

COMPLEX INVESTIGATION OF OPTICAL-METEOROLOGICAL PARAMETERS OF THE ATMOSPHERE NEAR COLIMA VOLCANO (MEXICO). PART II. MOIST SEASON

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Some results of field measurements of incident UV radiation intensity, total and aerosol optical depth of the atmosphere, ozone concentration, sulfur gas and aerosol content in the surface atmospheric layer during the moist season of 1995 (from June to October) are presented. We studied the aerosol washout by tropical rains and its reconstruction after the rains. The multielement analysis of aerosol samples and rain precipitation has been carried out. The intensification of volcanic matter emission that occurred late in August and early in September has also been analyzed.

1. INTRODUCTION

The effect of volcano and volcanic eruptions on the physicochemical processes in the lower atmosphere during the moist season should obviously manifest itself first in the character of the precipitation formation and in chemical composition of the precipitation. The volcanic products under the conditions of enhanced humidity should favor formation of additional condensation nuclei and microdroplets: gaseous products of both sulfur gas and hydrochloric acid type will continuously adsorb on cloud droplets and participate in reactions inside these droplets. All this will change the microstructure of cloud formations and their stability. One can assume that this effect is similar to the effect of industrial centers in both the phase transformations of water and the processes of precipitation formation in the lower atmospheric layers.^{1,2}

Under these conditions, the most interesting process from the climatology viewpoint is the washout of the volcanic emission products by tropical rains, because this washout results in a sharp decrease in the aerosol number density and in concentration of the sulfur gas in the troposphere and noticeably changes optical properties of the troposphere decreasing, in particular, the absorption and scattering of radiation in the UV and visible spectral regions under clear sky conditions thus increasing the atmospheric transmittance.

The study of the washout processes near a volcano allows one to more accurately estimate chemical composition and emission intensity of aerosol particles generated directly by the volcano and the underlying surface into the troposphere and the conversion intensity of sulfur gas into sulfuric acid and sulfates. The abundant precipitation obviously can influence the

processes in the upper layers of the lithosphere, particularly, the intensity of volcanic matter emission, as well as possible motion of the surface layer of the lithosphere.

2. BRIEF CHARACTERIZATION OF METEOROLOGICAL CONDITIONS DURING THE MOIST SEASON

The moist season near the Fuego de Colima volcano usually begins in the late decade of May with the arrival of moist air masses from the equatorial and southern parts of the Pacific Ocean. The invasion of a more cold and moist oceanic air first causes a sharp local wind gusts in the surface atmospheric layer, strong dusting of the dried soil, and a noticeable decrease in the atmospheric transmittance. The first showers are characterized by high intensity and short duration, as well as by large size of droplets. Visual observations show that droplet size varies approximately between 3 and 7 mm. After precipitation, more often in the afternoon, evening, or even at night-time, or in the morning of the next day, the cloudless weather sets on, and the air temperature in the surface layer does not significantly decrease in comparison with the preceding days (near the Center for Atmospheric Studies the midday temperature is 30–35°C).

In the surface atmospheric layer, calm or weak wind along the direction of $225^\circ \pm 40^\circ$ is observed. The diurnal variations of wind direction in the surface layer sets in late June.

The relative humidity of the air in the day-time hours (by 17:00 LT) during the period to July usually does not exceed 70%, and the marked growth of relative humidity up to 85–90% is observed in the evening hours. This growth is faster in low lands and closer to the coast, and it is a little bit slower near the

volcano foot. Then the cumulus clouds intensely develop above the volcano and close to the coast of the Pacific Ocean, and these clouds overcast the sky totally by 20:00–21:00 LT.

Intensity and time of precipitation varied depending on the preceding cycle: the more intense and long was the preceding precipitation, the later the next rain began. Occasionally, this period lasted up to three days. In the middle of July, precipitation occurred most often and every day. Since the third decade of July the character of precipitation changed. With a noticeable decrease in the air temperature in the surface layer especially at night (down to +18°C), the intensity of cumulus cloudiness formation sharply decreased, and the intensity and frequency of precipitation also decreased. The mean size of droplets has also decreased noticeably. The droplet diameter was about 1.5–3 mm during some rains. Since late August rains were observed by series: several days with rain and gaps of 3–5 days to the following series. Then progressive air heating was observed up to 30°C and higher (in the city suburbs) during day-time. At nights, the air temperature in the city did not drop below 22°C. At the rancho Refuhio and even closer to the volcano foot, the air temperature at night was much lower (up to +15°C). Late in August intensification of the volcano activity was observed visually. In some days, weak short-term shocks were recorded (earthquakes of up to 2–3 mark on the Richter scale).

3. PRECIPITATION OBSERVATION

Precipitation was collected on the inclined surface of 2500 cm² with sink into a large glass bottle of twenty liters at two sites (rancho Refuhio and University Center for Atmospheric Studies) using the technique similar to that described in Ref. 3. The main data was obtained from samples collected at the rancho Refuhio. The glass bottle was changed weekly at 10:00–11:00 LT on Saturdays.

In the first series of measurements, great number of large hard particles was detected in the samples (fragments of plants, pieces of soil, insects). These things were removed from the surface of a paper filter, through which all samples of the rain water were filtered out. Some portion of the water was settled during a week, and the settled water without coarse-disperse suspension was filtered through a paper filter again. Paper filters were weighed before and after the exposure and dried. The difference between the weights allowed us to determine the concentration of both insoluble substance captured by droplets and the substance settled on the receiving platform due to the gravity. The latter part was mainly far less than the substance captured by droplets.

After being filtered, a portion of water was evaporated in porcelain cups to determine the soluble substance in the rainwater. The main part of this component was sulfuric acid. This, quite simple and reliable, technique allowed us to estimate the amount

of substance weighed and washed out from the troposphere (from the cloud and undercloud layers).

Figure 1 shows the time behavior of aerosol washing out from the troposphere (the total concentration of substance in water and the concentration of both soluble and insoluble components).

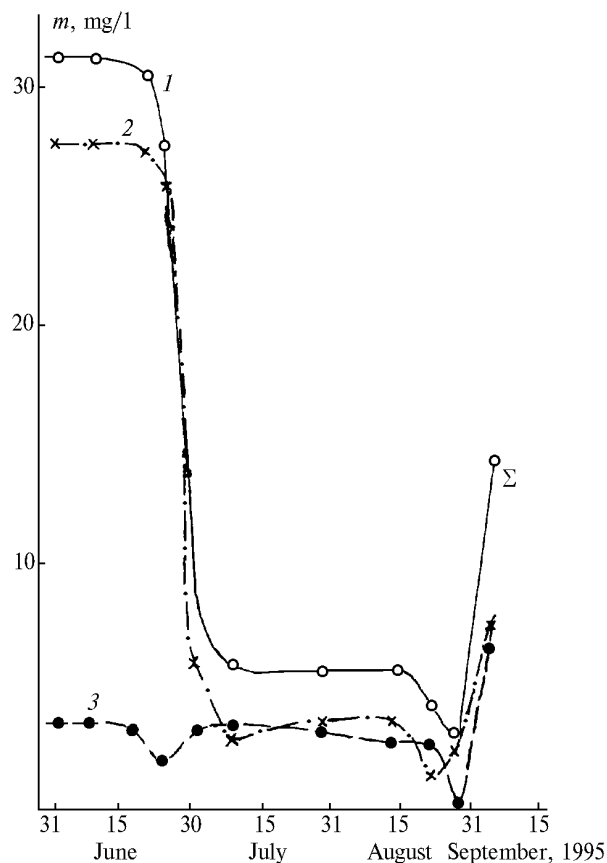


FIG. 1. Time behavior of aerosol washing out from the troposphere (rain water samples): total content of substances suspended in water (1), soluble substance (2), and insoluble substance (3).

The data on concentration of some chemical elements in the rain water samples (the total insoluble suspension, the suspension after settling of water during a week, and the substance in a test glass after long storage of the rain water sample) are presented in Tables I and II. The correspondence between all the data of the time dependence in Tables I and II is quite satisfactory. One can clearly see high degree of washing out of soluble substances in the first weeks of the moist season. Rather stable washing out of insoluble substances is also clearly seen. In August, some growth of the fraction of substance washed out from the troposphere is observed, what can be explained only by the growth of the dispersed matter emission into the troposphere.

