

Biogenic aerosol in the atmosphere

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In connection with the growing interest to estimates of the possible effect of biogenic aerosol on climate and chemical processes in the atmosphere, gas-to-particle conversion processes and properties of biogenic aerosol are reviewed.

Introduction

Among many reasons stirring the interest in atmospheric aerosol, the role of aerosol in global climate and its changes is perhaps most important, but least understood (especially in terms of quantitative estimates).¹⁻⁴⁸ The initial and entirely speculative estimates of the net contribution of greenhouse gases (warming) and sulfate aerosol (cooling) have eventually evolved into realization that the atmospheric aerosol has highly variable properties and varies widely in space and time. Unfortunately, of little use in this process has been the rich experience of domestic researchers of atmospheric aerosol (e.g., see Refs. 1-15, 29-31) who, in particular, tried to justify the utility of different models of atmospheric aerosol for different atmospheric conditions. However, little attention has been given until recently to aerosol of biogenic origin. Therefore, this review discusses the available information on biogenic aerosol in the atmosphere.

Biogenic trace gases and atmospheric aerosol

Nitrogen oxides and organic compounds

In the atmosphere with high nitrogen oxide (NO_x) concentration, fast reactions of volatile organic compounds (VOCs) with ozone, HO radicals, and NO_3 may contribute considerably to formation of not only oxidants, but also organic aerosol, thus substantially affecting the radiative transfer in the atmosphere. The gas-to-particle conversion of trace gases to submicron aerosol particles during oxidation of some VOCs is also of considerable interest since the newly formed particles may serve as cloud condensation nuclei and, thereby, influence cloud formation, atmospheric hydrological conditions, and climate.

At the initial stages of oxidation of high-molecular-weight VOCs in the troposphere, semi-volatile species are formed. Then their condensation (by a mechanism poorly understood yet) leads to formation

of secondary organic aerosol (SOA). The main SOA precursors are, probably, mono- and sesquiterpenes, as well as aromatic compounds. In regard to monoterpene hydrocarbons, most representative (most frequently detected in the free atmosphere) species of this group of biogenic VOCs are α - and β -terpenes, limonene, and sabinene. The contribution of biogenic VOCs to formation of tropospheric aerosol depends strongly on climate, type of vegetation, geographic location, etc.^{6,10-12}

Whereas the rates of chemical reactions with HO radicals, NO_3 , and ozone are rather well-known, the products of these reactions are still far less understood. Griffin et al.²⁵ undertaken a series of experiments in open "smog" chambers to determine the rate of aerosol formation from 14 VOCs. Because their oxidation products can be in both condensed and gas phases, it is important to determine the aerosol yield as a function of concentration of already existing particles, which can absorb VOC oxidation products. For the mass concentration of organic matter ranging from 5 to $40 \mu\text{g}\cdot\text{m}^{-3}$, the percentage of the aerosol component in VOC oxidation products varied in the ranges of 17-67% for sesquiterpenes, 2-23% for cyclic dienes, 2-15% for bicyclic alkenes, and 2-6% for acyclic ocimene triene.

Griffin et al.²⁵ performed experiments with bicyclic alkenes (α -pinene, β -pinene, Δ^3 -carene, and sabinene) at daylight temperature, but in the dark. Oxidation was initiated by ozone or only by NO_3 radicals. The experiments with NO_3 radicals were characterized by highly intense aerosol formation from β -pinene, sabinene, and Δ^3 -carene. Reference 25 gives also the estimates of the relative contribution of aerosol formation for every type of the reaction of bicyclic terpene oxidation.

The earlier researches have shown that dark reactions of terpenes with ozone produce more aerosol than photochemical processes in presence of NO_x do. Winterhalter et al.⁴⁶ discussed the results of laboratory study of the reaction of β -pinene with ozone in the gas phase aimed at obtaining more reliable information on the mechanism of the process and its products.

