Volcanogenic Nanosized Carbon Aerosol in the Stratosphere

V. V. ZUEV, N. E. ZUEVA, P. K. KOUTSENOGII and E. S. SAVELYEVA

Institute of Monitoring of Climatic and Ecological Systems, Siberian Branch of the Russian Academy of Sciences, Pr. Akademicheskiy 10/3, Tomsk 634055 (Russia)

E-mail: vvzuev@imces.ru

Abstract

The temperature anomalies and long-term depressions of ozone in the stratosphere observed after large-scale volcanic eruptions are poorly explained from the point of view of modern ideas about composition of the stratospheric aerosol of the volcanogenic nature. However, such post-volcanic phenomena could occur in case when the aerosol comp its surface. The basic opportunity of forming nanosized carbon aerosol (less than 0.1 μm in size) in the stratosphere in case of powerful Plinian type volcanic eruptions is shown in the paper. Estimates of the amount and lifetime of these particles allow explaining long-term temperature anomalies and the ozone depression in the stratosphere after volcanogenic perturbations.

Key words: volcanic eruption, eruptive column, stratosphere, temperature, solar radiation, ozone depression, sulphuric acid aerosol, carbon particles

INTRODUCTION

The source of the volcanogenic aerosol in the stratosphere is gas-ash eruptive columns that are formed in case of powerful Plinian-type eruptions reaching the stratospheric height. The lifetime of relatively heavy micrometre-sized ash particles is considered to amount to several months. It is considered that approximately in six months after Plinian eruptions, only submicron sulphuric acid aerosol remains in the stratosphere that is produced due to the cycle of the oxidation of sulphur dioxide SO_2 ejected from the volcano. The aerosol represents the microdroplets of 75 % aqueous solution of sulphuric acid; it exhibits high buoyancy, whereas the life time thereof in the stratosphere amounts to several years.

Optical properties of sulphuric acid aerosol are well studied. It virtually does not absorb the short-wave radiation in the visible and middle IR diapasons of the spectrum. Only the long-wave (thermal) part of the IR spectrum has low-intensity absorption bands. In this regard, heating the stratosphere layers with an elevated content of sulphuric acid aerosol after powerful volcanic eruptions is usually associated with the absorption of the rising long-wave thermal radiation of the Earth. For example, the analysis of radiosonde measurement data with taking into account quasi-biennial cycles (QBC), in the dynamics of the tropical stratosphere demonstrated that during almost half a year after the volcanic eruptions of the Agung (Indonesia, March 1963), El Chichon (Mexico, March–April, 1982) and Pinatubo (Philippines, June 1991), the stratosphere exhibits warming with a maximum deviation of 3 °C at the level of 50 mbar [1]. In general, warming of the stratosphere remained for two years. In the September of 1991, the stratospheric warming exceeding the long-term average one by 4 °C in aerosol layers formed in the equatorial region after the eruption of the Mount Pinatubo, at the level of 30 mbar there was registered [2].
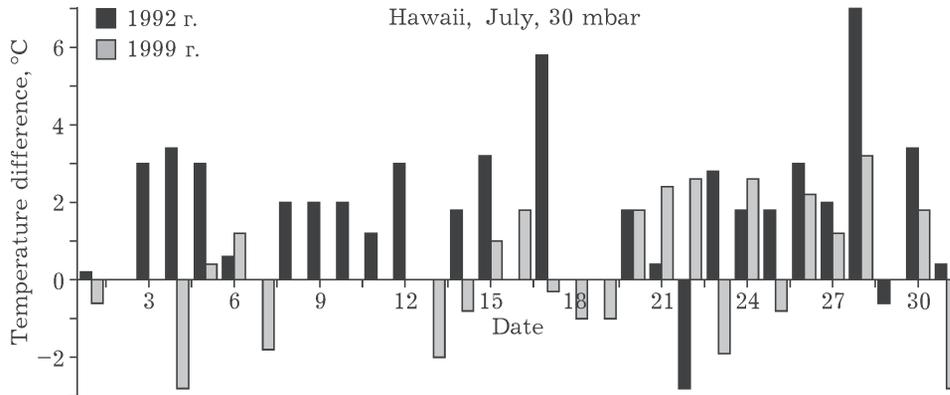
Fig. 1. Differences between daytime and night temperature values in July at the level of 30 mbar according to the Hawaiian station Lihue under the conditions of perturbed (1992) and background (1999) stratosphere.