During first weeks of the rain season, the amount of soluble substance in precipitation (mainly sulfuric

acid and sulfates) has reached the concentration of 400 mg/l. It approximately corresponds to the concentration in air of 400 $\mu\text{g}/\text{m}^3$ (at the liquid water content of 1 g/m^3). In the samples collected at the rancho Refuhio, these values were significantly less: 27 mg/l and 27 $\mu\text{g}/\text{m}^3$, respectively. These

amount of soluble substance captured by the rain water were observed in the precipitation even a month after the beginning of the rain season. Evidently, some overestimation of these values is possible due to oxidation of the sulfur gas in cloud droplets.

TABLE I. Concentration of the chemical elements in the samples of filtered rain water (Mexico, summer, 1995), in $\mu\text{g}/\text{l}$.

Sample No.	Collection date	Sample volume, ml	Concentration $C + \Delta C$ (the lower figure)												
			Al	Si	P	S	Cl	K	Ca						
1	27.05.-17.06	3.5	2000	23800	<5000	26900	2820	920	30600						
			1100	4400		2400	120	100	700						
2	17.06-24.06	3.5	5500	17700	<4000	11700	1840	790	32000						
			1300	1700		1700	200	230	6000						
3	24.06-1.07	23	2500	<1000	<2000	340200	-	130	37500						
			700			1600		60	500						
4	1.07-8.07	21.5	360	30900	<800	13300	730	130	5120						
			220	800		500	40	40	80						
5	8.07-15.07	23	630	31700	<900	14500	1260	270	8480						
			260	800		500	40	40	90						
6	15.07-22.07	22	810	7900	<1000	31200	1020	140	12370						
			370	600		600	40	50	110						
7	22.07-29.07	23	780	20500	<700	12900	740	320	5310						
			260	700		400	40	50	80						
8	29.07-5.08	22.5	500	17400	<1000	18200	9320	510	13070						
			380	800		600	80	50	110						
Sample No.	Concentration $C + \Delta C$ (the lower figure)														
	Ti	Cr	Mn	Fe	Ni	Cu	Zn	Ga	Se	Br	Rb	Sr	Y	Zr	Pb
1	<70	43	40	89	25	<10	730	<8	22	20	23	63	-	38	<10
		15	9	17	7		130		5	11	6	9		19	
2	<100	51	<20	90	19	<10	600	<8	7	21	29	49	-	<30	<20
		17		60	4		80		4	10	10	20			
3	<20	11	24	56	6	<3	3230	-	3	3	4	35	46	<5	17
		3	5	3	1		210		1	2	2	2	5		2
4	<20	<5	8	<6	5	<3	28	<1	4	4	<6	18	20	<6	3
			2		1		2		1	1		3	3		2
5	<20	<5	9	4	5	2	71	<1	2	2	12	13	11	<6	<3
			2	3	1	1	2		1	1	2	3	3		
6	<20	<6	6	<5	2	<3	25	<2	<2	2	6	13	6	<6	<3
			2		1		2			1	2	3	3		
7	<20	7	7	6	4	<3	12	<2	<2	3	3	10	9	4	2
		3	2	3	1		2			1	2	2	3	3	2
8	<20	8	8	16	6	4	217	<2	<2	18	<3	23	12	<5	<3
		2	2	3	1	2	3			2	2	2	2		

The insoluble aerosol substance was washed out most intense in the first two weeks of the rain season. The concentration of solid matter washed out during the first week reached 100 $\mu\text{g}/\text{m}^3$ in the troposphere, and for the largest particles ($d > 20 \mu\text{m}$) it was even 500 $\mu\text{g}/\text{m}^3$ provided that the geometrical depth of the washed out layer is 2 km. Two weeks after the beginning of the rain season, the amount of insoluble substance washed out by precipitation sharply decreased by an order of magnitude and even more, and then remained practically constant ($\approx 3.5 \text{ mg}/\text{l}$) by the end of August.

It follows from the data of multielement radiofluorescence analysis that the paper filter filtered only the most coarse-disperse insoluble fraction of aerosol particles. The main portion of aerosol substance remained in water. Washout of finely disperse particles containing Al, Si, Ca, Zn, Mn, Cr, and Fe decreased noticeably only in July, i.e., their concentration in air decreased. Practically, only Fe and, to a certain extent, Pb were efficiently filtered out by the paper filters, i.e., were mainly in the coarse-disperse fraction of insoluble aerosol particles. The sharp growth of their concentration in

precipitation samples in September should be pointed out separately.

As follows from the data of paper filter analysis, the concentration of S, Cl, Se, and Br is very low practically during all measurement period, whereas the multielement

analysis of rain water samples gives, for instance, that the sulfur concentration is about two orders of magnitude higher. Moreover, repeated sharp growths of sulfur concentration probably caused by sporadic emission of sulfur by Fuego de Colima volcano were observed.

TABLE II. Concentration of chemical elements in the samples of rain water collected in Mexico in May – October, 1995 (data of sediment analysis on filters).

Sample No.	Collection date Colima-city	Sample volume, l	Sediment mass, mg/l	Fraction	Concentration of the chemical elements in water, $\mu\text{g/l}$								
					Al	Si	P	S	Cl	K	Ca	Ti	
1	27.05 – 17.06	20		*	214	5600	<30	164	<1	72.5	140	42.6	
		20		**	9	11	8	<10	0.9	1.1	1.8	0.8	
2	17.06 – 24.06	20	19	*	26	253	11	21	3.7	4.4	6.6	1.2	
		14	1	**	31	46	17	<10	2.5	5.8	3.5	<0.8	
3	24.06 – 1.07	20		*	26	423	<10	11	2.0	5.5	9.8	1.5	
4	1.07 – 8.07	5.5	2	*	76	700	24	31	13.5	17	18.8	3.6	
		14	0.3	**	29	125	<10	<10	3.2	5.4	1.3	1.0	
5	8.07 – 15.07	19	3.3	*	50	1060	<10	27	<1	10.9	38	8.0	
		18		**	29	<20	<10	<10	1.3	1.4	2.3	<0.8	
6	15.07 – 22.07	1.15	18	*	390	730	120	410	43	55	290	13	
7	22.07 – 29.07	20.28		*	22	114	9	24	<1	2.1	40.5	4.2	
		20		**	18	14	9	11	1.6	2.4	0.7	0.6	
8	29.07 – 5.08	17.61		*	102	1451	<10	18	2.0	19.4	23.7	9.2	
9	3.09	1.17	13.7	*	350	<100	120	<100	<20	19	269	<10	
10	5.09	1.18	19.3	*	310	1820	<100	<200	82	34	360	17	
11	18.08 – 22.09	2.77	31.6	*	240	5240	<70	340	<8	42	347	48	
12	25.09	1.45	64.4	*	1010	10880	<100	<100	<10	132	2278	190	
13	2.10 – 3.10	4.79	19.1	*	160	6040	<70	183	<4	78	395	57	
Sample No.	Concentration of the chemical elements in water, $\mu\text{g/l}$												
	Cr	Mn	Fe	Ni	Cu	Zn	Ga	Se	Br	Rb	Sr	Zr	Pb
1	1.1	5.8	353.4	0.47	0.86	2.41	0.11	0.12	0.28	0.52	4.83	1.26	1.52
	1.0	0.8	2.3	0.71	0.22	0.08	0.21	0.32	0.25	0.16	<0.2	<0.2	0.61
2	0.3	<0.1	14.1	0.08	<0.08	2.24	0.05	0.11	0.06	0.09	0.26	0.27	0.23
	0.3	<0.2	2.0	0.26	<0.1	0.79	0.12	0.06	0.14	0.23	0.35	0.68	<0.1
3	0.2	0.3	16.6	0.16	0.08	1.02	0.07	0.08	0.10	0.28	<0.1	0.48	0.52
4	1.6	0.5	38.4	0.83	0.89	0.91	0.41	0.48	1.04	1.30	0.39	<0.7	1.72
	0.3	0.7	4.8	0.39	0.15	0.33	0.15	0.25	0.16	0.26	0.45	0.23	0.8
5	0.3	1.1	58.6	0.09	0.21	0.72	0.12	0.14	0.08	0.59	0.50	0.38	0.43
	0.4	0.2	0.7	0.13	0.22	0.38	0.19	0.14	0.22	0.14	0.27	<0.2	0.15
6	3.9	2.9	56	4.4	1.7	3.1	1.8	2.4	4.6	3.2	5.1	<3	3.6
7	0.7	1.4	33.4	0.58	1.01	1.70	<0.1	0.30	0.15	0.09	0.17	0.26	1.30
	0.2	<0.1	0.7	0.10	0.11	0.36	0.05	0.07	<0.08	0.36	0.31	1.64	0.14
8	0.4	0.8	67.6	0.27	0.08	0.81	0.09	0.11	0.27	0.24	0.50	0.17	0.66
9	<4	2.5	<4	1.0	<2	0.9	<1	<1	1.2	<2	5.5	<3	<2
10	6.0	4.0	47.5	<2	2.8	5.3	2.9	3.5	<2	3.2	2.9	<3	10.1
11	3.8	1.9	326.9	0.72	0.95	5.14	1.33	0.65	1.5	1.7	7.8	<1	3.2
12	16.5	20.1	1227	4.7	5.6	12.0	4.5	3.4	<2	2.2	24.1	<3	7.7
13	1.4	5.2	414.4	0.42	0.88	1.40	0.62	0.99	1.07	1.07	6.4	1.3	1.4

