Effect of biomass burning on chemical composition of the atmosphere

K.Ya. Kondratyev and V.A. Isidorov

Centre for Ecological Safety of the Russian Academy of Sciences/Nansen International Centre of Environment and Remote Sensing, St. Petersburg
St. Petersburg State University

Received January 31, 2001

The problem of biogenic emissions into the atmosphere is under discussion. The data on the effect of biomass burning on the chemical composition of the global atmosphere, as well as on gas-phase reactions of formation of atmospheric aerosol are analyzed. The principal attention is paid to consequences of biomass burning (forest, bush, and grass fires) in the tropics (Africa and South America) and, to a lesser degree, forest fires in mid-latitudes. The effect of biomass burning on the dynamics of tropospheric aerosol is considered separately. The influence of biomass burning on the global climate is briefly outlined as well.

Introduction

Biomass burning in the tropics is one of the main sources of minor gaseous constituents (MGC) and aerosol particles in the troposphere. Since MGC and aerosol affect significantly atmospheric chemical processes and the global climate, it is very important to have adequate information on the products of biomass burning emitted into the atmosphere.[1–42] The results obtained in this connection are the data of both field measurements and laboratory simulation.

1. Savannas and tropical forests

The tropics occupy about 40% of the land surface on the globe and are responsible for about 60% of primary global productivity. The diversity of plant species in the tropics is much wider than in other regions. However, nowadays the rate of transformation of tropical forests and savannas into agricultural lands and pastures is about 1% a year. This transformation involves biomass burning that affects markedly the chemical composition of the atmosphere.

In the process of biomass burning, a great amount of nonmethane hydrocarbons (NMHC), NO_2, and many other minor gases are emitted into the atmosphere. The analysis of satellite data shows that about 70% of biomass burning goes to the tropics (about a half of this value is in Africa). The maximum of biomass burning in the annual behavior (in the dry season) is observed to the north from the equator. Savannas and forests in the tropics also emit a great amount of biogenic compounds to the atmosphere.

Delmas et al.[3] describe the technical means for observation, methods of data interpretation, and the main results obtained within the framework of the international field observational experiment EXPRESSO conducted in 1994–1996 (the main period of observation includes the beginning of the dry season in November–December 1996). The aim of this experiment was to study the processes responsible for the change in the chemical composition of the troposphere under the effect of biomass burning in the Central Africa. The main observational facilities were (1) French aircraft-laboratory Focker–27 specially equipped for measuring the chemical composition of the troposphere and meteorological parameters at the altitude up to 4 km, (2) NOAA AVHRR, (3) equipment installed on the 65-m-high mast in the tropical forest in Congo.

The analysis of airborne measurements, used for studying peculiarities in the dynamics of the atmosphere and turbulence, demonstrated the complex structure of mesoscale atmospheric circulation near intertropical convergence zone. Processing of satellite images gave the maps of fire zones in forests and savanna. The effect of biogenic sources and biomass burning on the chemical composition of the lower tropospheric layers was characterized from joint interpretation of the airborne and mast data. The observational data were analyzed based on the corresponding results of numerical simulation of global-scale and regional processes.

Greenberg et al.[11] discussed the results of airborne and ground-based observations of MGC and aerosol emission in the period of biomass burning in the Central Africa. The observations were conducted within the framework of the EXPRESSO Experiment for Regional Sources and Sinks of Oxidants. Among NMHCs, isoprene is characterized by the maximum level of emission over savannas and tropical forests. The concentration of isoprene in the region of tropical forests and savannas is 700–1000 and 100–400 ppt, respectively, whereas for α-pinene it is equal to 30–100 and 20–30 ppt.

Direct measurements of the isoprene flow with the use of the correlation methods gave the values of about 890 μg isoprene/m^2 per hour for the period from mid-morning to noon in the case of humid tropical forests

0235-6880/01/02 93-09 $02.00

and semideciduous forests (about 10.6 mg isoprene/m^2 a day) and about 570 μg isoprene/m^2·h under conditions of transient and degraded forest landscapes (6.5 mg isoprene/m^2). These data agree well with model estimates obtained using landscape characteristics from the satellite data in combination with the data on MGC emission by leaves.

The obtained values of isoprene concentration and flows were used in Ref. 11 for estimating the balance of oxidants above tropical forest and savannas. The analysis of the calculated results on radiative fluxes has led to the conclusion that the observed sharp vertical gradient of the NO_2 photolysis rate coefficient is caused by extinction of photolytic radiation because of a large amount of absorbing aerosol that is likely generated as a product of biomass burning. Numerical simulation of chemical processes in the atmospheric boundary layer (ABL) based on the box model and with allowance made for the observed values of isoprene concentration and flow has shown that the above-mentioned extinction of the photolytic radiation almost halves the OH concentration as compared to the conditions of the aerosol-free ABL. Therefore, direct contribution of photochemical processes in the ABL to the ozone generation, especially, from the biogenic isoprene, turns out to be low.

Ruellan et al.[35] discussed the results of airborne observations of aerosol in the lower troposphere (at the altitudes up to 4 km) over the Central Africa. The observations were conducted in November 1996 within the framework of the EXPRESSO. In the context of studies of the products of biomass burning emitted into the atmosphere, Ruellan et al.[35] processed 24 aerosol samples to analyze the properties of black and organic carbon (BC and OC), water-soluble organic carbon (WSOC), polycyclic aromatic hydrocarbons (PAH), soluble ions, and aerosol morphology. Aerosol was sampled above tropical forests and savannas near the intertropical convergence zone (ITCZ).