The analysis of the temperature regime of the tropical stratosphere at the level of 30 mbar after powerful volcanic eruptions performed by us **revealed a systematic excess of daytime temperatures over night temperatures.** In particular, according to data obtained at the Hawaiian station Lihue [3], in July 1992, a year after the eruption of the Mount Pinatubo, the daytime temperature values at the level of 30 mbar were 2−3 °C higher than the night values with a maximum deviation amounting up to 7 °C (Fig. 1). Within the background period of 1999, the difference between the daytime and night temperature values are scattered in a random manner (see Fig. 1), which could be, to all appearance, caused by variations in stratospheric ozone content at these altitudes. Since the daily amplitude of temperature variations on the surface of the ocean away from the continents (the conditions of Hawaii) does not exceed 0.5 °C, whereas the daily modulation of thermal radiation rising flows is insignificant, the systematic excess of daytime temperature values at the altitude level of 30 mbar in July 1992 indicates that volcanogenic aerosol actively absorbs short-wave solar radiation. Consequently, the mentioned aerosol has a more complicated composition than the sulphuric acid aerosol. One could explain such temperature anomalies assuming that the composition of the volcanogenic aerosol in the stratosphere involve carbon black particles with the size less than 0.1 μm. Such a combined aerosol could efficiently absorb not only long-wave radiation, but also short-wave one.

Alongside with the temperature anomalies, after the volcanic disturbances in the stratosphere, as it is well known, there occurs an ozone depression. In particular, after the eruptions of the El Chichon and the Pinatubo, there was a long-term decrease observed in the average annual values of total ozone content (TOC) at a rate of 2.5 % for 10 years [4]. After entering the ash aerosol into the stratosphere, the ozone depression is initially caused by an active interaction between ozone and composite ash particles occurring on the surface of the latter. Depending on the phase state of the surface, wherewith the ozone molecules interact, in order to describe the heterogeneous reactions occurring one uses the two coefficients such as the accommodation coefficient α for the interaction of between the gas and a liquid surface and the reaction probability value γ for the gas interaction with a solid surface [5]. The accommodation coefficient reflects the probability of the absorption of gas molecules, whereas the value of γ corresponds to the probability of decomposing the gas molecules in collisions with the surface. Both parameters change within the range from 0 to 1 being comparable in magnitude. In particular, the probability of ozone decomposition on the surface of aluminium oxide Al_2O_3, whose content in ash particles is, as a rule, significant [6], attains the γ values equal to $(1.2\pm0.4)\cdot10^{-4}$ [7]. According to estimations performed by the authors of [8], this value is close to the level of significant effects on the stratospheric ozone layer. At the same time, the probability of absorb-
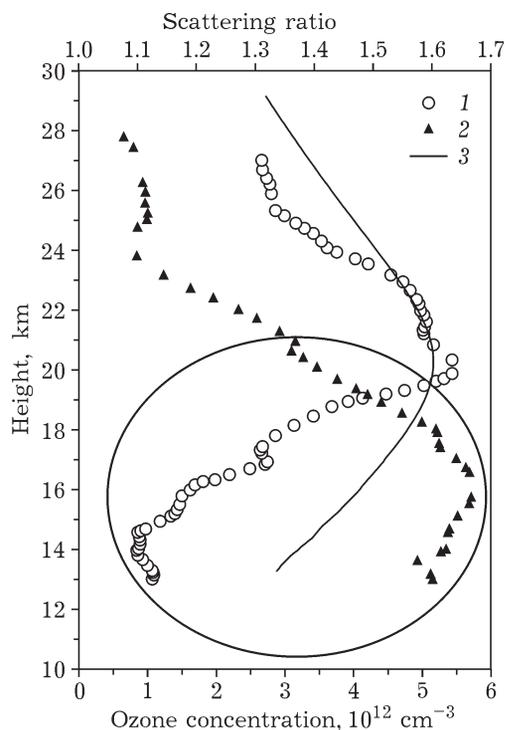
Fig. 2. Vertical profiles of ozone concentration (*1*) and the scattering ratio (*2*) at the wavelength of 532 nm, measured using a lidar in Tomsk, April 12, 1993, in comparison with the Krüger model (*3*); the oval area indicates ozone deficiency.