* sediment

** suspension

Time dependence $C(t)$ of sulfur concentration in water samples is quite different from the dependence $C(t)$ for other elements. Thus, the decrease of sulfur concentration in samples is accompanied by the growth

of silicon concentration. It should be also noted that very high calcium concentration in samples is closely comparable to concentration of sulfur and silicon. It corresponds, while not completely, to the popular

opinion that calcium is contained basically in the most coarse-disperse particles of the soil origin.^{4,5}

4. AEROSOL MEASUREMENTS

The measurements of the particle number density and dispersion were made with the photoelectric counter A3-5M in several measurement series from May to June, July, and from August to September during ten days (on the average) on the roof of the Center for Atmospheric Studies building (under the tarpaulin 120 cm above the roof surface level and about 5 m above the ground surface).

The measurements were carried out repeatedly during a rain. Various types of washout of aerosol particles in the surface layer were observed depending on the precipitation character. Washout was selective similar to that mentioned in Ref. 6. Particles of the size $d \geq 4 \mu\text{m}$ were washed out most efficiently. However, unexpectedly, restoration of their number density up to a certain level was also very fast. The only reason for this could be the activity of the Fuego de Colima volcano. Probably, a portion of the volcanic aerosol matter was emitted in the atmosphere above the cloud level, and in the absence of clouds it diffused and settled in the lower layers.

The variety of conditions of washout and reconstruction of the size spectrum of aerosol does not allow us to make unambiguous conclusions about the washout efficiency for particles of different size based on the experimental data obtained. Therefore, the data were simply averaged over the particle size spectra for three measurement series: the first series yielded 192 spectra obtained from May to June, the second one - 264 spectra from July to August, and the third series (from August to September) yielded 216 spectra. The data on obviously abnormal particle size spectra were excluded from this analysis.

Table III and Fig. 2 show the data on size-distribution of particle volumes $\Delta V/\Delta r$ (in $\mu\text{m}^2/\text{m}^3$). It was an unexpected fact that the particle number density in the range $0.6 \leq d \leq 1.0 \mu\text{m}$ grew up during the third measurement series (from August to September). It confirms definitely the growth of intensity of the volcanic matter emission in August - September. Since August 28 a sharp growth of the number density of aerosol particles in the size range $0.6 \leq d \leq 7.0 \mu\text{m}$ was recorded by the photoelectric counter. These fluctuations of particle number density lasted during some hours, then the particle distributions over size came back to those close to the initial ones.

The analysis of similar fluctuations has allowed us to conclude that these fluctuations have some common features in the evolution. As the beginning of these fluctuations we took the essential excess of the particle number density values in the size range $0.6 \leq d \leq 1.0 \mu\text{m}$ over the mean values. After that the results of seven clearly observed cases from August 28 to September 3 were averaged $[\Delta V(r) - \bar{\Delta V}(r)]$ (in $\mu\text{m}^3/\text{m}^3$). The time evolution of these spectra was

considered during the period from two hours before the fluctuation beginning and to six hours after the beginning (Table IV).

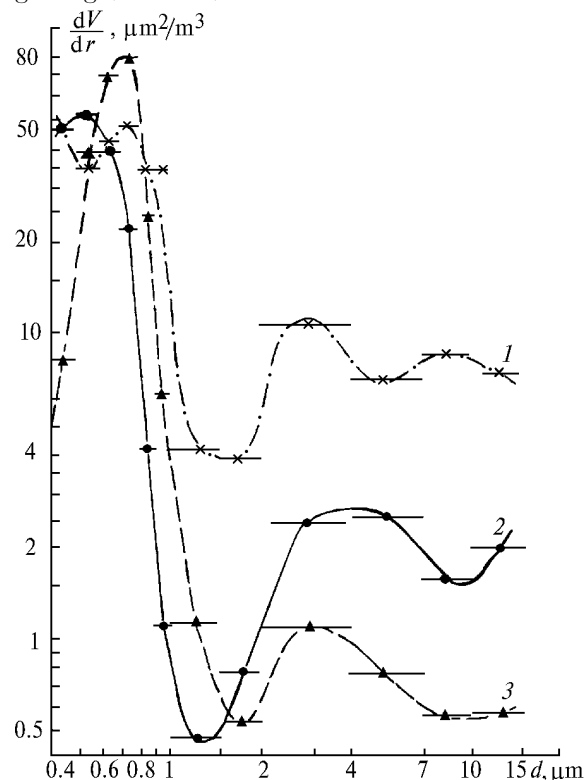


FIG. 2. Average distributions of particle volume over size $\Delta V/\Delta r$ (in $\mu\text{m}^2/\text{m}^3$) for three series of measurements in 1995: 20 of May - 24 of June (1), 3 of July - 14 of August (2), and 26 of August - 7 of September (3).

One can see from Table IV that a marked growth of the particle number density in the size ranges $0.9 \leq d \leq 1.0 \mu\text{m}$ and $2.0 \leq d \leq 4.0 \mu\text{m}$ is observed already two hours before the fluctuation beginning. The most noticeable growth of the particle number density in the size range $d \leq 1.0 \mu\text{m}$ is observed after the beginning. The decrease of number density down to the mean values and even lower takes place four hours after the beginning for particles with $d > (1.5-2.0) \mu\text{m}$. At the same time, for every case the pattern can significantly differ from the mean pattern, especially depending on the case intensity, however the common pattern corresponds to that presented in Table IV. Figure 3 shows the spectra $\Delta V(r)$ (in $\mu\text{m}^3/\text{m}^3$) for $t = 0, +1, \text{ and } 3-4$ hours.

The strongest spectrum changes are observed in the size range $1.0 \leq d \leq 3.0 \mu\text{m}$. This spectrum deformation obviously can be rather reliably recorded both with the photoelectric counter and other optical methods, for example, by the aerosol scattering and attenuation in the near IR spectral range ($\lambda = 1.0 - 3.0 \mu\text{m}$).

The data of the multielement analysis of aerosol samples in the moist season (Tables V and VI) testify to a rather stable multielement structure of aerosol particles. By the degree of correlation in temporal

behavior of the total content of chemical elements in the aerosol state, we can distinguish separate groups of chemical elements: (I) Si, Al, Cl, K, Ca, Ti, V, Cr, Mn, Ni, Zn, Rb, Sr, S and (II) Fe, Cu, and Zr. Such

elements as Pb, Br, and W are close in temporal variation, while the behaviors of Ga, Se, and P (particularly, because of high errors of estimation) are not close to any other.