At all altitudes, the number density of particles (from 10 to 14000 nm in diameter) was high [(3100 ± 2060) cm^{-3}]. The fraction of particles of soil origin proved to be lower than expected [the mass concentration was (20 ± 18 μg/m^3)]. On the other hand, the content of pyrogenic particles and black carbon turned out to be rather significant. The BC concentration was (3.8 ± 2.3) μg/m^3 (atmospheric boundary layer over a forest), (9.8 ± 3.9) μg/m^3 (savanna), and (8.7 ± 1.6) μg (harmatan layer).

The data on other minor constituents (oxalate, PAN, etc.) demonstrate a strong effect of fires in savanna on their content in the regional troposphere. The obtained results are also indicative of the existence of vertical and horizontal exchange between different tropospheric layers through ITCZ.

The fraction of WSOC in the samples under study was (46 ± 9)% relative to the total content of organic carbon. This fraction turned to be more significant [(85 ± 18)%] in the harmatan layer. This points to the possible significant role of such products of biomass burning as cloud condensation nuclei. To estimate aging of such particles, different chemical indicators were used; among them was the WSOC/OC condensation ratio that increased by two to three times with altitude when entering the harmatan layer.

Within the atmospheric boundary layer above a forest, the high concentration of organic acids (format, acetate, and oxalate) of biogenic origin was measured. The observational results under discussion were obtained at the beginning of the dry season, when the effect of savanna fires on the atmosphere prevailed, and the flow of dust aerosol due to harmatan was still weak. Under these conditions, nitrates were mostly conserved in the gaseous state, and therefore the corresponding nitrogen nutrients remained within the considered region.

In recent years, it becomes clear that emissions into the atmosphere due to biomass burning not only radically affect the chemical composition of the atmosphere in the tropics, but also influence the global atmosphere thus contributing to the global climate change. Biomass burning in Africa, where more than half of savanna biomes is located, has the strongest effect on the chemical composition of the atmosphere. Biomass burning emits a great amount of such greenhouse gases as CO_2 and CH_4, as well as intensifies generation of tropospheric ozone.

From November to March the fire region covers the Western and Central Africa (in the Northern Hemisphere), and from July to October fires spread in the Eastern and Southern Africa (in the Southern Hemisphere). The global atmospheric circulation (first of all, through the intratropic convergence zone) causes the aerosol and gaseous products of biomass burning transport above the equatorial zone of the Atlantic Ocean.

For further research into consequences of biomass burning (first of all, from the viewpoint of spatial distribution of carbon dioxide), in November–December of 1996 Cautenet et al.[2] conducted airborne measurements of the chemical composition and meteorological parameters of the troposphere. These measurements also were a part of the EXPRESSO. They were aimed at obtaining the data on regional sources and sinks of oxidants. To solve this problem, the NOAA AVHRR data were used. These data served as input information for the regional atmospheric model (RAMS) estimating atmospheric emissions of products of biomass burning.

The level of emissions into the atmosphere depends on characteristics of the burnt biomass and can be estimated from the AVHRR data using two independent techniques (1) with allowance for classification of vegetation cover (CV) and (2) based on the net primary productivity (NPP). Satellite images were processed to determine the area subjected to burning. The part of burnt biomass (or biomass burning factor α) was estimated using numerical simulation; it was roughly 40%. Information of such a kind is used for calculation of carbon monoxide and

CO_2 redistribution due to fires. These calculated results were then compared with the data of airborne observations.

Reference 2 considers two such events covering the time intervals of 4 and 5 days, when the aircraft flew above forests and savannas, respectively. The obtained results indicate that the main factor of spatial distribution of minor gaseous constituents – the products of biomass burning – was mesoscale circulation. The results of numerical simulation of the CO concentration field (using the RAMS) are in a good agreement with the data of airborne observations above forests and savanna. The application of the CV or NPP techniques to calculations of the CO concentration field causes the discrepancy no higher than 20–30% (such a small discrepancy complicates revealing of the most reliable technique).

In connection with widespread occurrence of fires in savanna and their significant influence on the environment (chemical composition of the atmosphere, composition of soil, biological diversity, etc.), Nielsen[27] has analyzed the peculiarities of the space-time distribution of fires in the Central Africa (the region being studied within the EXPRESSO) based on the NOAA AVHRR data for the periods of dry seasons from November 1994 to December 1997. Three characteristics were used to describe the variability of fires: (1) probability of a fire at the western point in a certain time; (2) probability of repeated fires at the western point for a certain time interval; (3) the size and temperature of the burning savanna affecting the conditions at a given point.

Processing of satellite images shows that appearance of a fire is not a spatially random process. The probability of a fire increases, for example, in the presence of fires near the considered point. The combined analysis of characteristics of time and space variability of fires allows justification of 12 typical fire modes, as well as the dependence of a fire character on the vegetation cover. Although it is undoubted that fires in savanna are caused, as a rule, by human activity rather than natural factors, some specific causes of fires (connected with some or other activities) are still unclear. From the viewpoint of time variability, it is worth classifying fires with allowance for the beginning of the fire season, the rate of fire development, and the duration of the fire season. In this context, the types of fires can be distinguished by peculiarities of their dynamics: fast, late, or long.

