nucleation (a similar process but with two or more gases participating); (3) heterogeneous heteromolecular condensation (already formed particles increasing in size due to gas adsorption).

The photochemical reactions responsible for the initial transformation of the "highly volatile" gas into a gas component which becomes a source of aerosol formation are very complex and as yet have been poorly described. The following processes appear to be the most important: (1) reactions of sulphur dioxide with hydroxyl radicals which lead to the formation of molecules of sulphuric acid and sulphuric aerosol; (2) reactions between non-methane hydrocarbons and ozone and/or hydroxyl radicals. As a

result, aldehydes, alcohols, carbonic and dicarbonic acids are formed (as a rule the secondary products of these reactions interact with nitrogen oxides, forming organic nitrates). Ozone and HO and HO_2 radicals play a very important part in atmospheric chemistry. These radicals are either direct or indirect products of photochemical reactions (this is why the gas-phase processes resulting in particle formation are usually highy dependent on daylight.

Organic particles are some of the most important types of atmospheric aerosols. Because the organic compounds emitted into the atmosphere are so diverse and participate in so many reactions, it is extremely difficult to study them. The concentration of soot particles is very high. Over oceans it reaches mean values of about 0.5 $\mu g\ m^{-3}$, which is comparable with mineral aerosol concentrations. It seems that the origin of the organic aerosol is half natural and half anthropogenic. The ocean accounts for about half of the natural aerosol.

As a rule, the effect of aerosol on various processes is determined by a whole combination of chemical and physical processes. These are significantly influenced by the size of the aerosol particles. In order to obtain an adequate description of a real aerosol, it is necessary to carry out a comprehensive appraisal of its various characteristics. In most cases it is the mass concentration of the aerosol that is determined. But this characteristic is usually the least informative one, because it carries no information about the sources, composition and possible effects of the aerosol.

Aerosol cycles are closely connected with moisture transformation in the atmosphere: clouds and rain play an important part in the formation and transformation of the aerosol and its removal from the atmosphere. The aerosol in its turn has a significant effect on microphysical processes in the clouds. It is not just a coincidence that the life of the aerosol in the lower and upper troposphere is one to two weeks, while that of water vapour is ten days. It is impossible to have a full understanding of the processes of aerosol formation and transformation without reliable data on cloud physics and chemistry. For this reason, studies of the nucleation mechanism are extremely important.

There is good reason to fear that the increase in anthropogenic aerosol content may affect the climate by altering both the global radiation regime and the hydrological cycle. Though there is much evidence that natural and anthropogenic aerosol is dispersed to great distances from its source, there are still no reliable data to confirm the connection between man's economic activity and the trend of the global aerosol content to increase. The great spatiotemporal variability of the aerosol makes it difficult to isolate the anthropogenic component. This would become feasible only after the cause of this variability has been established. But for this an extensive programme of combined studies of the atmospheric aerosol would have to be carried out.

The aerosol affects climate mainly through its influence on the transmission of short and long wavelength radiation. Besides that, climatic changes can induce regional and global alterations in the content and composition of atmospheric aerosols.[4] In addition to the direct radiative effects, one should also take into account the indirect effects, e.g. the effects that are connected with changes in the microphysical characteristics of clouds. The great variability of the spatial distribution and properties of aerosols from different sources (wind erosion of soil, volcanic eruptions, sea foam, forest fires, biospheric and anthropogenic sources, gas-phase reactions, etc.) and shortage of data prevent us from obtaining a reliable picture of aerosol distribution over the globe. The optical properties of the aerosol depend on its concentration, its microstructure, and the complex refractive index.

It is convenient to use four parameters in examining the radiative effects of the aerosol: the relationship between the absorption strength of the particles in the short wavelength radiation range and backward scattering, the long wavelength radiative strength, underlying surface albedo, and the height of the sun. Priority should be given to the following objectives: (1) development of realistic aerosol models suitable for studying climatic sensitivity to aerosol effects; (2) development of parametric models for radiation transmission and the assessment of the radiative effect of aerosols in the above models; (3) application of the parametric models in climatic models in order to evaluate radiative effects; (4) development of the means for obtaining global information on aerosols (recommended for this reason it is that a draft programme for global aerosol monitoring be prepared).