TABLE III. Diurnal behavior of volume density of the aerosol particle distribution over size $\Delta V/\Delta r$ (in $\mu\text{m}^2/\text{m}^3$) in the surface layer for three measurement series (Colima city, Center for Atmospheric Studies).

d , μm	Time, hour											
	01 - 02	03 - 04	05 - 06	07 - 08	09 - 10	11 - 12	13 - 14	15 - 16	17 - 18	19 - 20	21 - 22	23 - 24
10 - 15	6.24	5.10	8.03	11.0	9.68	10.4	11.9	9.57	9.13	4.62	3.99	4.72
	2.64	1.54	1.19	2.20	2.33	1.86	1.46	1.92	1.81	1.74	2.82	1.76
	0.22	0.044	0.15	0.53	0.92	1.34	0.93	0.77	0.64	0.55	0.46	0.37
7 - 10	4.60	2.68	3.64	5.16	6.84	7.15	7.09	8.52	6.27	9.14	22.0	16.9
	0.88	0.85	0.83	1.40	1.74	1.24	1.09	1.29	1.20	1.76	3.20	2.84
	0.28	0.15	0.22	0.44	0.74	0.69	0.90	0.95	0.78	0.37	0.56	0.47
4 - 7	4.10	3.56	5.17	8.16	7.76	9.84	10.1	8.34	5.43	6.72	11.6	10.1
	2.02	1.84	1.77	4.08	2.53	2.18	1.73	1.98	1.72	1.45	5.03	2.72
	0.65	0.31	0.31	0.57	1.13	1.05	0.94	0.91	0.76	0.82	0.92	0.84
2 - 4	4.10	3.54	28.4	40.4	7.47	6.48	6.30	7.26	5.42	6.04	5.76	4.63
	2.19	2.10	1.38	2.68	3.03	2.86	2.45	2.20	2.10	2.24	2.97	3.19
	0.72	0.60	0.58	0.85	1.84	1.51	1.79	1.36	0.91	1.03	0.90	0.81
1.5 - 2	2.01	1.83	1.05	2.08	2.96	3.32	9.88	5.62	4.72	2.88	5.19	5.46
	0.54	0.32	0.56	1.45	0.86	0.60	0.79	0.66	0.71	0.73	1.14	0.84
	0.34	0.23	0.22	0.47	1.07	0.65	0.81	0.58	0.49	0.47	0.43	0.42
1.0 - 1.5	0.86	0.70	0.55	0.68	0.98	8.82	24.7	7.03	2.48	1.86	0.83	0.56
	0.40	0.40	0.42	0.57	0.46	0.49	0.43	0.41	0.34	0.35	0.93	0.39
	0.92	0.77	0.66	0.29	0.35	0.59	3.32	2.66	0.98	0.93	1.25	1.10
0.9 - 1.0	1.83	2.19	3.78	3.74	6.04	46.2	164	129	19.0	10.6	16.6	9.97
	0.64	0.28	0.32	0.70	0.80	1.65	1.82	1.28	1.29	1.33	1.01	2.07
	7.18	9.66	10.8	6.58	1.38	3.68	6.62	9.20	9.35	1.74	4.14	5.48
0.8 - 0.9	3.35	3.60	9.79	5.95	10.7	45.8	141	106	30.4	10.4	2.78	37.9
	0.83	0.70	1.10	0.99	7.96	10.2	13.7	5.18	1.60	1.47	1.74	4.12
	11.2	12.5	13.7	13.6	12.8	33.8	91.6	60.8	26.2	2.58	7.68	9.90
0.7 - 0.8	6.66	9.12	17.0	38.6	10.7	45.8	157	170	67.0	0.48	1.96	36.7
	1.98	2.11	2.24	2.53	28.6	56.2	45.0	26.1	39.0	28.8	49.8	5.55
	84.9	70.4	59.4	40.0	49.3	74.0	87.4	88.6	90.0	95.9	112	97.7
0.6 - 0.7	18.6	40.6	37.6	55.0	43.6	59.0	109	62.8	30.4	6.18	5.94	37.8
	5.12	7.89	24.1	18.0	61.8	52.8	57.0	65.2	55.4	53.4	44.6	19.5
	72.3	70.8	72.0	66.8	74.4	66.4	55.0	57.6	62.2	67.2	75.3	73.8
0.5 - 0.6	51.2	39.9	32.9	38.2	53.5	63.6	27.6	11.8	12.0	21.2	27.6	37.8
	23.2	34.2	47.4	73.4	49.0	41.8	49.4	58.5	46.5	45.3	73.8	67.6
	37.8	43.0	45.2	52.1	27.4	25.8	24.4	43.2	54.2	31.5	30.2	33.5
0.4 - 0.5	50.2	37.0	27.5	19.6	62.6	58.5	0.05	12.9	62.0	92.6	83.0	56.2
	78.0	78.4	79.0	60.2	17.4	23.9	27.8	24.2	32.7	47.8	33.7	59.0
	7.70	8.75	10.4	11.8	16.0	5.10	4.80	7.75	11.0	3.80	4.50	6.05

Note: The first row shows mean values over the measurement series during May - June 1995; the second row corresponds to the measurement values during July - early August, and third row shows the measurement values in late August - September.

Calculations of the correlation coefficients for the dependence of concentration of some species and between species for the whole data array during dry and moist seasons (from December 1994 to October 1995) for both aerosol samples and the precipitation samples show that practically all species contained in aerosol particles are mainly of the volcanic origin. At the same time, the multielement structure of aerosols

emitted by the Popocatepetl volcano differs somewhat from the structure of particles emitted by the Fuego de Colima volcano. The most close correspondence between the multielement structure of the rain and aerosol samples was observed at the beginning of the period of tropical rains, that testifies to good washing out of aerosol substance of the volcanic origin.

TABLE IV. Variations of volume concentration of aerosol particles of different size $\Delta V(r) - \Delta \bar{V}(r)$ during the period of fluctuation (averaging over seven cases) (in $\mu\text{m}^3/\text{m}^3$).

Size range, $\Delta d, \mu\text{m}$	Time from the beginning Δt , hour									
	-2	-1	0	+1	+2	+3	+4	+5	+6	
0.4 - 0.5	+0.12	+0.04	-0.10	-0.16	-0.30	-0.20	-0.32	-0.30	-0.28	
0.5 - 0.6	+0.75	+0.06	-0.43	-1.0	-1.4	-1.0	-1.5	-1.1	-0.38	
0.6 - 0.7	-0.70	0	+1.0	0	+44	+0.34	0	+1.7	+1.0	
0.7 - 0.8	-0.80	0	+1.2	0	+52	+0.40	0	+0.8	+1.2	
0.8 - 0.9	-0.50	-0.50	+0.12	+6.0	+7.5	+7.2	+14	+11	+6.5	
0.9 - 1.0	+0.65	+0.48	+1.3	+14	+8.5	+2.0	+1.8	+6.5	+5.4	
1.0 - 1.5	-0.18	-0.22	-0.14	+20	+27	+3.0	+2.0	+10	-0.15	
1.5 - 2.0	+0.08	-0.02	0	+1.4	+4.5	+0.80	+0.06	+1.2	-0.08	
2.0 - 4.0	+0.43	0	+0.54	+0.43	+0.43	+1.0	+0.11	+0.11	-0.43	
4.0 - 7.0	+0.20	0	+0.25	+0.20	+0.20	+0.47	+0.06	-0.03	-0.18	
7.0 - 10.0	+0.18	+0.04	+0.08	+0.10	-0.15	-0.03	-0.06	-0.03	-0.18	
>10	+0.11	+0.07	+0.04	-0.03	-0.16	-0.03	-0.14	-0.13	-0.12	

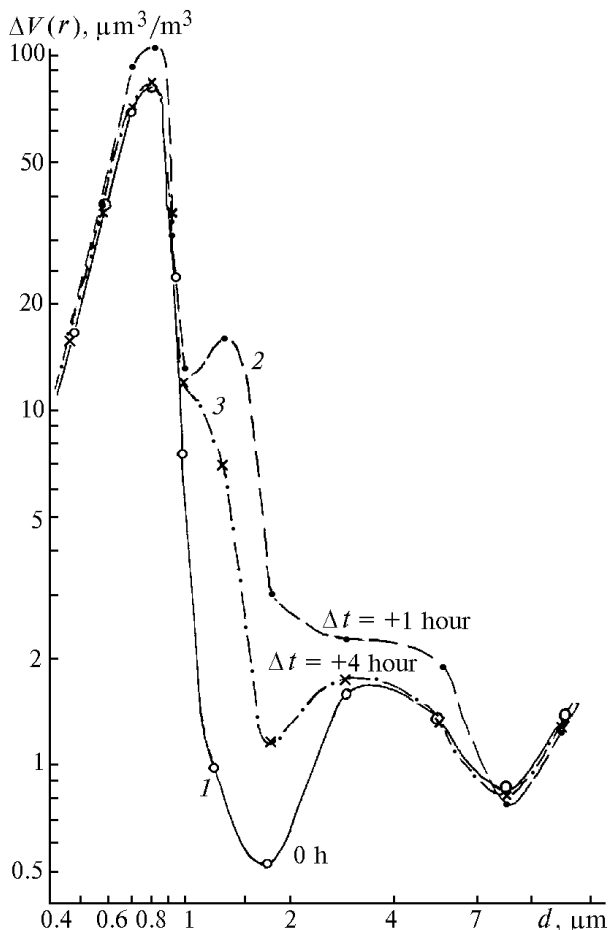


FIG. 3. Average spectra of aerosol volume concentration $\Delta V(r)$ (in $\mu\text{m}^3/\text{m}^3$) during the fluctuation of volcanic matter emission: the initial moment ($t = 0$) (1), one hour later ($t = +1$ hour) (2), and 3 - 4 hours later ($t = 3 - 4$ hours) (3).