The contribution of savanna fires is more than 40% of the global level of biomass burning. They emit, in particular, such minor atmospheric constituents as nonmethane hydrocarbon compounds, carbon monoxide, methane, and others, as well as aerosol. According to the available estimates, for the period of 1975–1980 from 40% to 75% of savannas were burnt annually, and about 60% of such fires took place in Africa. In 1990 about $2.0 \cdot 10^9$ t of biomass were burnt; as a result, the atmosphere received 145 Tg CO. This is about 30% of total anthropogenic emissions of CO. The amount of emissions of C_2–C_3 alkanes, alkenes, and benzine to the atmosphere due to fires in African savannas can be 20–95% relative to global industrial emissions of these compounds. The relative contribution of the emissions mentioned above to the greenhouse effect can achieve 25%. Biomass burning has also a significant effect on the global carbon cycle (consequently, on the CO_2 concentration).

In connection with the circumstances mentioned above, Hoffa et al.[14] studied the regularities in the seasonal behavior of atmospheric emissions due to fires in savanna of the Western Province of Zambia in the dry season of 1996 (early June–early August). Their aim was to analyze the effect of the humidity content on the burning dynamics. Observations showed that biomass burning at the beginning of the dry season emits less products of complete combustion (CO_2), but more products of incomplete combustion (including CO).

For the period of observations, the fires created at 13 points in various savanna regions have been analyzed. The fire development was traced in the process of the dry season evolution from the moment of fire setting. The firing rate varied from 1884 to 3314 kg/ha in the dambo savanna and from 88953 to 132332 kg/ha in the miombo savanna. The humidity content of green grass decreased for the period of fires from 127 to 69% (dambo) and from 119 to 33% (miombo). The combustion factor CF (fraction of the fuel burnt in a fire) increased from 44 to 98% (dambo) and from 1 to 47% (miombo). The power linear intensity of burning varied from 288 to 5271 kW/m (dambo) and from 25 to 5274 kW/m (miombo). Thus, in the course of the fire development (evolution of the dry season), the character of the fire and its atmospheric emissions changed significantly.

Laboratory simulation of fires involving the burning of various plant species (with the use of an IR Fourier spectrometer for determining properties of the products of burning) has shown such organic compounds as formaldehyde, methanol, vapor of acetic and formic acids to be in abundance among the products of burning. Goode et al.[9] have discussed the results of three new experiments on studying the grass-burning products. The data has been obtained on the content in emissions of carbon dioxide, nitrogen oxide, water vapor, carbon monoxide, methane, ammonium, ethylene, acetylene, isobutane, methanol, vapor of acetic and formic acids, formaldehyde, and hydroxyacetaldehyde. These data characterize the composition of smokes emitted by burnt plants of various types. Formaldehyde, methanol, and acetic acid were emitted under such conditions of the grass burning, at which the relative content of CO was ~1–2% and about 1% when burning other oxidized compounds. All these compounds are important, because they have a significant effect on chemical processes with participation of O_3 and NO_x proceeding both in smoke plumes and in the free troposphere.

The spectroscopic analysis has shown that prevalent C_4-compound in emissions was isobutene

0235-6880/01/02 93-09 $02.00

(C_4H_8), rather than 1-butene. Estimates have led to the conclusion that (67 ± 9)% of nitrogen contained in the fuel is accounted for the MGC under study, and NH_3 and NO_x are responsible for the fraction of (22 ± 8)%. These data contradict the earlier results, according to which about 90% of nitrogen (including 55% of NH_3 and NO_x) in the fuel are transformed into the gas phase. The reasons for this discrepancy are still unclear.

Using the 3D global model of atmospheric circulation with the allowance for chemical processes, Guenther et al.[12] have performed numerical simulation, the results of which showed that doubling of isoprene and monoterpene emissions changes the concentrations of such minor gases as OH, MPAN, NO_x, H_2O_2, O_3, and CO by 10–30%. This conclusion is important for interpreting the data of the EXPRESSO field experiment aimed, in particular, at estimating the emissions of isoprene and monoterpenes in forests and savannas of the Central Africa.

The comparison of the results of numerical simulation with the data of airborne and mast observations have shown that mean emissions can be estimated accurate to the coefficient 2, if the data of ground-based measurements are used as input parameters of the model. In Ref. 12, the annual income of isoprene into the atmosphere of the Central Africa has been estimated as 35 Tg C. This value is only 14% lower than that determined earlier with the use of an approximate model. The values calculated for individual points at different time moments differ from the observed ones up to 5 times. This is indicative of the presence of very significant errors in the numerical simulation.

Since there is few measurements of the molecular hydrogen concentration in the atmosphere, the available information is rather contradictory. According to the available data, the near-ground H_2 concentration varies within ~540–590 ppb under conditions of clear troposphere and reaches ~800 ppb under urban conditions. The background H_2 concentration in the Northern Hemisphere (NH) is about 5% higher than that in the Southern Hemisphere (SH). However, according to the data obtained between 71°N and 90°S, the H_2 concentration in the SH (~520 ppb) is higher than in the NH (~490 ppb). According to the observational data, for 1986–1989 the H_2 concentration increased by (0.6 ± 0.1)% a year.

Four main sources of H_2 in the troposphere are currently known: two photochemical sources (oxidation of methane and nonmethane hydrocarbons) and two sources due to products of combustion (such "technological" sources as burning of fossil fuel and biomass). The biogeochemical cycle is characterized by some interaction with the cycles of methane and carbon oxide through the reactions of formaldehyde formation and destruction. Hydrogen is removed from the troposphere through the reaction with OH:

$$H_2 + OH \rightarrow H_2O + H$$

and through H_2 deposition onto the surface. Novelli et al.[28] have considered the results of 5-year observations of the H_2 concentration by analyzing air samples collected at 50 points of the remote marine atmospheric boundary layer. The processing of observational data for 1991–1996 has shown that the globally mean value of the ratio of H_2 mixture is (531 ± 6) ppb. The variability of the H_2 concentration is therewith characterized by the pronounced annual behavior in the both hemispheres at identical levels of the seasonal maximum equal to ~530–550 ppb. However, the minimum of the H_2 concentration (in the annual behavior) in the Northern Hemisphere turns to be 70 ppb deeper than in the Southern Hemisphere (respectively, about 450 and 520 ppb), and therefore the amount of H_2 in the SH is about 3% higher than in the NH.