The main products of reactions (with relative yields in parentheses) are HCHO (0.65 ± 0.04), nopinon (0.16 ± 0.04), 3-hydroxi-nopinon (0.15 ± 0.05), CO₂ (0.20 ± 0.04), CO (0.030 ± 0.002), HCOOH (0.020 ± 0.002), secondary β -pinene ozonide (0.16 ± 0.05), and *cis*-pinic acid (0.02 ± 0.01).

At the first stage of the process, ozonides are formed, and then they are spontaneously destroyed to form formaldehyde and excited Criegee biradicals consisting of nine carbon atoms (0.84 ± 0.04). The second pair of the products, CH₂OO biradicals and nopinon, had the lower yield (0.16 ± 0.04). About 40% of excited biradicals-C₉ stabilized and reacted with HCHO, HCOOH, and H₂O. To be noted is more intense formation of nopinon (0.35 ± 0.05), as well as H₂O₂ (0.24 ± 0.03), from stabilized Criegee biradicals and H₂O. This is of great interest from the viewpoint of chemical processes occurring in the atmosphere, because hydrogen peroxide photolyzes to form hydroxyl radicals.

The products of oxidation of β -pinene and sabinene by ozone were also studied by Grosjean and Grosjean.²⁶ Using a 60-m³ "smog" chamber, they observed not only intense formation of aerosol and well-known gas products, but also a number of trace gases not observed before. It was shown that the sabinene-O₃ and Δ^3 -carene-O₃ reactions produce over 10 oxidized compounds containing carbonyl, hydroxyl, and carboxyl groups in the percentages of 34–50, 57, 29–67, and 24%, calculated from amount of carbon contained in β -pinene, sabinene, α -pinene, and Δ^3 -carene reactants, respectively. The relative percentages of these products were over 83, about 100, over 90, and 61%, respectively (however, with accuracy to within $\pm 50\%$). One of the main products of α -pinene oxidation is pinic acid formed by a mechanism not explained convincingly yet. Nonetheless, a series of products, such as pinic, pinonic, norpinonic, and hydroxypinonic acids, as well as hydroxypinonaldehydes can serve as molecular tracers of the secondary biogenic aerosol.

The organic compounds contained in the polar atmosphere play an important role as tracers of long-range transport, as well as they affect considerably the physical and chemical processes determining the chemical composition of the atmosphere and snow cover. The data of Table 1 obtained from observations in Alert, Canada, in February–June 1991 characterize the chemical composition of arctic aerosol.²⁸ In relation to the total aerosol mass, the carbon content in aerosol varies in the range of 2.4–11%. However, considering that a portion of this carbon may be bound to oxygen in such compounds as carboxyl acids, the fraction of carbon-bearing species is even larger.

The dominating water-soluble compounds are low-molecular-weight (LMW) dicarboxyl acids (C₂–C₁₁) and, to a lesser degree, ketocarboxyl acids (C₂–C₉). The relative percentages of individual components in the total concentration of diacids are 44% (oxalic acid, C₂), 17% (malonic acid, C₃), 15% (succinic acid, C₄),

5% (gluten acid, C₅) and 19% (others). The total concentration of diacids (varying in the range of 10–100 ng/m³) has a well-defined annual behavior with a maximum in early spring.

The percentage of organic compounds in water-soluble aerosol is less than 20%. In the case considered here, the concentration of aerosol LMW species, i.e., diacids, correlates well with the concentration of aerosol Br and I playing an important role in ozone destruction. The arctic aerosol is also found to contain the compounds of the class of lipids (Table 1), including *n*-alkanes (C₁₈–C₃₅), polycyclic aromatic hydrocarbons (PAH), *n*-alcohols (C₁₃–C₃₀), fatty acids (C₇–C₃₂), and α , ω -long-chain dicarboxyl acids (C₆–C₂₆). The data on concentration of these compounds bear the useful information on the relation between natural and anthropogenic sources of aerosol organic matter.