TABLE V. Concentration of chemical elements in the atmospheric samples of the near-ground aerosols during the moist season, ng/m^3 (Colima city, University Center for Atmospheric Studies, August to October of 1995).

Species	Date of sample collection						
	28.08	29.08	30.08	31.08	1.09	2.09	12.10
	-	-	-	-	-	-	-
Al	1200	2300	3800	2600	300	1900	8200
Si	9800	9700	25500	6300	15500	1400	100300
P	200	<400	800	2200	1200	700	<600
S	40800	21500	38400	14800	18900	4400	70600
Cl	200	400	1200	1100	3100	800	4600
K	680	1660	1940	1690	1920	860	2610
Ca	1270	1720	3680	920	3440	230	8690
Ti	98	124	167	227	380	72	590
V	45	50	117	45	112	26	72
Cr	4	9	<20	23	37	13	31
Mn	26	20	<10	8	30	6	69
Fe	930	6470	2310	1210	1970	260	4780
Ni	5	3	14	9	27	8	15
Cu	6	8	<8	<5	<9	27	62
Zn	18	29	47	28	29	8	58
Ga	1	<2	<4	<2	<5	2	5
Se	<2	<2	3	<3	<7	<2	6
Br	14	19	8	22	14	2	48
Rb	70	9	54	5	24	14	37
Sr	21	15	42	5	62	17	90
Zr	24	51	70	27	294	81	54
W	<7	<3	-	<10	<20	14	<7
Pb	66	104	41	41	981	237	88

Note: The statistical measurement error for different species is equal to 5 - 50%, on the average.

TABLE VI. Average distribution of chemical element content in different layers of the cascade filter for the moist season in per cent (near Colima city).

Chemical elements	Layer		
	1st	2nd	3rd
Si	85	4	11
Ca	82	6	12
Fe	81	4	15
Ga	86	–	14
Cl	78	7	15
Al	68	10	22
Zn	53	13	34
K	52	18	30
Sr	66	21	13
Zr	68	25	7
Ti	48	27	25
Br	45	40	15
S	36	18	46
Pb	36	34	30
V	29	26	45
Ni	25	42	33
Cu	26	13	61
Rb	9	47	44
W	–	60	40
Se	–	71	29
P	23	60	17
Cr	11	59	30
Mn	21	47	32

The species can be divided into the following groups according to the content of the species analyzed in the particles of different sizes: (1) Si, Al, Cl, K, Ca, Fe, Zn, Ga, Sr, and Zr are contained basically in the largest aerosol particles (first layer of the cascade filter), (2) S, Ti, V, Ni, Br, and Pb are rather uniformly distributed over particles of different size, (3) Cu, Rb, and W are contained basically in the finest particles, and (4) P, Cr, Mn, and Se are contained mainly in particles of the medium size range $0.8 \leq d \leq 2.5 \mu\text{m}$. It is also possible to separate out the species distributed with a gap in the medium part of the size spectrum. Those are Al, Cl, K, Fe, Cu, Zn, and Ga.

The analysis of temporal variability of the species groups and their content in the particles of different size testifies to the differences in the transition of species into the aerosol state. Almost all species contained mainly in large particles (Si, Al, Cl, K, Ca, Zn, and Sr) enter into the first group, except for Fe, Ga, and Zr. These latter species, in their behavior, form the common group with Cu detected mainly in fine particles. The first group includes also the following species: (1) W is contained mainly in the fine particles, (2) S, V, Ti, and Ni are rather uniformly distributed, (3) Cr and Mn are contained in particles of the medium size, and (4) Al, Cl, K, and Zn are distributed with the gap in the medium part of the size spectrum.

The analysis of data on the species content in particles of different size during the fluctuations of the volcanic matter emission from late August to early September and after the earthquake allowed us to reveal some features in the process of transition of

different species into the aerosol state. At the initial stage of intensifying of the volcanic matter emission, there are both the growth of S, Ti, Ni, Se, Zn, and Pb content in largest particles (integration of aerosol particles) and the growth of the portion of fine particles for species Si, Mn, Fe, and Rb, as well as Cu, Se, and K. As the emission intensifies, the growth of the portion of both large and fine particles (U-shaped distribution) is observed for Ca, Br, P, and Pb species.

After long intensification of the volcanic matter emission, the growth of the portion of fine particles containing Al, Cl, Cr, Mn, Cu, Br, and Sr is observed. The growth of the content of large particles containing K, Ca, Ti, Cr, Mn, Fe, Se, Rb, Sr, and Pb is obviously connected with the strong shifts of the surface layer of the lithosphere (earthquakes and shocks caused by volcanic eruptions).

By the behavior of the size spectrum variation for particles containing some species, it is possible to separate out four groups of species: (1) Si, Ti, Cr, Ni, Zn, and Sr, (2) Al, Cl, V, and Ga, (3) Fe, Cu, and Zr, and (4) K, Ca, and Mn. Figure 4 shows typical curves of temporal transformation of the content of these species groups for particles of different size at the volcanic matter emission.

Obviously, additional observations are needed to make a more thorough interpretation of these results. It is desirable to carry out such observations at closer distances to the volcano crater, as well as in different atmospheric layers.

5. MEASUREMENTS OF OZONE AND SULFUR GAS CONCENTRATION

The systematic measurements of ozone during June–September of 1995 were carried out on the roof of the Center for Atmospheric Studies. The diurnal behavior of ozone concentration in the surface layer for all months was rather similar (Fig. 5). In June–July the morning growth of ozone concentration was observed in earlier hours, than in the consequent months. The highest values of the ozone concentration, exceeding $350\text{--}400 \mu\text{g}/\text{m}^3$, were recorded in the midday hours in July. Some fluctuations of the ozone concentration usually coincide with the appearance of cloudiness and shower precipitation. The small secondary maximum of the ozone concentration was recorded frequently in hours before dawn (3:00–5:00 LT).

We failed to reveal the dependence of ozone concentration on concentration of aerosols similar to that reported in Ref. 7. However, on some days noticeable deviations from standard curves of diurnal behavior of ozone concentration were observed, first in late August. Probably, they are caused by the intensification of the Fuego de Colima volcano activity. Thus, on August 28 a sharp decrease of the surface ozone concentration in day-time hours was observed. To a lower degree, this decrease was observed also on August 29. The values of the ozone concentration fell down to $30\text{--}60 \mu\text{g}/\text{m}^3$ instead of characteristic values of $250\text{--}300 \mu\text{g}/\text{m}^3$.

