thought to be attributed to the main plume was 0.6 km^3. If it has a bulk density of 0.5 g cm^{-3} because of loose packing (*3*), the average mass mixing ratio at the volcano would be approximately 0.025, and the acceleration caused by mass loading would be $-0.025g$ or 32 percent of the required mean value. Dilution by entrainment would reduce the mean value of this term, so that even if the mass is underestimated by a factor of 2, the dominant term must be the last, the mixing term. Thus, qualitatively, the very small percentage of the plume volume attributed to the volcano is supported. If a larger percentage is assumed, the mean exit velocity increases. Since the required deceleration increases with the square of the exit velocity, a much larger entrainment is required, opposing the assumption. A large entrainment of horizontal momentum also helps explain the rapid adjustment of the plume to the winds.

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Gaseous Constituents in the Plume from Eruptions of Mount St. Helens

Abstract. *Measurements in the stratosphere of gaseous constituents in the plume of Mount St. Helens were obtained during five flights of the NASA U-2 aircraft between 19 May and 17 June 1980. Mixing ratios from gas chromatographic measurements on samples acquired about 24 hours after the initial eruption show considerable enhancement over nonvolcanic concentrations for sulfur dioxide (more than 1000 times), methyl chloride (about 10 times), and carbon disulfide (more than 3 times). The mixing ratio of carbonyl sulfide was comparable to nonvolcanic mixing ratios although 3 days later it was enhanced two to three times. Ion chromatography measurements on water-soluble constituents are also reported. Very large concentrations of chloride, nitrate, and sulfate ions were measured, implying large mixing ratios for the water-soluble gaseous constituents from which the anions are derived. Measurements of radon-222 present in the plume are also reported.*

As part of an investigation of the distribution in the stratosphere of precursor gases and their role in sulfuric acid aerosol formation, we conducted a series of experiments in California and Alaska during the summer of 1979 (*1*). Typical mixing ratios by volume were about 0.4 to 0.1 part per billion (ppb) for OCS (carbonyl sulfide) and 0.04 to 0.05 ppb for SO_2 at altitudes from 15 to 21 km. An upper limit of about 1 part per trillion (ppt) at an altitude of 15 km was attributed to CS_2.

The 18 and 25 May and 13 June 1980 eruptions of Mount St. Helens presented an opportunity to study the input of volcanic emissions into the stratosphere. Between 19 May and 17 June 1980, we participated in five sampling flights over the northwestern United States on the NASA U-2 aircraft, in locations predicted to be in the trajectory of the plumes.

A flow-through cryogenic collection method, in which condensable constituents are trapped in a glass sampler at liquid-nitrogen temperature (*2*), was used to sample large volumes of air. Four cryogenic collectors were used on each flight, and 19 samples were collected.

After the residual air in each sample was removed by evacuation with a sorption pump, the samples were transferred to glass bulbs (200 to 250 ml). The samples were analyzed by gas chromatography. Sulfur constituents were separated by Chromosil-310 or Porapak-PS columns and measured with a flame photometric detector. A photoionization detector was used in CH_3Cl measurements. We adapted ion chromatographic methods for measurement of anions derived by dissolving the water-soluble constituents (*3*). Because of the large enrichment (over 1000-fold) of the cryogenically collected samples, we estimated a lower limit of measurement to be a few parts per trillion by volume.

All measurements were quantified by calibration based on reference standards. Primary standards were prepared from pure gases, each separately mixed with CO_2 and stored in concentrations approximating the enriched stratospheric samples. Commercial standards were also used, either directly or for preparing secondary standards. The accuracy of the standards ranged from 2 to 10 percent, depending on the constituent and method of preparation.

The 19 samples collected were analyzed for OCS and SO_2. Table 1 shows the results of gas chromatography analysis for those constituents with enhanced mixing ratios. In the first set of analyses of the sulfur constituents of the samples taken at 15.2 and 16.5 km on flight 36, several replicate trials were within the normal scatter for SO_2 measurements. Only one injection was made for the sample collected at 14 km in the first analysis. A decrease in the level of the SO_2 signals was observed in the second analysis a day later; the decay may have been caused by some chemistry that occurred in the sample bottle. The mixing ratios of the three SO_2 samples from flight 36 (Table 1) are derived from the first analysis and are considered lower limits. Some samples in Table 1 showed a marked decrease in the SO_2 signal between the first and second trial. This is the result of temporary column degradation or chemical decay of SO_2 in the sample bulb, or both. This effect is not observed in analyses of reference standard mixtures.