As to the components of the global budget of H_2, the main source of H_2 in the troposphere is oxidation of methane, and the main sink is its assimilation by soil. The size of the global cycle of H_2 is 75 Tg H_2/year. Such a cycle together with the calculated content of the hydrogen in the troposphere (155 Tg) determines the lifetime equal to ~2 years.

Although the available information on the global distribution of sources and sinks of H_2 and the factors determining its content remains incomplete, it is undoubted that the lower level of the minimum concentration of H_2 in the Northern Hemisphere can be explained by the influence of asymmetry of H_2 assimilation by soil in both hemispheres. The annual behavior of the H_2 concentration in the Southern Hemisphere is likely caused by the effect of biomass burning.

2. Boreal forests and other sources of emission

Fires in boreal forests contribute only insignificantly (about 2%) to atmospheric emissions of carbon, but affect markedly the chemical processes in the high-latitude troposphere, especially, those connected with formation of tropospheric ozone and oxidation power of the troposphere. Fires in boreal forests affect significantly the radiative properties of the atmosphere as well and thus lead to formation of the primary and secondary aerosols.

The analysis of the chemical composition of snow accumulated in northern glaciers and the Greenland ice sheet opens up unique opportunities for evaluating the evolution of fires in the past under the effect of natural (climate change) or anthropogenic factors. In this connection, Jaffrezo et al.[18] have discussed the results of analysis of the concentration of aerosol oxalate ($C_2O_4^{2-}$) in daily snow samples taken on Mt. Summit of the Greenland ice sheet (72°30′N, 38°00′W, the height of 3210 m above the sea level) in summer seasons of 1992–1995. Four cases of the increased concentration of oxalate were observed. These cases can be interpreted as a result of passage of a plume of products of biomass burning over the sampling point.

At least, in two cases the regions of fires were localized in the Northern Canada. The analysis of the aerosol corresponding to one of these cases revealed a significant increase in the number density of particles of the accumulative mode, although the increase in the total number density was insignificant. The chemical composition of the aerosol was characterized by the presence of typical products of biomass burning: fine aerosol, aerosol containing K, high concentration of ammonium (NH_4^-), aerosol formic acid ($HCOO^-$), and acetate (CH_3COO^-), as well as organic compounds of glycolate type.

The microstructure of the aerosol containing K, oxalate, and glycolate is shifted towards the accumulative mode, and its shape corresponds to the microstructure of the sulfate aerosol. This is indicative of the presence of internal mixing of the considered components in aerosol particles. The values of the molar ratio S/K suggest that sulfur is in aerosol due to long-range transport (likely, by gas-phase formation of sulfates). The measured concentrations of the components mentioned above in the samples of fog particles showed a good agreement between the relative variability of the aerosol and fog concentrations from the viewpoint of content of various compounds (acetate, formic acid, chloride, nitrate, and sulfate).

In April 1997, Yokelson et al.[41] have conducted airborne measurements of the concentration of minor gases above the point of biomass burning in North Carolina (USA). Toward this end, a Fourier transform IR spectrometer (AFTIR) with a flow-through multipass cell was installed aboard a King Air B–90 aircraft. This allowed the concentration of minor gases to be measured *in situ*. The list of the gases under study included water vapor, carbon dioxide, carbon monoxide, methane, formaldehyde, formic acid, methanol, ethylene, and ammonia. The concentrations of formaldehyde, acetic acid, and methanol measured in relation to the concentration of carbon oxide were (2.5 ± 1)%. This value agrees well with the results of similar laboratory simulation experiments. However, these values markedly exceed the values obtained earlier when studying "fresh" smokes.

The calculations made in Ref. 41 based on the use of a simple photochemical model showed that numerical simulation of the processes of ozone formation in plumes of biomass burning should take into account the reactions with participation of oxidized organic compounds generated in great amounts (as HO_x) at biomass burning. The results under discussion indicate that the oxidized biogenic and other organic compounds, whose content was measured only in rare cases, play a significant part in chemical processes with participation of HO_x, NO_x, and O_3 in the troposphere.

Methyl bromide (MeBr) has the highest concentration in the atmosphere among organic bromide gases. Although it is destroyed in the troposphere through the reaction with hydroxyl OH, a part of methyl bromide comes to the stratosphere and, as a result of photolysis, becomes a source of the bromine atoms destroying ozone. Unlike chlorfluorocarbon compounds, methyl bromide has both natural and anthropogenic origin. It is difficult to estimate the anthropogenic contribution and, thus, to reveal its effect on the global environment, although in recent years serious efforts were made to study sources and sinks of methyl bromide.

At the total content of methyl bromide in the global atmosphere roughly equal to 145 Gg and the lifetime about 0.7 years, the levels of its mutually compensating source and sink should be about 207 Gg/year, and the level of unknown sources reaches about 80 Gg/year. The studied sources of MeBr include emissions connected with the use of chemical control agents in agriculture (with fumigation), burning of biomass and benzine, as well as emissions due to the World Ocean. The ocean that is both a source and a sink of methyl bromide was considered as a resulting source until the studies of emissions in the eastern sector of the Pacific Ocean in the latitudinal zone from 44°N to 45°S alternated the sign of those estimates. It is important that cold polar water is a significant source of MeBr.