Table 1. Chemical composition of arctic aerosol

Compound	Concentration	
	Range	Mean
Aerosol total concentration, ng/m ³	2500–9100	5200
Total carbon (TC), ng/m ³	88–639	359
Total nitrogen (TN), ng/m ³	16–154	86
Weight ratio C/N	2.4–7.1	4.5
TC/atmosphere, %	2.4–11.1	6.8
TN/atmosphere, %	0.48–2.4	1.6
Water-soluble organic carbon (WSOC), ng/m ³	47–300	186
WSOC/TC, %	30–72	53
WSOC/atmosphere, %	1.2–5.5	3.4
Dicarboxyl acids (C ₂ –C ₁₁), ng/m ³	7.4–84.5	36.6
Ketoacids (C ₂ –C ₆), ng/m ³	0.76–8.9	3.7
α -dicarbonyls (C ₂ –C ₃), ng/m ³	0.05–2.8	0.88
Diacids: C/TC, %	1.5–9.1	3.8
Ketoacid: C/TC, %	0.18–0.78	0.34
α -Dicarbonyl: C/TC, %	0.019–0.17	0.073
<i>n</i> -alkanes (C ₁₈ –C ₃₅), ng/m ³	0.15–2.7	0.85
PAH, ng/m ³	0.0002–0.85	0.11
<i>n</i> -alcohols, ng/m ³	0.24–0.95	0.50
Fatty acids (C ₇ –C ₃₂), ng/m ³	1.3–6.5	3.2
Long-chain diacids (C ₂₂ –C ₂₆), ng/m ³	0.074–0.56	0.27

The analysis of the chemical composition of snow samples has shown that the main natural sources of light-weight carboxyl acids are biogenic species released from vegetation and oxidation of various hydrocarbons in the atmosphere. Volcanic eruptions and forest fires, whose products are transported far away from a source, also strongly affect the chemical composition of snow.

Available observations indicate that the organic aerosol (OA) is widespread in the atmosphere over both ocean and land. This aerosol may be of both natural (such as dimethylsulfide released by ocean) and anthropogenic (due to biomass burning etc.) origin. Cloud condensation nuclei (CCN) contain about 10–20% (by mass) of organic aerosol. In recent studies of the relative role of sulfate, sea salts, and organic

components in aerosol of the marine boundary layer, it was found, in particular, that (1) purely sulfate aerosols do not dominate in this case and (2) much (about 10%) of sea-salt aerosols are composed of organic substances.

An important role of OA was emphasized by Ellingson et al.²⁴ who proposed an observation-based model of OA chemical composition and changes ("processing") in the atmosphere. It was assumed that OA particles are liquid nuclei covered with a hydrophobic organic monolayer consisting of organic substance of biogenic origin. Ellingson et al.²⁴ justified a chemical mechanism by which the organic surface layer changes in interaction with radicals contained in the atmosphere. The final result of interaction of the surface layer with the surrounding oxidizing atmosphere is conversion of the inert hydrophobic film into an optically active hydrophilic layer. This may favor the growth of converted organic aerosol particles by accretion of water and formation of CCN that influence radiative transfer in the atmosphere.

The radiative transfer may be also influenced directly by chromophores remained on the surface of aerosol particles after chemical conversion.

By comparing this model with the experiment, it is possible, in particular, to verify the dependence of the percentage of organic matter present in particles on particle diameter (according to this model, most aerosol mass in the upper troposphere resides in the organic component). "Processing" of organic aerosol particles in the atmosphere must lead to tropospheric injection of small organic fragments playing an important role in homogeneous chemistry of the atmosphere. Seemingly, OA can supply the atmosphere with organics and other water-insoluble compounds. Supposedly, the biomass burning may lead to formation of coating on the surface of aerosol particles that is analogous to the above-mentioned. This coating consists of substances coming from the Earth's surface. Ellingson et al. argued that hydrophobic-to-hydrophilic conversion of the surface layer of aerosol particles may provide an additional mechanism by which the biosphere influences (by means of chemical processes) the radiative transfer, the radiative budget, and climate.