It is especially important for us to study volcanic aerosols, because volcanic eruptions can be regarded as a natural "experiment" that allows us to really test models for the study of climatic effects.[6,7,9,10] Accordingly, it is important that a special international programme of observation, ready for implementation at the next big eruption, should be prepared. This would allow us to obtain comprehensive documentation of the climatic consequences of the eruption and other associated phenomena.

It is only very recently that the first attempts were made to use complicated three-dimensional climatic models to assess the climate-forming role of aerosols. The study by Coaxley and Cass is an interesting example of such computer modelling of the climate.[21]

Usually, the natural tropospheric background aerosol is not taken into account in computer modelling of the general atmospheric circulation (GAC). However, calculations show that the aerosol causes a reduction by 5.0 $W\ m^{-2}$ in the short wavelength radiation balance at the underlying surface level and one of 3.5 $W\ m^{-2}$ at the top of the atmosphere. This means that it creates radiation disturbances of about the same magnitude (but with the opposite sign) as doubling of CO_2 concentration (one should of course also take into account the effect of aerosol on the heat radiation field).

In contrast to the relatively homogeneous global radiative disturbances caused by CO_2, aerosol has a spatially heterogeneous effect on the radiation regime. This is connected with the spatial variability of the aerosol content and the underlying surface albedo, as well as with the varying height of the sun above the horizon. Calculations of climatic sensitivity to the effect of aerosol were carried out on a GAC model developed at the National Centre for Atmospheric Research, USA (NCAR). Present disturbances of short wavelength radiative heat flux similar to that received in July was initially introduced into the model.[21] The distribution of snow cover, sea ice, and ocean surface temperature (OST) were also fixed, as was the sun's height.

As the OST distribution in this model is rigidly fixed, the aerosol should have a weak effect on the temperature field. Special attention was given to isolating the weak aerosol signal from the intrinsic climatic background variability common for this model. An aerosol-created radiative disturbnce equivalent to the above mentioned 1.5 $W\ m^{-2}$ increase in the radiation absorbed by the atmosphere was introduced on the (arbitrary) 201st day of integration. Subsequently it lasted up to 600 days (the same period as the control experiment with no aerosol). An analysis of the averaged results for seven thirty-day intervals from the last 350 arbitrary days was carried out: these intervals were divided by

20-day breaks to ensure the statistical independence of the averaged results.

Examination of the averaged meridional profile of the surface temperature shows that there is a general cooling with local subarctic warming. The aerosol-induced large scale cooling can be considered statistically significant. The average global temperature drop is 0.08 K (with fixed OST this corresponds to a drop of 0.32 K). Computation of the average vertical temperature profile for the northern hemisphere points to a cooling of the whole thickness of the atmosphere. A statistically significant (90% confidence level) cooling of the lower troposphere (1000–500 hPa) amounted to 0.17 K. Computation of the surface temperature on the basis of the energy-balance climate model (EBCM) shows that the changes should be greater by an order of magnitude. This discrepancy can be attributed, first, to the fact that the EBCM takes the albedo feedback into account; second, that it deals with average annual conditions; and third, that it assumes that an equilibrium has been achieved. In a GAC model the latter depends to a great extent on the preset OST.[7] The internal variability of the model itself is extremely important. Without it, errors may arise which will impart to the aerosol effect a wrong sign.[21]

The effect of the atmospheric aerosol (in all its various types) on the development of the temperature field can be assessed with the help of a 15-level global spectral model of the climate (which deals with wavenumbers up to 15). It was developed at the European Centre for Medium Range Weather Forecasting (ECMWF).[22] Fifteen series of integrations over a 90-day period with averaging of the last 30 days (summer weather conditions) at fixed ocean surface temperatures were carried out. Eight of the series were used to evaluate the aerosol effect in different seasons.

Table 7. Optical parameters specific to various types of aerosol.[4]

Type of aerosol	$\tilde{w}_0$ (0.55 μm)	$1-g$	$\tilde{w}_0$ (10 μm)	$\frac{\sigma_e\ (10\ \mu m)}{\sigma_e\ (0.55\ \mu m)}$
Soot	0.209	0.66	0	0.038
Oceanic	1	0.22	0.692	0.250
Dust	0.653	0.12	0.558	1.08
Water soluble	0.957	0.37	0.209	0.019
Marine	0.989	0.26	0.680	0.19
Continental	0.891	0.36	0.486	0.097
Urban	0.647	0.41	0.173	0.033
Sulphuric acid (75% H_2SO_4)	1	0.27	0.010	0.050
Volcanic	0.947	0.30	0.130	0.035

An analysis of the zone-averaged temperature fields indicates that the induced heating of the stratosphere by about 2 K due to the presence of the aerosol is compensated by greater cooling at long wavelengths. This means that in conditions of a stratospheric disturbance, radiative equilibrium is restored. At the same time, in the troposphere (and first of all near the underlying surface) the heating caused by absorption of short wavelength radiation by the aerosol is balanced mainly by nonradiative factors (IR-cooling reduced the heating only by about a quarter). As a result, there is no significant change of the temperature field. The higher the location of the aerosol, the greater its effect.