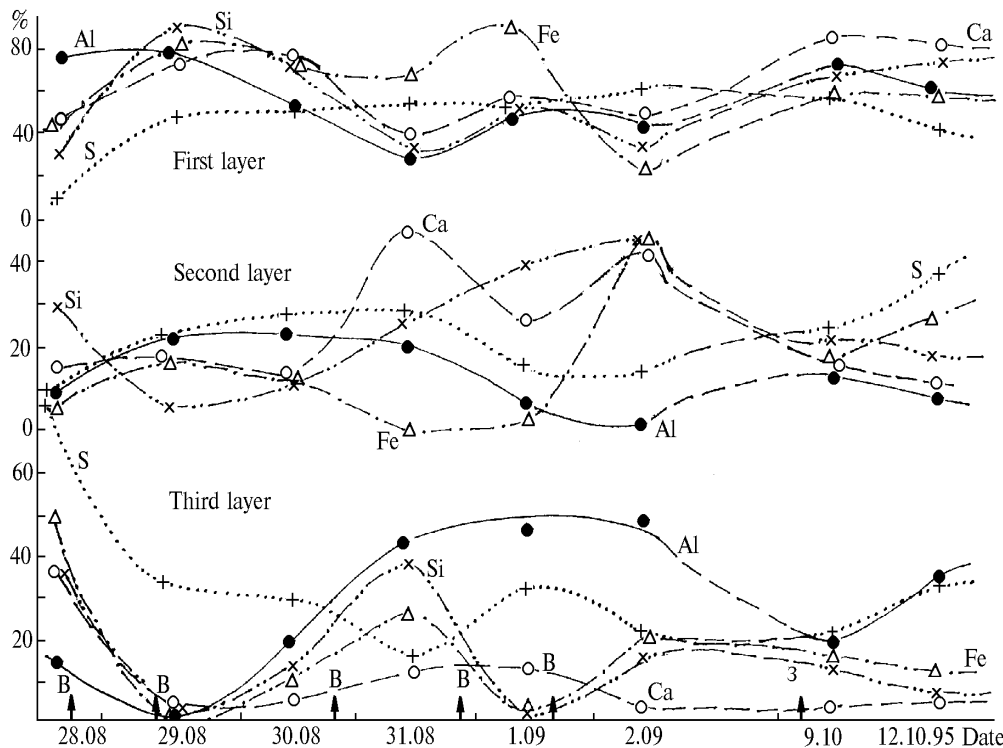


FIG. 4. Curves of temporal transformation of content of some groups of species in particles of different size during the intensification period of the volcanic matter emission.

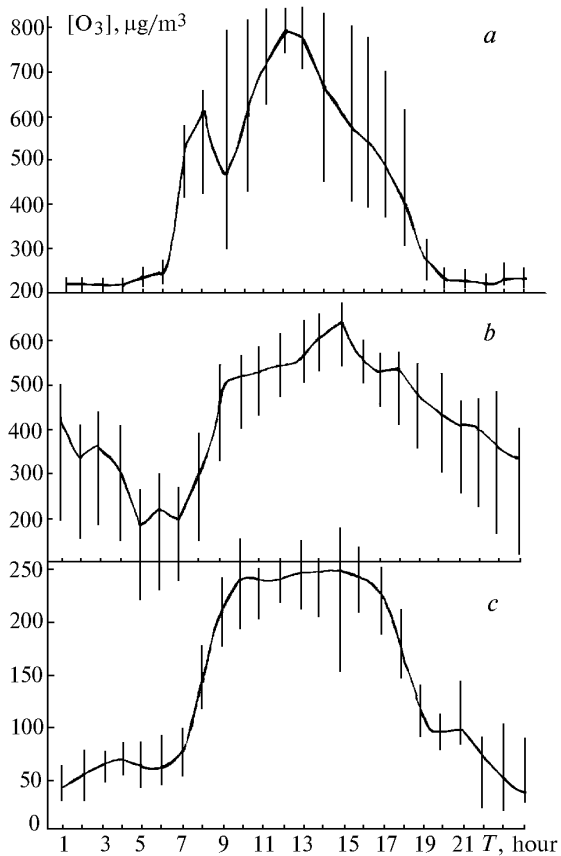


FIG. 5. Characteristic and average diurnal behavior of ozone concentration in the surface layer: July (a), August (b), and September of 1995 (c).

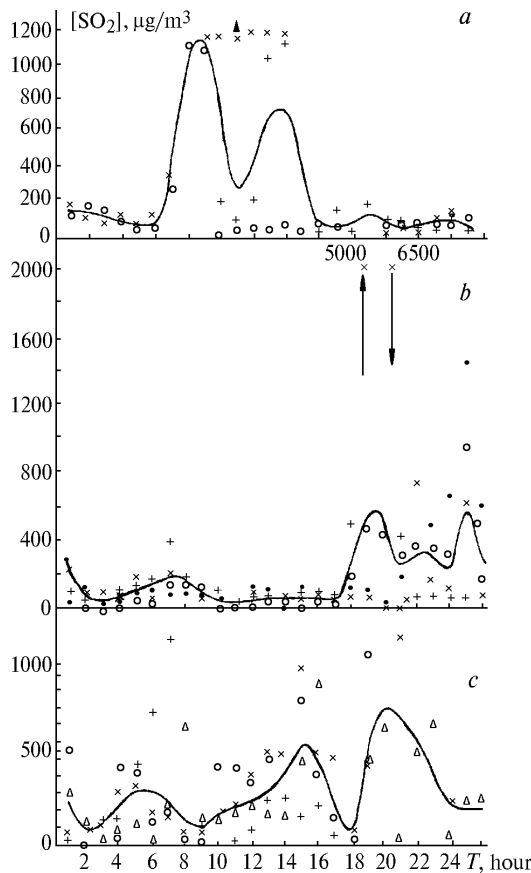


FIG. 6. Average diurnal behavior of sulfur gas concentration in the surface layer: July (a), August (b), and September of 1995 (c).

No marked diurnal behavior of sulfur gas concentration was observed in the surface layer (Fig. 6). However, some characteristics of sulfur gas behavior can be noticed:

- 1) the relative increase of sulfur gas concentration in the surface layer in the morning (6:00–8:00 LT) and evening hours (18:00–20:00 LT) is observed almost always;
- 2) in September, during almost all days when the observation was carried out, the rise of sulfur gas concentration in the afternoon hours (13:00–16:00 LT) was also recorded;
- 3) for some days (July 22 to 24) the curves of diurnal behavior similar to the curves for ozone were observed;
- 4) some abnormally high peaks of sulfur gas concentration were recorded from late August to early September, and no temporal variation in their appearance was detected.

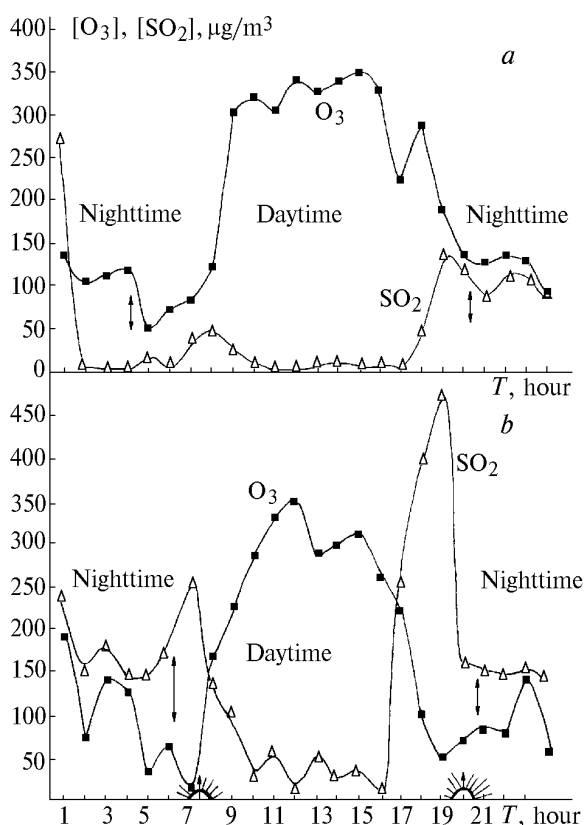


FIG. 7. Comparison of diurnal behaviors of the ozone and sulfur gas concentration in the surface layer (characteristic cases): August 30 (a), August 31 1995 (b).

We tried to find the correlation between the ozone and sulfur gas behavior. For some days it was observed quite clearly (Fig. 7). The growth of sulfur gas concentration in day-time hours was usually accompanied by a decrease of the surface ozone concentration. In night-time hours, the behaviors of the ozone and sulfur gas were similar. Most likely, it

is explained by interaction of two processes: (1) photochemical process of ozone formation and destruction and (2) process of vertical mass exchange (convection and turbulent diffusion).