Observations have shown that soils serve as a significant sink of MeBr [(42 ± 32) Gg/year], but these estimates need in further refinement, as well as the data on emissions of methyl bromide by plants. Conflicting data of the World Meteorological Organization indicate that the emissions of MeBr due to benzine burning in 1991–1992 achieved 15 Gg/year. But, according to other information, they were only 0.5–1.5 Gg/year (one more available estimate is about 3–4 Gg/year). For the emissions due to biomass burning, two estimates were obtained: 19 and 14–24 Gg/year. Williams et al.[39] have discussed the measured results on the methyl bromide flow for six agricultural fields in the process of their fumigation, including measurements of flows both above soil (using gas chambers) and at a depth up to 90 cm (measurements were conducted in various regions of California). The measurements showed that from 21 to 74% methyl bromide was emitted to the atmosphere. The mean relative level of emissions is (49 ± 19)% (chamber measurements) and (52 ± 20)% (soil data). In Ref. 39, the main factors determining the level of methyl bromide emissions have been analyzed.

The main factors determining sources and sinks of NO, N_2O, and CH_4 are microbe (biogeochemical) processes in soils proceeding due to the presence there of nitrogen, carbon, oxygen, and water. The atmospheric flows of minor gases formed in such a way are characterized by strong spatiotemporal inhomogeneity. This complicates estimation of the budget of ozone and the minor gases mentioned above. The application of nitric fertilizers also affects significantly the flows of nitrogen and methane. To study the spatiotemporal variability of the NO, N_2O, and CH_4 flows, a three-year-long program of field observations (with the use of gas chambers) was conducted in Costa Rica in balsa plantations (Ochroma lagopus) both subjected and not subjected to fertilization.

0235-6880/01/02 93-09 $02.00

The flows of the minor gases under study in soil were measured manually at 36 randomly distributed points in the balsa forest, and the averaged atmospheric emissions were measured in seven chambers. The observational data are indicative of the wide variability of flows of the minor gases within two selected 40×40 m^2 areas, except for the nitrogen oxide flows that varied only slightly. Fertilization intensified emissions of nitrogen oxide, but did not cause their spatial variability. Roughly for 6 weeks, the emission of nitrogen oxide on the fertilized area came back to the normal level observed before the fertilization. If the soil was relatively dry, then fertilization restricted the CH_4 assimilation by soil.

3. Biomass burning and tropospheric ozone

It is believed now that the annual maximum of total tropospheric ozone content (TTOC) observed in the tropics of the Atlantic Ocean in the Southern Hemisphere is caused by biomass burning in Africa and Brasilia in spring. Biomass burning emits a significant amount of such precursors of tropospheric ozone as CO, NO_x, and hydrocarbons into the atmosphere. This causes the TTOC growth in the troposphere about 10–15 D.u.

Interpretation of the data on the southern part of the Atlantic Ocean, however, is complicated by the fact that the variability of numerous meteorological parameters is characterized by the structure similar to the spatial distribution of TTOC with the zonal wavenumber equal to 1. This allows us to assume a significant influence of meteorological factors on the filed of TTOC. Numerical simulation has demonstrated, for example, that the TTOC maximum can be also formed in the absence of biomass burning due to the sedimentation process in the troposphere and the horizontal transport of air.

On the other hand, TTOC anomalies about 10–20 D.u. were observed in the region of Indonesia in the period of El Niño of 1997–1998 (large-scale fires were also observed at that time in humid tropical forests of Indonesia). This reflects the need to take into account both biogenic and dynamic factors. The effect of the stratosphere on the troposphere with its characteristic dependence on the solar activity and quasi-biennial oscillations also can play a marked part. Changes of the total ozone content in the stratosphere affect the income of UV solar radiation to the troposphere and, thus, the course of photochemical processes in the troposphere.

In connection with the circumstances mentioned above, Ziemke and Chandra[42] have analyzed the causes of TTOC variability using the data of satellite observations (Nimbus-7) for 20 years (1979–1998) in order to estimate the role of biomass burning and large-scale transport. Consideration of the observational data for the tropics revealed three regions characterized by specific peculiarities in the annual behavior and interannual variability of tropospheric ozone: eastern and western sectors of the Pacific Ocean, as well as the Atlantic Ocean.

In the latter region, the maxima of TTOC typically take place at roughly the same time (September–October) both to the north and to the south from the equator, whereas in the north-to-south direction from the equator the amplitude of the annual behavior of tropospheric ozone increases from 3 to 6 D.u. On the other hand, the yearly variability of TTOC is weak in both sectors of the Pacific Ocean with maxima in March–April (Northern Hemisphere) and September–November (Southern Hemisphere).

The interannual variability of tropospheric ozone in the three considered regions also differs significantly. In the Atlantic Ocean, the dominant factor of variability is quasi-biennial oscillations that, however, do not coincide in phase with manifestation of such oscillations in the stratosphere. Such a regularity agrees with the assumption on the influence of the modulation of the UV radiation incoming to the troposphere on tropospheric photochemical processes with the time scales characteristic of quasi-biennial oscillations and determining variations of TTOC. However, the photochemical model predicts changes of TTOC that are far lower than the observed ones. This reflects the critically important role played by dynamic factors.