ing the ozone onto sulphuric acid aerosol is low being characterized by coefficient $\alpha < 10^{-6}$ [9].

However, the results of the lidar observations of stratospheric ozone vertical profiles and of scattering ratio (Fig. 2) [10] demonstrate that a significant deficiency of stratospheric ozone with respect to the long-term average (Krüger model) was maintained for two years after the eruption of the Mount Pinatubo. It was observed within the range of the maximum values of scattering ratio values those describe the vertical structure of the layer of volcanogenic aerosols in the stratosphere.
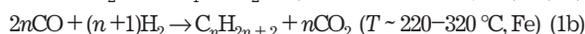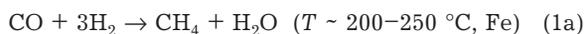
It is considered that for such a long period after the eruption, only a sulphuric acid aerosol could remain in the stratosphere, whose presence could not be connected with the distinct shortage observed for the stratospheric ozone, because of the fact that the probability of ozone molecule sorption on the surface thereof is low. However the depression of ozone observed, in particular, after the eruption of the Mount Pinatubo, could be explained assuming

that there are nanometre-size carbon particles in the stratosphere, since the probability of ozone destruction on the surface of carbon black amounts to $\gamma = 3.3 \cdot 10^{-3}$ [11], which is an order of magnitude higher as compared with the value of r inherent in Al_2O_3.

Until recently, the formation of black carbon particles in the course of volcanic eruptions was traditionally not considered, since it was assumed that elemental carbon in soot aerosol can be formed only *via* an incomplete combustion of an organic material. We have attempted to demonstrate that there is principal possibility for the formation of black carbon nanoparticles in the stratosphere as a result of volcanic eruptions in an amount necessary to maintain the above-described temperature and ozone anomalies.

FORMATION OF CARBON PARTICLES IN AN ERUPTIVE COLUMN

The idea that the volcanism is not the source of carbon particles is most likely based on some well-established judgments, rather than on any strong evidences [12−14]. However, the reactions of carbon oxidation-reduction as well as the presence of carbon proper in the emissions indicates the presence of carbon monoxide CO in the volcanic gases in the concentration amounting to 0.01−1.5 vol. % [15]. Methane that is a part of the volcanic emissions of at a concentration amounting to about 0.3 % [16] initiates the processes of soot formation *via* the thermal decomposition thereof in the central part of the eruptive column where there are high-temperature conditions (~1000 °C). In fact, the eruptive column in the central part represents as a naturally occurring analogue of an industrial chemical reactor for the production of carbon black nanoparticles (soot) [17]: high temperature, oxygen deficiency, turbulence and subsequent cooling down to stratospheric temperature values ($T < -50$ °C). In the peripheral parts eruption column, there are all the conditions for occurring the reactions of synthesis gas (Fischer−Tropsch process) under the hydrogenation of CO in the presence of catalysts (Group VIII metals). As the result, predominantly methane as well as other alkanes C_nH_{2n+2} and alkenes C_nH_{2n} are formed [18, 19]:

$CO + 3H_2 \rightarrow CH_4 + H_2O$ ($T \sim 200-250$ °C, Fe)   (1a)

$2nCO + (n+1)H_2 \rightarrow C_nH_{2n+2} + nCO_2$ ($T \sim 220-320$ °C, Fe) (1b)

$2nCO + nH_2 \rightarrow C_nH_{2n} + nCO_2$ ($T \sim 220-320$ °C, Fe) (1c)

Under the specific conditions inherent in the gas-vapour mixture in the eruptive column there can be also possible synthesizing other, more complex organic compounds [20]. The hydrocarbons synthesized can be drawn by turbulent flows from the periphery to the central part of the column.