Sulfuric compounds

Much of the earlier models of the global sulfur cycle employ highly parameterized mechanisms of chemical processes for prescribed NO_x and oxidant fields. These models cannot be used to predict the NO_x and oxidant concentrations with account of varying anthropogenic and biogenic emissions of different trace gases. The trace gases can be divided into two groups: inorganic and organic. The chemically active inorganic gases include primarily NO , NO_2 , SO_2 , and CO ; whereas organic tropospheric trace gases include thousands both natural and anthropogenic species.

Whereas the chemical processes involving inorganic trace gases are rather well studied, all organic gases cannot be considered individually because of (a) computer time limitations, (b) absence of reliable information on emissions, and (c) unavailability of adequate data on reaction rates and products. This necessitates the validation of a combined photochemical mechanism (CPCM) describing quite accurately the chemistry of tropospheric hydrocarbons (and kinetics of the corresponding processes) on regional to global scale.

Previously, this problem was solved using (a) "surrogate" trace gases, (b) "composite" molecule, and (c) combined structure of chemical processes (CSCP), with the last two being most reliable and, hence, most popular of all. The use of CSCP is most appealing because it employs a minimum number of trace gases and reactions. Zaveri and Peters⁴⁸ proposed a new CPCM designated as CBM-Z; it is based on the earlier developed Carbon Bond Mechanism (CBM-IV) method. It can be used for numerical simulation in a wider range of space and time scales.

Comparison of the results calculated using CBM-Z, CBM-IV, and its partially refined version, as well as the improved regional model RADM2 of acid sediments within the framework of box versions of these models, has shown that (for conditions of hypothetical scenarios of the urban and rural atmosphere for the period of 30 days) CBM-Z and refined RADM2 agree to within $\pm 20\%$, whereas the CBM-IV versions differ by as much as 50–95%. Consideration of reactions with organic nitrates and alkyl peroxide was most important for reliable work of the CBM-Z (accurate calculation of NO_2 and O_3 concentrations).

Understanding of gas-to-particle conversion processes of biogenic aerosol formation facilitates the solution of the problem of identification of this aerosol under conditions of the real atmosphere, but usually only through a complex (and sometimes ambiguous) analysis of observations of real aerosol characteristics.

The first field Aerosol Characterization Experiment (ACE-1) conducted from November 15 to December 14, 1995, over south-western Pacific (to the south from Australia) was the first in the series of observational programs devoted to the study of physical, chemical, and nucleation properties of atmospheric aerosol and scheduled as a part of the first International Global Atmospheric Chemistry (IGAC) Project.¹⁹ The ACE-1 involved 47 research groups from 11 countries.

The observations were made from aboard the NASA C-130 research aircraft and two research vessels, as well as from island sites. One research program concentrated on analysis of the influence of physical, chemical, and biological characteristics of four water masses in the target area on the content of various trace gases in the atmosphere. In this regard, it is important to note that the ocean may supply the atmosphere with such biogenic constituents as dimethylsulfide,

hydrocarbons, methyl nitrates, and methyl halides. The ocean can also be a source of biogenic calcium bicarbonate that favors higher alkalinity of the sea salt aerosol and leads to intensification of ozone-induced oxidation of sulfur dioxide contained in the "aerosol" water.

Earlier publications suggest that in the target area the sea salt aerosol is a dominating aerosol component (this is so for 90% of particles over 130 nm in diameter and up to 70% of particles over 80 nm in diameter). In 50% of aerosol particles larger than 160 nm, there exist organic components associated with sea salt. Thus, the sea salt aerosol must be accounted for in climate models inasmuch as it determines not only the scattering of solar radiation, but also the CCN concentration.

The Bates¹⁹ results showed that, even in a distant ocean region, the anthropogenic impact on the atmosphere and aerosol properties is well pronounced. For instance, above the height of 3 km, Bates observed the layers that contained aged biomass burning products. About 11–46% of sulfate aerosol particles over 100 nm in diameter contained soot that probably arose from biomass burning in South Africa.