Biomass burning has likely a marked (but less significant than the atmospheric dynamics) influence on the variability of tropospheric ozone over the Atlantic Ocean. The dominant factor in the interannual variations of tropospheric ozone over the Pacific Ocean is El Niño, during which tropospheric ozone has minimum values in the eastern sector of the Pacific Ocean and maximum values in the western sector. Such a signature of variability reflects the combined action of the convection-induced transport and the intensity of biomass burning in Indonesia. To draw maps of tropospheric ozone with high spatial resolution and to study long series of data on tropospheric ozone, the STOR technique has been proposed. This technique is based on the use of a low variability of TTOC near the International Date Line.

In the region of the river Amazon and in the Central Brasilia, fires in tropical forests and serrado in the period of dry winter of the Southern Hemisphere (July–October) result from man's activities. Biomass burning emits many minor gases (CO, CO_2, NO_x, hydrocarbons, etc.) and aerosol into the atmosphere. Secondary minor gases including, in particular, tropospheric ozone are also formed through reactions between products of combustion. In this connection, in the period from August 16 to September 10 of 1995 in the Cuiaba region (Central Brasilia, 16°S, 56°W), the SCAR-B field observational experiment was conducted. The goal of the experiment was to study physical properties of the smoke produced at biomass burning and its influence on the radiative budget and climate.[24a]

Balloon observations during the experiment revealed an increase in the concentration of tropospheric ozone (as compared to the mean conditions of the dry season), which varied widely depending on the character of atmospheric circulation. Photometric

observations of the aerosol optical depth and the near-surface concentration of soot carbon gave a quantitative characteristic to the smoking conditions of the atmosphere. The analysis of the air mass trajectories led to the conclusion that the especially high increase of the ozone concentration took place in August 26–29. It was likely connected not only with the direct effect of products of biomass burning, but also with the influence of atmospheric emissions of minor gases from large cities situated on the Atlantic coast of Brasilia. This conclusion is supported by the data of lidar sensing of clouds from aboard the ER-2 aircraft.

Acid minor gases take an active part in the chemical processes proceeding in the troposphere. In particular, they are the main products of oxidation processes, and dry and wet deposition of HNO_3 and H_2SO_4 from the atmosphere is the main sink for tropospheric NO_x and SO_2. In the remote (background) regions of the atmosphere, monocarboxylic acids HCOOH and CH_3COOH often turn to be the dominant acid minor gases, as well as components of cloud water and precipitations. In the cloud water, formic acid is the main sink for hydroxyl radicals.

Talbot et al.[36] described the main peculiarities in the large-scale distribution of HNO_3, HCOOH, and CH_3COOH above the central and southern regions of the Pacific Ocean in the Southern Hemisphere. The data were obtained within framework of the field observational experiment PEM-Tropics in the spring period. Since the considered regions are far from continents, it was assumed that the concentration of acid minor gases was low. However, it turned out that at the altitudes of 2–12 km above the southern part of the Pacific Ocean the ratios of acid minor gases mixture were increased (up to 1200 ppt in volume). As a rule, such situations characterized the layer of 3–7 km in the latitudinal belt of 15–65°S. In most cases, there exists a correlation with the ratios of CH_3Cl, PAN, and O_3 mixture. This correlation indicates that all these components have common sources caused by photochemical processes and biomass burning. However, no correlation was observed between acid minor gases and typical gaseous pollutants (for example, C_2Cl_4 or CH_3CCl_3).

The pollutants due to car exhausts were characterized by significant aging at the concentration ratio C_2H_2/CO varying within 0.2–2.2 ppt/ppb. The relation between the content of acid minor gases and this ratio was similar to that observed in "old" air masses (that came >3–5 days after they left a continent) of the western sector of the northern Pacific Ocean. The C_2H_2/CO concentration ratio equal to 0.6 observed in the marine atmospheric boundary layer in the southern Pacific Ocean indicates that this region was not subjected to the direct effect of biomass burning emissions. In this region, the lowest mixture ratios of the acid minor gases were observed at the mean values equal to 14 (HNO_3), 19 (HCOOH), and 18 ppt (CH_3COOH). These values agree with the low concentrations of NO_x (10 ppt), CO (about 50 ppm), O_3 (<20 ppm), and long-living hydrocarbons (for example, C_2H_6 < 300 ppt).

On the whole, the analysis of the PEM-Tropics data points to the significant effect of "old" emissions of products of biomass burning on the spatial distribution of the acid minor gases concentration above the Southern Pacific region in spring. The role of these emissions in the chemical processes proceeding in the atmosphere of the Southern Hemisphere occurred to be far more significant than expected.

Conclusion

The problem of biogenic atmospheric emissions in general and biomass burning emissions in particular has been realized only recently. It attracted attention to anthropogenic influence on the chemical composition of the atmosphere affecting the global climate.[17,21–23] Earlier estimates show that the climate radiative forcing due to the aerosol produced at biomass burning is about -1.0 W/m^2 (in the case of a purely scattering aerosol the uncertainty of these estimates is from -0.3 to -2.2 W/m^2). Thus, this effect is comparable with the effect produced by the anthropogenic sulfate aerosol and, on the other hand, with the greenhouse effect that has the opposite sign (from the beginning of industrial revolution the greenhouse effect has achieved the value of 2–3 W/m^2).

Aerosol particles generated at biomass burning consist mostly of condensed organic components, elemental or black carbon, but they also include nitrates, sulfates, and other components. Although the concentration ratio of black carbon to liquid components is low, it is important that black carbon significantly absorbs solar radiation. This determines the heating effect on the atmosphere (likely, within several tenths of W/m^2) and can affect the process of convection.