The thermal decomposition of complex hydrocarbons requires, as a rule, for temperature values of higher than 1200 °C. However, methane, that predominates in the composition of the resultant mixture of hydrocarbons is subjected to thermal decomposition at a temperature $T \sim 800$ °C [21], inherent in the central part of eruption column. Therefore, the formation of nanodispersed (<0.1 μm) particles of soot are quite possible:

$CH_4 \rightarrow C + 2H_2$ ($T \sim 800$ °C)   (2)

In the peripheral parts, at $T > 250$ °C there are favourable conditions for the formation of carbon nanostructures in the presence of Fe particles as the result of the reducing pure carbon according the Bell–Boudoir reaction of:

$2CO \rightarrow CO_2 + C$ (3)
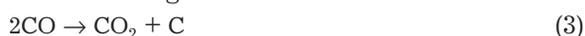
It should be noted that the peripheral parts of the eruptive column are more subjected to the turbulent friction, so they cannot reach the stratosphere. At the same time, the turbulent involving in the vertical transfer could result in capturing a part of «quiescent» atmosphere.

It is obvious that in the case powerful volcanic eruptions, in the eruptive column there are all necessary conditions for the formation of nanodispersed carbon particles.

EVALUATION OF THE LIFETIME AND NUMBER OF VOLCANOGENIC CARBON PARTICLES IN THE STRATOSPHERE

In the stratosphere, the volcanic "black carbon", formed in the eruptive column as a result of chemical reactions can stay in the form of stable nanodispersed carbon particles (such as carbon black and pure carbon), which provides heating the stratospheric air with an efficient ozone destruction on their surface thereof [22]. At the same time, the carbon particles are either contained in the sulphuric acid aerosol acting as condensation nuclei, or precipitated onto the aerosol due to coagulation, which provides an efficient absorption of short-wave solar radiation by sulphuric acid aerosol. The intensity of solar radiation absorption by carbon particles is determined by their dispersity level, concentration and the altitude, where they stay in the atmosphere, whereas the impact on the climate depends on the life time thereof. It is known that the sink of aerosols from the atmosphere is mainly caused by washing out the aerosol particles by clouds, fog, precipitations, and sedimentation and dry deposition onto obstacle surfaces. The absence of cloud cover, the processes of convective and advective transport of air masses in the stratosphere, the absence of the diffusion flux of particles from the stratosphere to the troposphere significantly extend the lifetime of the stratospheric aerosol [22]. Model calculations demonstrate that the exponential decay time for carbon particles with the radius $r = 0.08$ μm within the altitude range of $20-57$ mbar and those with $r = 0.03$ μm within the altitude range of $100-150$ mbar is equal to almost four years [23]. The exponential decay time of sulphuric acid aerosols, according to the lidar observations and model estimations, amounts up to one year [10, 23].

The powerful eruption of the Mount Pinatubo in 1991, with an index of volcanic explosion VEI = 6 resulted in ejecting about $1.1 \cdot 10^{10}$ m^3 gas-and-ash products into the atmosphere [24]. The carbon content in the Earth's crust is approximately equal to 0.3 %, so at the average density of the Earth's crust and the magma amounting to 2500 kg/m^3 the carbon emissions in the case of such an eruption should be equal to about $8.25 \cdot 10^{10}$ kg. In this case, the mass of the carbon ejected into the stratosphere (m_C) will be the following: $k8.25 \cdot 10^{10}$ kg, where k is the coefficient characterizing the fraction of the eruptive mass of carbon that reached the stratosphere. It is easy to calculate that at the height of the eruption column of the Mt. Pinatubo equal to 40 km and 15 km of tropopause altitude, about 95 % of the total emissions reached, the stratosphere, *i. e.* $k = 0.95$. In this case, the mass of carbon that reached the stratosphere $m_C = 7.84 \cdot 10^{10}$ kg. Let us denote the fraction of carbon transformed into carbon nanoparticles as k_{tr}, then the mass of

the carbon particles (m_{BC}) should be equal to $k_{tr} \cdot 7.84 \cdot 10^{10}$ kg.