The ACE-1 data can be used to estimate the role of biogenic components in formation and growth of new aerosol particles. There are also some evidences of formation of new particles from sulfuric acid in regions of "emissions" from clouds. The results of numerical simulation suggest that about 30–50% of dimethylsulfide (DMS) is converted to SO₂ and the main sink for this sulfurous gas is ozone-induced oxidation in "aerosol" water. Non-sea-salt sulfates were contained largely in supermicron salt particles in percentages of (35 ± 10)% in summer and (58 ± 22)% in winter.

McArdle et al.³⁴ analyzed aerosol samples taken at Mace Head, the western coast of Ireland, and found that 30% of non-sea-salt sulfate in summer arises due to gas-to-particle conversion of ocean-emitted DMS. In this regard, the isotopic composition of sulfate aerosol deposited in three distant (background) regions in Wales and Mace Head was examined to estimate the contribution of DMS oxidation to aerosol formation. The samples of aerosol and sediments were taken between March 1993 and September 1994. The value of $\delta^{34}\text{S}$ defined as

$$\delta^{34}\text{S} = \left[\left(\frac{{}^{34}\text{S}}{{}^{32}\text{S}} \right)_{\text{sample}} \left(\frac{{}^{34}\text{S}}{{}^{32}\text{S}} \right)_{\text{reference}}^{-1} - 1 \right] \cdot 1000,$$

where ${}^{32}\text{S}$, ${}^{34}\text{S}$ is the concentration of sulfur isotopes, was found to be maximum for non-sea-salt sulfates and to reach 11.9‰ for aerosol and 9.7‰ for sediments in summer months.

A well-pronounced (3–4 nmole/m³) summer maximum was observed in the aerosol methane-sulfonate concentration. Assuming that the studied samples contained only sulfur from anthropogenic (land) sources, sea salts, and marine biogenic sources (DMS oxidation), McArdle et al.³⁴ estimated, from analysis of the isotopic composition of sulfur, the

contribution of DMS aerosol to total sulfate aerosol. Generally, the biogenic contribution was found to be small (less than 10%), however reaching 40% in marine air masses. Comparison of $\delta^{34}\text{S}$ for aerosol and sediments revealed no significant isotopic fractionation in the process of sulfur dioxide oxidation.

Dibb et al.²² discussed the results of airborne (DC-8 research aircraft) measurements of atmospheric concentration of water-soluble ions contained in atmospheric aerosol over the vast Pacific territory in the Southern Hemisphere. The observations were made in September–October 1996 as a part of GTE Pacific Exploratory Mission in the Tropics (PEM-Tropics).

The measured values of all ionic components were found to be surprisingly low throughout the free troposphere (2–12 km) despite the influence of biomass burning plumes coming to the studied region from the west. On the other hand, the activity of extraterrestrial radionuclide ⁷Be associated with aerosol often exceeded 1000 fCi/m³ throughout the troposphere. The observations imply that the considered ionic components do should be washed out of plumes by precipitation, however in regions far removed from the observation site in the direction opposite to the dominating wind (otherwise, the ⁷Be concentration would also be low). This is also confirmed by the evidence that HNO₃ and carbonyl acids increase in many plumes despite their high solubility in water and, consequently, high probability of being washed out by precipitation.

Over the south Pacific region, the NH₄⁺ mixing ratio decreases with altitude; this argues for recent hypothesis that NH₃ emissions from ocean constitute a significant NH₃ source far removed from the continents. Analysis of observational data for altitudes below 2 km supports earlier ground-based and shipborne data on the latitudinal distribution of molar ratio MSS/nssSO₄²⁻ (methyl sulfonate/sulfates not produced from sea salts), growing from less than 0.05 in tropics to almost 0.6 near 70°S. Very large (0.2–0.5) values of this ratio were observed at the height of about 10 km over the extratropical convergence zone near 10°N. The high values of the ratio MSS/nssSO₄²⁻ in the tropical upper troposphere are likely due to humid-convective "pumping" of dimethyl sulfide from the marine atmospheric boundary layer. This complicates interpretation of the observed values of the ratio mentioned above with the purpose of identifying source region for biogenic sulfur compounds survived long-range transport.