Since it is difficult to estimate sufficiently reliably the effect of the soot aerosol component, Iacobellis et al.[16] have calculated the radiative forcing with allowance made for the following seven sources of aerosol: (1) burning of tropical forests, 2) burning of savannas, (3) burning of forests in middle latitudes, (4) burning of boreal forests, (5) burning of fire-wood, (6) burning of agrowaste, (7) production and burning of charcoal. The tabulated data characterize the scales of these components in various regions.

The calculations of the radiative forcing using different techniques for parameterization of radiative transfer and the calculated aerosol field (annually and globally mean aerosol content is equal to $3\cdot10^{-3}$ g/m^2) gave its value from -0.6 to -1.0 W/m^2 (the errors of calculations are mostly determined by uncertainties in input parameters). Mutual compensation of systematic errors due to different factors is an important circumstance, as well as the conclusion on stronger effect of the aerosol generated at biomass burning on the backscattering intensity (as compared to the sulfate aerosol) under conditions of cloudy sky, that is mostly caused by the shorter solar zenith distance in the tropic regions where most biomass is burnt.

0235-6880/01/02 93-09 $02.00

Table. Distribution of the scales of dry biomass burning (Tg/year) in different regions

Regions	Sources						
	Tropical forests	Savanna	Mid-latitude forests	Boreal forests	Domestic fuel	Agrowaste	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
Western Europe	0	0	0	0	40	170	0.2
Former USSR and Eastern Europe	0	–	–	–	–	–	–
Mid-latitude 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

References

1. M.O. Andrea, T.W. Andrea, H. Annegarn, J. Beer, H. Cachier, P. Canut, W. Elbert, W. Maenhaut, I. Saima, F.G. Wienhold, and T. Zenker, J. Geophys. Res. **103**, No. D24, 32119–32128 (1998).
2. S. Cautenet, D. Poulet, C. Delon, R. Delmas, J.-M. Gregoire, J.M. Pereira, S. Cherchali, O. Amram, and G. Flouzat, J. Geophys. Res. **104**, No. D23, 30641–30657 (1999).
3. R.A. Delmas, A. Druilhet, B. Cros, P. Durand, C. Delon, J.M. Lacaux, J.M. Brustet, D. Serca, C. Affre, A. Guenther, J. Greenberg, W. Baugh, P. Harley, L. Klinger, P. Ginoux, G. Brasseur, P.R. Zimmerman, J.M. Gregoire, E. Janodet, A. Tournier, P. Perros, T. Marion, A. Gaidichet, H. Cachier, S. Ruellan, P. Maslet, S. Cautenet, D. Poulet, C. Bouka Biona, D. Nganga, J.P. Tathy, A. Minga, J. Loemba-Ndembi, and P. Ceccato, J. Geophys. Res. **104**, No. D23, 30609–30624 (1999).
4. O. Dubovik, B.N. Holben, Y.J. Kaufman, M. Yamasoe, A. Smirnov, D. Tanre, and I. Slutsker, J. Geophys. Res. **103**, No. D24, 31903–31924 (1998).
5. F. Echalar, P. Artaxo, J.V. Martins, M. Yamasoe, F. Gerab, W. Maenhaut, and B. Holben, J. Geophys. Res. **103**, No. D24, 31849–31864 (1998).
6. M.A. Fenn, E.V. Browell, C.F. Butler, W.B. Grant, S.A. Kooi, M.B. Clayton, G.L. Gregory, R.E. Newell, Y. Zhu, J.E. Dibb, H.E. Flueberg, B.E. Anderson, A.R. Bandy, D.R. Blake, J.D. Bradshaw, B.G. Heikes, G.W. Sachse, S.T. Sandholm, H.B. Singh, R. Talbot, and D.C. Thornton, J. Geophys. Res. **104**, No. D13, 16197–16212 (1999).
7. R.J. Ferek, J.S. Reid, P.V. Hobbs, D.R. Blake, and C. Liousse, J. Geophys. Res. **103**, No. D24, 32107–32118 (1998).
8. J.F. Gleason, N.C. Hsu, and O. Torres, J. Geophys. Res. **103**, No. D24, 31969–31978 (1998).
9. J.G. Goode, R.J. Yokelson, R.A. Sussott, and D.E. Ward, J. Geophys. Res. **104**, No. D17, 21237–21246 (1999).
10. V.G. Gorshkov, V.V. Gorshkov, and M. Makarieva, *Biotic Regulation of the Environment. Key Issues of Global Change.* (Springer/PRAXIS, Chichester, U.K., 2000), 364 pp.
11. J.P. Greenberg, A.B. Guenther, S. Madronich, W. Baugh, P. Ginoux, A. Druilhet, R. Delmas, and C. Delon, J. Geophys. Res. **104**, No. D23, 30659–30671 (1999).
12. A. Guenther, B. Baugh, G. Brasseur, J. Greenberg, P. Harley, L. Klinger, D. Serca, and L. Vierling, J. Geophys. Res. **104**, No. D23, 30625–30639 (1999).
13. L.S. Guild, J.B. Kauffman, L.J. Ellingson, D.L. Cummings, E.A. Castro, R.E. Babbit, and D.E. Ward, J. Geophys. Res. **103**, No. D24, 32091–32100 (1998).
14. E.A. Hoffa, D.E. Ward, W.M. Hao, R.A. Susott, and R.H. Wakimoto, J. Geophys. Res. **104**, No. D11, 13841–13853 (1999).
15. G. Holdsworth, K. Higuchi, G.A. Zielinski, P.A. Mayewski, M. Wahlen, B. Deck, P. Chylek, B. Jonson, and P. Damiano, J. Geophys. Res. **101**, No. D18, 23317–23334 (1996).
16. S.F. Iacobellis, R. Frouin, and R.C.J. Somerville, J. Geophys. Res. **104**, No. D10, 12031–12045 (1999).
17. V.A. Isidorov, *Organic Chemistry of the Earth's Atmosphere* (Springer Verlag, Berlin, Heidelberg e.a., 1990), 218 pp.
18. J.-L. Jaffrezo, C.I. Davidson, H.D. Kuhns, M.H. Bergin, R. Hillamo, W. Maenhaut, J.W. Kahl, and J.M. Harris, J. Geophys. Res. **103**, No. D23, 31607–31078 (1999).
19. Y.J. Kaufman, C.O. Justice, L.P. Flynn, J.D. Kendall, E.M. Prins, L. Giglio, D.E. Ward, W.P. Menzel, and A.W. Setzer, J. Geophys. Res. **103**, No. D24, 32215–32238 (1998).
20. M.D. King, S.-C. Tsay, S.A. Ackerman, and N.F. Larsen, J. Geophys. Res. **103**, No. D24, 31989–32000 (1998).
21. K.Ya. Kondratyev, *Multidimensional Global Change* (Wiley/PRAXIS, Chichester, 1998), 761 pp.
22. K.Ya. Kondratyev *Climatic Effects of Aerosols and Clouds* (Springer/PRAXIS, Chichester, 1999), 264 pp.
23. K.Ya. Kondratyev and C.A. Varotsos, *Atmospheric Ozone Variability: Implications for Climate Change, Human Health, and Ecosystems* (Springer/PRAXIS, Cichester, 2000), 716 pp.
23a. X. Liu, P.V. Espen, F. Adams, J. Cafmeyer, and W. Maenhaut, J. Atmos. Chem. **36**, No. 2, 135–155 (2000).
24. J.M. Lobert, W.C. Keene, J.A. Logan, and R. Yevich, J. Geophys. Res. **104**, No. D7, 8373–8390 (1999).
24a. K.M. Longo, A.M. Thompson, V.W.J.H. Kirchhoff, L.A. Rewer, S.R. de Freitas, M.A.F.S. Dias, P. Artaxo, W. Hart, J.D. Spinhirne, and M.A. Yanasoe, J. Geophys. Res. **104**, No. D10, 12113–12122 (1999).
25. J.V. Martins, P. Artaxo, C. Liousse, J.S. Reid, P.V. Hobbs, and Y.J. Kaufman, J. Geophys. Res. **103**, No. D24, 32041–32050 (1998).
26. J.V. Martins, P.V. Hobbs, R.E. Weiss, and P. Artaxo, J. Geophys. Res. **103**, No. D24, 32051–32058 (1998).
27. T.T. Nielsen, J. Geophys. Res. **104**, No. D23, 30713–30723 (1999).