Let as assume that the volcanic cloud was uniformly distributed by the stratospheric winds in the torrid zone between $-10°$ and $+10°$ within the lower stratosphere. In this case, the total area thereof is $S = 8.85 \cdot 10^{13}$ m². Consequently, the surface density of the carbon nanoparticles in the torrid zone after the eruption of the Mount Pinatubo should be equal to $m_{BC}/S = k_{tr}8.9 \cdot 10^{-4}$ kg/m².

According to model calculations [23], the presence of the nanoparticles of "black carbon" in the stratospheric torrid zone having the radius of 30 nm, with the surface density of $6.7 \cdot 10^{-6}$ kg/m² should lead to heating of the stratosphere at the level of 30 mbar up to 55 °C and to decreasing the level of global TOC down to 45 % for 10 years. After the eruption of the Mount Pinatubo the temperature and ozone anomalies were an order of magnitude lower: heating the tropical stratosphere at the level of 30 mbar was registered on average by 4 °C as well as lowering the global TOC down to 2.5 % during 10 years was observed. It is obvious that, in order to provide this kind of stratospheric anomalies, it is necessary and sufficient that $k_{tr} \sim 10^{-3}$.

On the other hand, the major amount of carbon in the course of eruption is ejected as CO_2, which is equal to $15-20$ % of the total amount of volcanic gases [24]. The fraction of methane and other hydrocarbons in this case is about two orders of magnitude lower than CO_2 [16]. For such a non-optimized chemical reactor, as an eruptive column, the yield of nanodispersed carbon particles due to the thermal decomposition of hydrocarbons could hardly exceed 10 %. In this case, the fraction of carbon transformed into carbon nanoparticles could be evaluated equal to 10^{-3}.

It is obvious that, in the course of the volcanic eruptions like the Mount Pinatubo, a sufficient amount of nanosized carbon aerosol is ejected into the stratosphere, interacting actively with the incident solar radiation with the participation in heterogeneous chemical processes in the stratosphere.

CONCLUSIONS

Carbon particles are hydrophobic, according to the nature thereof. However, in the real atmosphere the surface of the particles rapidly acquires hydrophilic properties under the action of oxidizing agents, whose role in the troposphere is played by organic compounds, whereas in the stratosphere the mentioned oxidizers are presented by ozone and hydroxyl radical OH. As the result, finely dispersed carbon particles become condensation nuclei for water droplets and acidic aqueous solutions. In the troposphere, owing to a high humidity level, the presence carbon particles within a day or two results in the formation of drops of sulphuric acid aerosol that is quickly washed away with precipitations. In the "dry" stratosphere, the factor of wet washing out that limits the lifetime of aerosol particles is almost absent. Therefore, the nanodisperse carbon particles could exist for a long time either in the free state or in the state bound with the sulphuric acid aerosol, being located within to serve as condensation nuclei or to precipitate thereon as the result of coagulation.

A high efficiency of solar radiation absorption by the carbon aerosol, including that within the short-wave region, and significant probability of ozone destruction on the surface of carbon particles allows to connect the observed long-term temperature and ozone anomalies in the stratosphere after Plinian eruptions with the presence of carbon nanoparticles of volcanogenic origin. The estimations performed demonstrate that the presence of carbon in the Earth's crust and in the magma, as well as thermal conditions in the eruption column in the course of volcanic eruptions do not exclude the formation of stratospheric nanodispersed carbon particles with the lifetime amounting up to several years.

So far, the effect of volcanic eruptions exerted on climate and atmospheric processes is poorly understood. The underestimation of relatively small volumes (with respect to the total amount) of gas emissions and the by-products of chemical transformation thereof do not allow correctly assessing the extent and duration of possible aftermath. It is obvious that targeted experiments are required for the search of nanosized carbon particles in the stratosphere.

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