Ruellan et al.⁴² have discussed airborne aerosol observations in the lower troposphere (at heights up to 4 km) over Central Africa. These experiments were conducted in November 1996 as a part of the field observational Experiment for Regional Sources and Sinks of Oxidants (EXPRESSO). In context of the study of biomass burning emissions to the atmosphere, Ruellan et al.⁴² analyzed 24 aerosol samples to determine the properties of black and organic carbon

(BC and OC), water-soluble organic carbon (WSOC), polycyclic aromatic hydrocarbons (PAH), and soluble ions, as well as elemental composition and morphology of aerosol. Aerosol samples were collected over tropical forests or savannas near the intertropical convergence zone (ITCZ).

At all altitudes, the number concentration of aerosol particles (with diameters ranging from 10 to 14000 nm) was high $[(3100 \pm 2060) \text{ cm}^{-3}]$. The number concentration of soil particles was found to be $(20 \pm 18) \mu\text{g}/\text{m}^3$, somewhat less than expected. On the other hand, pyrogenic particles and black carbon were found in significant amounts. The BC concentration was $(3.8 \pm 2.3) \mu\text{g}/\text{m}^3$ for the atmospheric boundary layer over forest, $(9.8 \pm 3.9) \mu\text{g}/\text{m}^3$ for savanna, and $(8.7 \pm 1.6) \mu\text{g}/\text{m}^3$ for the harmattan layer.

The data on other minor constituents (oxalate, peroxyacetyl nitrate (PAN), etc.) demonstrate that the content of these compounds in the troposphere depends strongly on savanna burning. The obtained data indicate also that the vertical and horizontal exchange exists between different tropospheric layers across ITCZ.

The percentage of WSOC in studied samples was $(46 \pm 9)\%$ relative to total organic carbon. This percentage was higher $[(85 \pm 18)\%]$ in the harmattan layer, thus suggesting that aerosol particles generated by biomass burning possibly play an important role as CCN. The aging of these particles was estimated using different chemical indicators, such as WSOC/OC concentration ratio, found to be 2–3 times larger in the harmattan layer than below it.

In the atmospheric boundary layer over forest, measurements revealed the high concentration of organic (formate, acetate, and oxalate) acids of biogenic origin. The observations discussed here were made at the beginning of the dry season when savanna burning had a dominating effect on atmospheric properties, whereas harmattan-induced flow of dust aerosol was still weak. Under these conditions, nitrates were predominately in the gas phase, so that existing nitric nutrients stayed within the studied region.

Andreae et al.¹⁶ analyzed weekly impactor samples of atmospheric aerosol taken at the Cape Grim Baseline Air Pollution Station (CGBAPS) near the north-western tip of Tasmania (Australia) during 20 months in 1988–1990. These results included the data on soluble ionic components such as methane sulfate (MS^-), ammonium, nitrate, and basic ions contained in sea salt. Analysis of the data has shown that, whereas sea salt component has only weak annual behavior, the non-sea-salt (nss) ions typically have well-pronounced summer peaks.

The comparison of data on nss-ions for two summers has revealed a considerable interannual variability. Both fine and coarse aerosol fractions (the latter is likely connected with sea salt particles) were characterized by the presence of nss-sulfate and MS^- ions. In winter, the percentage of nss-sulfate was larger in the coarse fraction than in the fine one. The

observations discussed here indicate that the oxidation processes in liquid-water cloud and haze droplets play an important role in formation of the nss-sulfate aerosol.