28. P.C. Novelli, P.M. Lang, K.A. Masarie, D.F. Hurst, R. Myers, and J.W. Elkins, J. Geophys. Res. **104**, No. D23, 30427–30444 (1999).
29. D. Poppe, R. Koppmann, and J. Rudolph, Geophys. Res. Lett. **25**, No. 20, 3823–3826 (1998).
30. E.M. Prins, J.M. Feltz, W.P. Menzel, and D.E. Ward, J. Geophys. Res. **103**, No. D24, 31821–31836 (1998).
31. J.S. Reid and P.V. Hobbs, J. Geophys. Res. **103**, No. D24, 32013–32030 (1998).
32. J.C. Reid, P.V. Hobbs, C. Liousse, J.V. Martins, R.E. Weiss, and T.F. Eck, J. Geophys. Res. **103**, No. D24, 32031–32040 (1998).
33. L.A. Remer, Y.J. Kaufman, B.N. Holben, A.M. Thomson, and D. McNamara, J. Geophys. Res. **103**, No. D24, 31879–31892 (1998).
34. J.I. Ross, P.V. Hobbs, and B.N. Holben, J. Geophys. Res. **103**, No. D24, 31925–31942 (1998).
35. S. Ruellan, H. Cachier, A. Gaudlichet, P. Maslet, J.-P. Lacaux, J. Geophys. Res. **104**, No. D23, 30673–30690 (1999).
36. R.W. Talbot, J.E. Dibb, E.M. Scheuter, D.R. Blake, N.J. Blake, G.L. Gregory, G.W. Sachse, J.D. Bradshaw, S.T. Satadholm, and H.B. Singh, J. Geophys. Res. **104**, No. D5, 5623–5634 (1999).
37. I.V. Trosnikov and C.A. Nobre, J. Geophys. Res. **103**, No. D24, 32129–32138 (1998).
38. A.M. Weitz, M. Keller, and P.M. Crill, J. Geophys. Res. **104**, No. D23, 30097–30107 (1999).
39. J. Williams, N.-Y. Wang, and R.J. Cicerone, J. Geophys. Res. **104**, No. D23, 30087–30096 (1999).
40. M.A. Yamasoe, Y.I. Kaufman, O. Dubovik, L.A. Remer, B.N. Holben, and P. Artaxo, J. Geophys. Res. **103**, No. D24, 31893–31902 (1998).
41. R.J. Yokelson, J.C. Goode, D.E. Ward, R.A. Susott, R.E. Babbitt, D.D. Wade, I. Bertschi, D.W.T. Griffith, and W.M. Hao, J. Geophys. Res. **104**, No. D23, 30109–30125 (1999).
42. J.R. Ziemke and S. Chandra, J. Geophys. Res. **104**, No. D17, 21425–21442 (1999).

0235-6880/01/02 93-09 $02.00