Two geographical features are typical of the aerosol effect during all four seasons. One is that desert aerosol reduces net radiation. In the Sahara desert and on the Arabian peninsula the net radiation decrease amounts to 60 W m^{-2}. This leads to an appreciable drop in ground surface temperature (up to 3 K near a 20°N., 30°W. location). The other feature that becomes evident in the field of disappearing long wavelength radiation is the reduction of cloud cover in the strip from the north-eastern coast of Brazil to Texas. The maximum reduction of cloud cover observed near 15°N., 50°W. location amounted to 0.1 and caused an abnormal increase in radiation.

A rough averaged estimate gives the following values for aerosol-induced changes in the radiation regime:[1] transmitted long wavelength radiation, 0; global albedo, +0.0075; absorbed short wavelength radiation, −3.5 W m^{-2}; radiation from the ground, −1.5 W m^{-2}; total radiation, −8.5 W m^{-2}; cloud cover −0.007; terrestrial surface temperature, −0.3 K; average ambient temperature, +0.5 K.

The other 7 computer modelling series of the abovementioned 15 were used for evaluating the contributions of 7 different types of aerosol (summer weather conditions). For this purpose, one (arbitrarily chosen) type of aerosol was excluded from the computation in each series. Computations revealed the well defined nonlinear nature of the interaction between different contributions. The sum of the effects differs considerably from the effect of the sum (sometimes even the sign changes). If one compares the overall effect of all types of aerosols with the effect of a single type one can see that the closest parallelism is observed in the case of the stratospheric aerosol. The background tropospheric aerosol takes second place. The stratospheric aerosol inhibits to some degree the Hadley circulation, and also slows down the zonal air transfer in the tropical and subtropical upper troposphere.

Further studies of the atmospheric aerosol and its impact on climate should develop along the following main lines:[23] (1) effect of aerosol on climate; (2) influence of aerosol on long distance observation from satellites of climatic parameters; (3) properties of aerosols; (4) climatology of aerosols; (5) consideration of aerosol in the modelling of climate. Investigation of the climate-forming role of aerosol includes four main objectives: observation of the spatiotemporal variability of the content and properties of the tropospheric and stratospheric aerosol; development of realistic aerosol-radiation models suitable for computer climate modelling; consideration of affects of aerosol in the theory of climate; study of the interdependence between aerosol content and various climate-forming processes (land transformation, glaciation, etc.) for the purpose of developing models that would take interactive account of the presence of aerosol.

The following basic characteristics determine the influence of the aerosol on radiation transmission and its corresponding effect on climate: the bulk extinction coefficient σ_e (data on the vertical profile of σ_e allow us to calculate the optical thickness of the atmosphere τ), the bulk scattering coefficient σ_s (or the albedo of a single scattering $\tilde{\omega}_0 = \sigma_s/\sigma_e$) and the bulk scattering indicatrix. The latter can be approximately described by introducing the indicatrix asymmetry coefficient g. The ratio of the optical thickness in the 8–12 μm transparency window to the averaged optical thickness for the visible range of the spectrum is an important parameter. Some of these parameters for various types of aerosols that conform to the standard atmospheric radiation model developed by the International Radiation Committee are listed in Table 7.[4]

Assessment of the effect of aerosol on climate is reduced in most cases to computation of the influence of the aerosol parameters on the global radiation balance (GRB) and the temperature of the ground surface. Changes in GRB are mainly determined by the albedo variation of the "ground surface–atmosphere" system. In a cloudless atmosphere, the sign of the change in the albedo of the system (increase or decrease) is determined by the content and optical properties of the aerosol (in the first place by the single-scattering albedo), the underlying surface albedo, and the height of the sun. It would appear that, overall, there is a decrease of the overall GRB because of the aerosol-induced increase of the albedo.

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