Sulfur and nitric compounds at Cape Grim have well-correlated annual variations, indicating that the oxidation due to dimethylsulfide is a dominating sulfur source in summer, whereas for remainder of the year a considerable contribution to formation of nss-sulfate aerosol comes from non-biogenic sulfur sources. The correlations between concentrations of condensation nuclei/cloud condensation nuclei (CN/CCN) and concentrations of nss-sulfate, MS^- , and wind velocity reflect the fact that the DMS-induced oxidation processes and, to a lesser degree, formation of sea spray contribute significantly to formation of CN and CCN (whose number concentrations are, respectively, 100–500 and 30–50 cm^{-3}). The weak annual behavior of sea-salt aerosol concentration contrasts with the well pronounced annual variations of both sulfur compounds and CCN, indicating the key role of biogenic DMS particles as CCN precursors in the studied region, at least, when marine bioproductivity is high.

Conclusion

According to recent estimates, global climate warming due to the greenhouse effect is comparable with cooling caused by the sulfate aerosol.³⁰ This problem, however, is still far from complete solution, because atmospheric aerosol is highly variable and its distribution strongly varies in space and time (unlike that of most greenhouse gases). Of special importance is still unanswered question of how aerosol influences the optical properties (primarily, albedo) of clouds.

In this context, of great interest is dimethylsulfide emitted by ocean and its subsequent conversion to sulfate aerosol influencing significantly the radiative forcing of climate. At present, the global DMS emissions from oceanic phytoplankton are estimated to be 12–54 Tg/yr, i.e., 10–40% of total emission of gaseous sulfur into the atmosphere.³⁰

The DMS oxidation involving OH and NO_3 radicals leads to formation of such sulfur-bearing compounds as sulfur dioxide and methanesulfonic and sulfuric acids. Because of the gas-to-particle conversion of DMS into sulfate aerosol, the DMS impact on the climate was hypothesized, though not without some doubt. The point is that the DMS oxidation in the atmosphere is still poorly understood, preventing reliable estimation of sulfate aerosol formation from DMS.

In this regard, Campelongo et al.²⁰ undertaken a numerical simulation of the possible role of multiphase chemical reactions in tropospheric chemistry with special emphasis on the study of the temperature dependence of the methane sulfate to non-sea-salt sulfate concentration ratio, $\alpha = \text{MSA}/\text{nss} - \text{SO}_4^{2-}$. The numerical simulation was based on the kinetic model of hydroxyl-initiated homogeneous gas-phase DMS

oxidation in the atmosphere extended to include liquid-phase reactions.

Analysis of the calculated results has shown that the temperature dependences of interactions between gas- and liquid-phase reactions may be largely explained by the influence of the temperature dependence of the $\text{MSA}/\text{nss-SO}_4^{2-}$ ratio. It was found that the multiphase reactions in the atmosphere are important for formation of not only SO_2 species, but also other products of DMS oxidation. The latitudinal α variations can be explained adequately only considering multiphase reactions in the troposphere. Campelongo et al.²⁰ pointed out to the model limitations to be removed in the future. They include neglect of such a sink as SO_2 , its trapping by sea-salt aerosol particles, and subsequent deposition. This might have resulted in overestimation of the rate of SO_2 conversion to sulfate aerosol.

Thus, the problems of estimating the processes of formation of the global DMS concentration field, subsequent gas-to-particle conversion into sulfate aerosol, and its possible impact on the climate are still far from complete solution.

The recently recognized problem of biogenic emissions into the atmosphere, both total and from biomass burning only, has attracted worldwide attention, in particular, to man-induced changes in the atmospheric chemical composition leading to impact on the climate.^{14,20-31}

Earlier, the radiative forcing of the climate by the biomass burning aerosol was estimated as about -1.0 W/m^2 (with the accuracy to within -0.3 – -2.2 W/m^2 in the case of purely scattering aerosol), which is comparable with the radiative forcing due to anthropogenic sulfate aerosol and, on the other hand, is balanced by the negatively valued radiative forcing due to the greenhouse effect (estimated to be 2 – 3 W/m^2 for the period from the beginning of industrial revolution to present).

Biomass burning aerosol particles are composed primarily of condensed organic components and elemental or black carbon, but they also contain nitrates, sulfates, and other components. While the concentration ratio of black carbon to organic liquid

constituents is small, it is important that black carbon absorbs effectively solar radiation. So, it has a warming effect (seemingly, within a few tenths of W/m^2) and thus can influence convective processes.