Analysis of the correlation in surface concentration of sulfur gas and aerosols did not reveal a clear picture. At least, the growth of one component concentration is not accompanied by a growth of the other component concentration at the same time. However, during a day, i.e., with a delay by several hours, this effect was observed almost always. The difference in time between growth of one component concentration and consequent growth of other component concentration can reach 6–7 hours. And, what seems of great interest for interpretation of this dependence, the increase in aerosol concentration usually came before an increase in the sulfur gas concentration. It is especially clearly seen for the cases of sharp growth of the volcanic matter emission in late August to early September. The number density of particles in the size range $1.5 \leq d \leq 4.0 \mu\text{m}$ increases first, then the number density of finer particles, with $0.6 \leq d \leq 1.5 \mu\text{m}$, increases later on the number density of particles in a wide size range $0.6 \leq d \leq 7 \mu\text{m}$ increases, and only after that a sharp growth of sulfur gas concentration is observed. Since all the measurements were carried out at the distance about 40 km from the volcano, correct and certain interpretation of the observed phenomenon is difficult nowadays.

6. OPTICAL MEASUREMENTS

In the season of rains, measurements of UV solar radiation by the Epply piranometer and determination of the atmospheric optical depth were rather difficult. Obviously, measurement results may be, in particularly, distorted by rain droplets falling onto the hemispheric surface of the instrument housing. Additional errors also appear in calculations of optical depths because of inaccurate account for molecular and aerosol components, i.e., because of the neglect of real vertical profiles of gas density and temperature, influence of the multiple scattering in clouds, and peculiarities of the ray geometry when passing through the broken cumulus cloudiness.⁸ Thus, the calculated residual (aerosol) atmospheric optical depth may take negative values, and the measured intensity of the global radiation may exceed the model values obtained for cloudless days. In some cases, the values of optical characteristics even cannot be calculated. As an example, we can present the values of intensity and optical depth obtained on August 1 and 11 (Figs. 8 and 9). It should be noted that the optical characteristics were relatively more stable in the beginning of the rain season (Fig. 10).

The results presented in these figures, as well as those obtained for other days under relatively stable conditions show that a rather strong washing out of aerosols from the atmosphere took place as compared to the period from May till the middle of June.

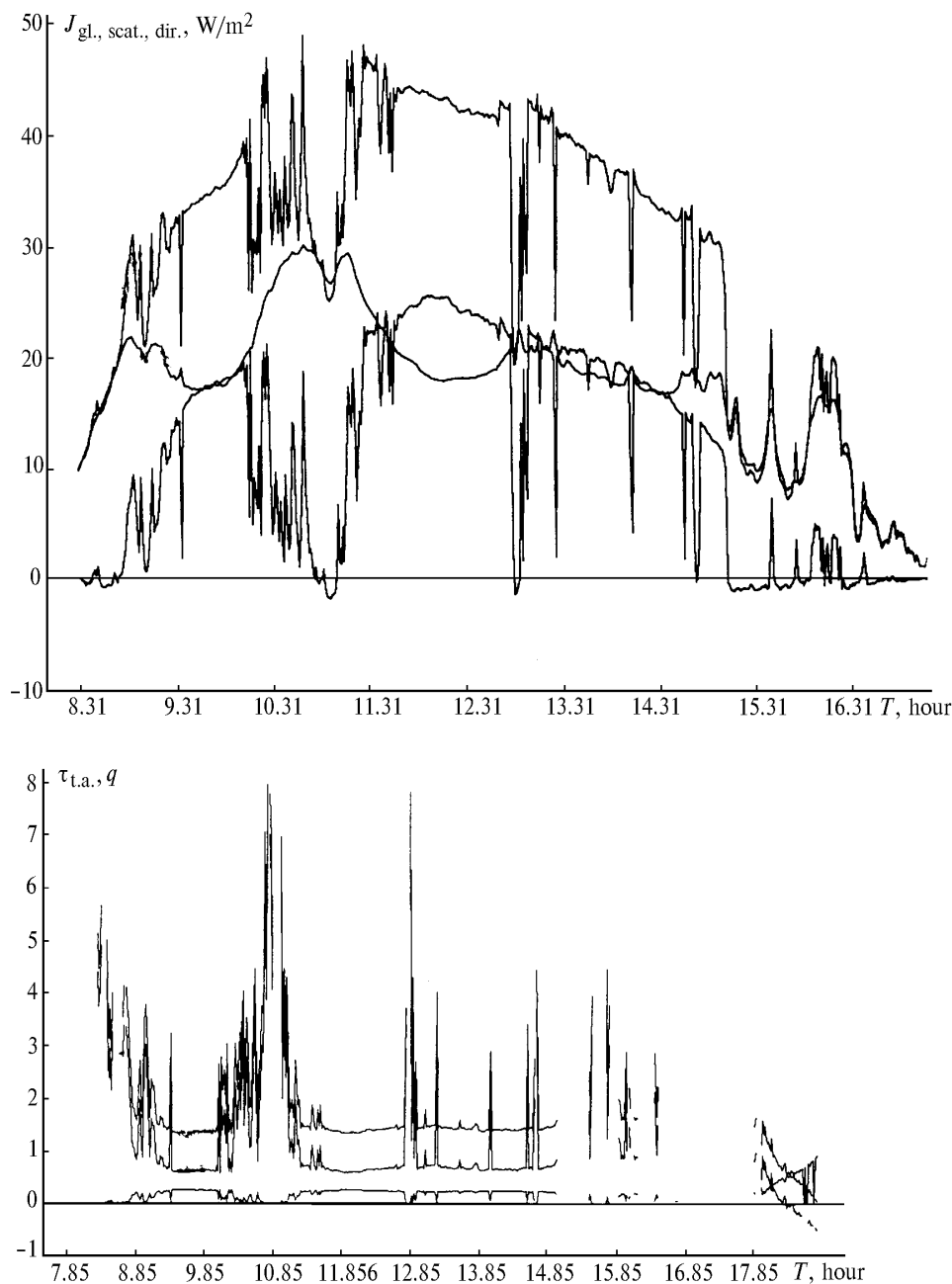


FIG. 8. Diurnal behavior of solar radiation intensity: the global intensity ($J_{gl.}$), the scattered radiation intensity ($J_{scat.}$), direct radiation intensity ($J_{dir.}$); and diurnal behavior of the atmospheric optical depth: τ_t (total), τ_a (aerosol), and C (atmospheric transmittance) (August 1 of 1995).

At the same time, we should obviously assume that a significant portion of the volcanic matter, particularly, sulfur gas and the finely dispersed aerosols, enter the atmosphere above the cloud layer, and they are poorly washed out by clouds and precipitation. This also corresponds to data of microphysical measurements, in which no decrease in the number density of aerosol particles with $d \leq 0.8 \mu m$ is observed, and moreover their noticeable increase is observed from late August to early September.

The essential difference in temporal behavior of the optical characteristics of the atmosphere under overcast and broken cloudiness conditions is of a certain interest.

In the case of broken cloudiness, the observed intensity of UV radiation and the corresponding optical depth vary extremely widely toward both large and small values. Obviously, the reason for this not quite usual phenomenon should be studied separately.

We have observed close relation of variations of these characteristics at the synchronous measurements of UV radiation and the surface ozone concentration. The decrease of UV radiation intensity practically immediately caused the decrease of ozone concentration and, accordingly, the increase of UV radiation intensity caused the increase of the surface ozone concentration (Fig. 11). However, this dependence was not linear.

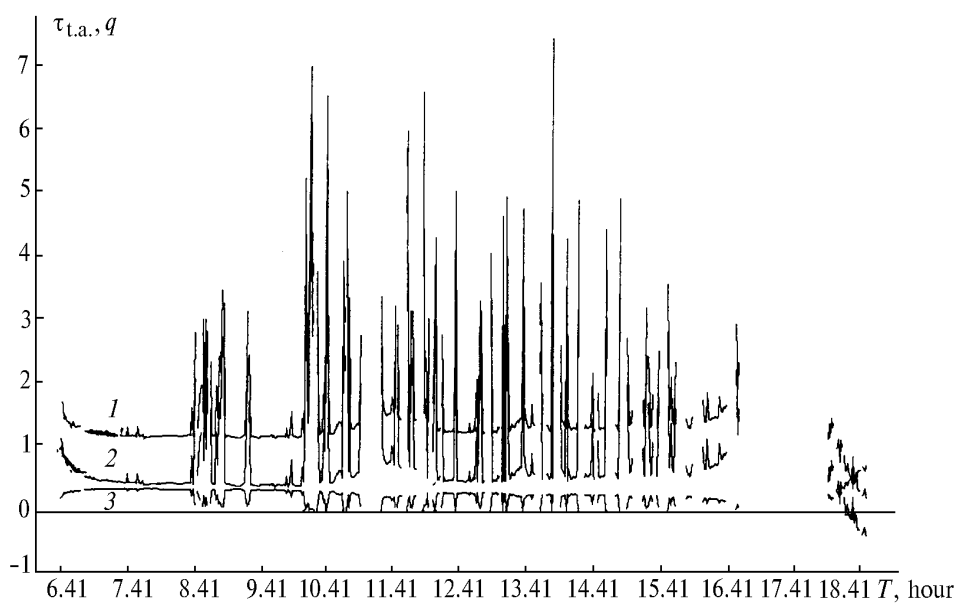
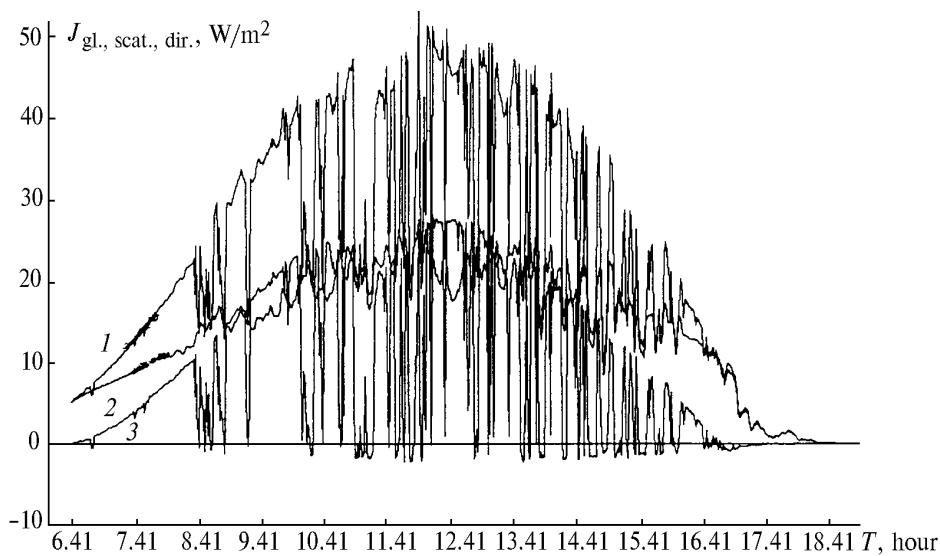


FIG. 9. The same as in Fig. 8, but for August 11, 1995.

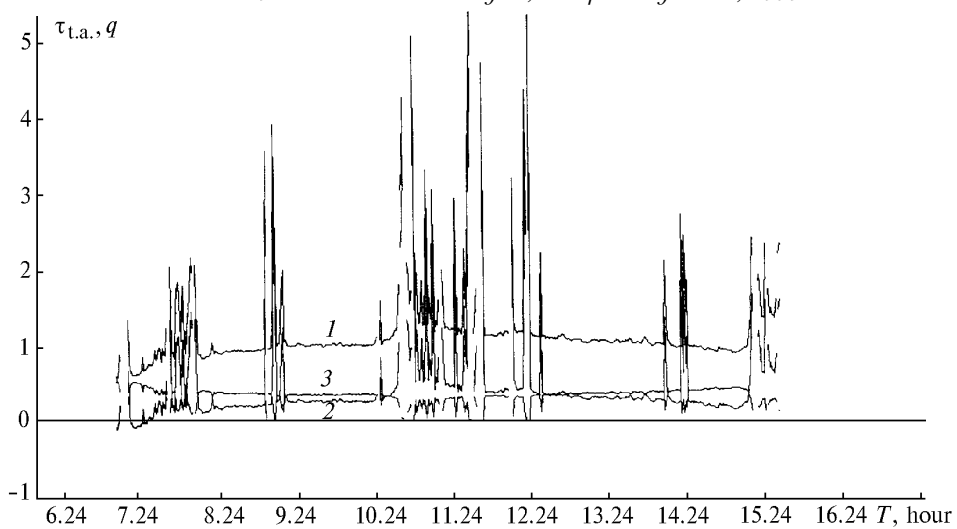


FIG. 10. Diurnal behavior of the atmospheric optical parameters τ_t , τ_a , and C (July 3, 1995).

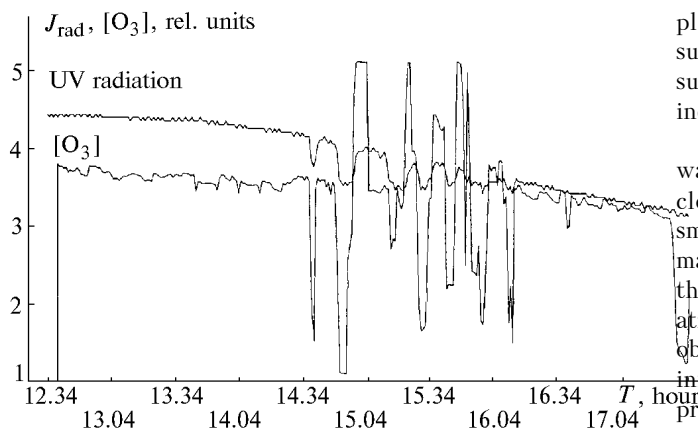


FIG. 11. Correlation between the ozone concentration and intensity of UV radiation in the surface layer (synchronous measurements).

Measurements of UV radiation with high spectral resolution are necessary for unambiguous interpretation of this dependence. In this case, the question arises on the nature of variations of the UV radiation intensity. In particular, those may likely be caused by spatial discontinuity of the stratospheric ozone field. Then it is completely obvious that stratospheric ozone minima (ozone holes) above certain places on the Earth surface will stimulate generation of the surface ozone.

Another possible reason for these intensity variations of the incident UV radiation may be the sulfur gas clouds in the troposphere (sulfur has the absorption bands in spectral range used in this study). Although this version seems less realistic, it well explains the phenomenon of invisible cloud formations having sharply outlined boundaries (of the jet stream type).

7. CONCLUSION

The analysis of results obtained in the dry and rain seasons testify to the determining role of the Fuego de Colima volcano in existence of unusual optical-meteorological phenomena in the lower atmospheric layers nearby this volcano. A number of these phenomena are connected with the significant emission of the volcanic matter, first of all, sulfur gas and aerosols, to the atmosphere. In the rain season, these components actively participate in physical-chemical processes in the troposphere. The presence of chemical compounds actively participating in photocatalytic reactions in the aerosol substance, as well as the increased intensity of UV solar radiation as compared to the midlatitudes favors these processes.

Inhomogeneities of the underlying surface and their different albedo in the visible spectral range favor the active air exchange in the vertical direction and, particularly, formation of cumulus clouds.

Significant part of the chemical transformations of the volcanic gaseous and aerosol substances takes

place in clouds. High concentrations of various substances, first of all of soluble ones: sulfuric acid, sulfates, and chlorides in precipitation are also indicative of this circumstance.

Despite rather a high efficiency of impurities washout from the lower atmospheric layers by cloudiness and precipitation, this effect is noticeably smoothed by the increase in intensity of the volcanic matter emission in the second half of the rain season. In this case, a portion of the volcanic matter enters the atmospheric layers above the cloudiness level and obviously spreads over a significant area, thus influencing the optical properties of the atmosphere, probably, on a regional scale. In any case, this influence is decisive for the whole territory of the Colima State.

Therefore, we can draw a conclusion that the influence of permanently active volcanoes, such as Fuego de Colima and Popocatepetl, should necessarily be taken into account in climatological estimates and forecasts. More thorough and detailed studies of this influence, particularly, in the immediate vicinity to the crater accompanied by measurements of the vertical profiles of meteorological and microphysical structural characteristics of the troposphere are needed.

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