Because the influence of soot aerosol is quite difficult to be estimated reliably, Iacobellis et al.²⁷ recalculated radiative forcing with account of seven aerosol sources: tropical forest burning, savanna burning, midlatitude forest burning, boreal forest burning, charcoal combustion, agricultural waste combustion, as well as charcoal production and combustion. The data of Table 2 give the magnitude of these components in different geographic regions.

Different radiative transfer parameterizations and calculated fields of aerosol abundance (whose globally and annually average value was taken to be $3 \cdot 10^{-3} \text{ g/m}^2$) were used for calculation of the mean radiative forcing found to range from -0.6 to -1.0 W/m^2 (the calculation errors are determined primarily by uncertainty of the input data). The calculations showed that the systematic errors caused by different factors influencing radiative forcing can be mutually cancelled out and that under cloudy conditions the biomass burning aerosol stronger affects the backscattered intensity than the sulfate aerosol does, primarily because of the shorter zenith distance of biomass.

Spänkuch et al.⁴⁴ first estimated the influence of the coarse fraction of biogenic aerosol on the spectral distribution of infrared downward flux (IRDF) in the atmosphere over the wavenumber region from 700 to 1300 cm^{-1} . To do this, they used Fourier spectrometric measurements of IRDF spectra at zenith made at Potsdam, Germany. From analysis of observations made in May 1998 it follows that IRDF increases by 10.40 W/m^2 as the concentration of piny pollen increases by $2000 \text{ particles/m}^3$ a day, i.e., to about 8 times higher level than normally. This IRDF enhancement is twice as large as that due to the 10% increase of the total atmospheric moisture content in midlatitude summer or, equivalently, to atmospheric aerosol at visibility of about 5 km. For a medium pollen concentration, the IRDF enhancement is 1 – 2 W/m^2 .

Table 2. Distribution of biomass burning aerosols (Tg/yr) in different geographic regions

Region	Sources						
	Tropical forests	Savanna	Midlatitude forests	Boreal forests	Domestic fuels	Agricultural wastes	Charcoal
Tropical America	590	770	0	0	170	200	7.5
Tropical Africa	390	2430	0	0	240	160	9.3
Tropical Asia	280	70	0	0	850	990	3.3
Tropical Oceania	0	420	0	0	8	17	0
USA and Canada	0	0	0	0	80	250	0.5
West Europe	0	0	0	0	40	170	0.2
Former USSR and East Europe	0	0	0	0	0	0	0
Midlatitude forests	0	0	224	0	0	0	0
Boreal forests	0	0	0	56	0	0	0
Total	1260	3690	224	56	1438	2017	21

The pollen effect on the spectral IRDF distribution is fairly uniform (weakly selective) with a maximum of $11 \text{ mW}/(\text{m}^2 \cdot \text{s} \cdot \text{cm}^{-1})$ at the wavenumber of 1000 cm^{-1} . The quite deep decline in IRDF enhancement unattributable to known atmospheric absorbers is observed in the wide $850\text{--}1000 \text{ cm}^{-1}$ band. Outside of the $720\text{--}1300 \text{ cm}^{-1}$ region, the pollen effect was found to be minor.

Based on the data obtained, pollen-induced spectral variations of IRDF at zenith were compared with those due to changes in the total atmospheric moisture content and contributions of aerosol of different types. Near the $4.67 \mu\text{m}$ wavelength lying in the main absorption band of carbon monoxide (recall that this spectral interval is used for retrieval of total CO in the atmosphere), up to 80% (about 20% on the average) pollen-induced IRDF enhancement was observed.

Undoubtedly, the biogenic pollen, as an optically active atmospheric component, should be considered as an important factor in greenhouse forcing of the atmosphere, as well as in some atmospheric remote sensing applications. In this regard, more representative data on biogenic aerosol are required. Hopefully, aerosol remote sensing data will contribute significantly to solution of this problem.^{29,30}

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