The OCS results obtained from flight 36 samples show mixing ratios that do not appear to be enhanced compared with those of the unperturbed stratosphere (*1, 2*). On the other hand, CH_3Cl mixing ratios are enhanced compared with those reported for the unperturbed stratosphere (*4*). Measurements on samples from a higher altitude plume (flight 37, Table 1) showed persisting enhancement of the CH_3Cl mixing ratio. The SO_2 mixing ratio, however, decreased to about that for the unperturbed stratosphere, except for the sample taken at 20.1 km. In contrast, the OCS mixing ratios are enhanced in samples from this flight except for the one taken at 20.7 km. These results indicate nonuniform distribution of these gases in the plume.

We also detected CS_2 in flight 36 samples. Because the signals were small and difficult to quantify, the CS_2 mixing ratios are reported with an uncertainty of about a factor of 2. For the 14.0-km sample, the mixing ratio is ≤ 55 ppt and for the 15.2-km sample, 2.8 ppt. We have not observed any H_2S signals in our measurements.

For ion chromatography measurements, solutions were prepared by dissolving in water a portion of the sample (Table 2). Air was not excluded in preparing these solutions, and easily oxidized solutes were expected to become oxidized in this process. Tests with added H_2O_2 confirmed this. Therefore, we expect that dissolved SO_2 will be converted to SO_4^{2-}. We are not aware of any other substantial stratospheric gas-phase source of SO_4^{2-}. Also, dissolved HNO_3, NO_2, and NO are responsible for any NO_3^- in the solution.

In the ion chromatography measurements (Table 2), the characteristic narrow peaks of Cl^- signals were strongly perturbed by a broad underlying feature. The perturbing feature may result from the presence of organic anions, either formate or acetate ions, or both (*5*). The Cl^- is presumably derived mainly from the HCl in the plume. We estimate that about 1 to 10 percent of the total signal is due to Cl^- in the samples from flights 38 and 39. We presume that this relation applies to the samples from flights 36 and 40. The estimate of Cl^- contribution to the total signal implies a large mixing ratio in the sample from flight 38 taken at 18.3 km, which was thought to have been obtained outside the plume. The high Cl^- mixing ratio, estimated to be about 4 to 50 ppb, cannot be reconciled with estimates of the total halogen abundance of about 3 ppb in the stratosphere (*6*).

The SO_4^{2-} data (Table 2) may now be compared with the SO_2 data (Table 1). The SO_4^{2-} mixing ratio of 174 ppb from flight 36 at 14.0 km is an upper limit estimate for that of SO_2. Hence, the mixing ratio in the plume is 111 to 174 ppb. Similarly, for the 15.2-km sample, the SO_2 mixing ratio is 10.4 to 42 ppb. In the flight 38 sample at 18.3 km, the SO_2 mixing ratio of 0.26 to 5.7 ppb is one to two orders of magnitude larger than in the unperturbed stratosphere (*1*). The NO_3^- mixing ratio in the same flight sample (Table 2) is quite high compared with that of HNO_3 plus NO_2 of about 1 ppb in the unperturbed lower stratosphere (*6*). These results suggest that the gaseous constituents measured in this sample may have originated from the volcanic emission, although the sampling was considered to have been made outside the plume.

The NO_3^- measurements show enhanced mixing ratios of 222 ppb in flight

Table 1. Mixing ratios by volume of gas constituents in the plume of Mount St. Helens determined by gas chromatography. Error limits represent root-mean-square estimates of all known sources of uncertainty.

U-2 flight					Mixing ratio (ppb)		
No.	Date (1980)	Time*	Coordinates† (°N, °W)	Altitude (km)	OCS	SO_2	CH_3Cl
Plume of 18 May eruption‡							
36	19 May	1606	44.4, 108.6	14.0	0.87 ± 0.11	111.0 ± 24§	2.89 ± 0.38
		1539	45.2, 111.0	15.2	0.47 ± 0.04	10.4 ± 1.0§	1.96 ± 0.25
		1508	45.8, 114.0	16.5	0.067 ± 0.009	1.78 ± 0.39§	0.280 ± 0.036
37	22 May	1838	46.1, 113.3	18.6 to 20.1	0.38 ± 0.11	0.091 ± 0.011	1.33 ± 0.17
		1938	47.0, 113.5	20.1 to 20.7	1.20 ± 0.36	0.082 ± 0.037	5.0 ± 1.2
		2009	46.3, 114.0	20.1	0.91 ± 0.36	4.20 ± 0.55‖	3.19 ± 0.41
		1938	47.3, 112.6	20.7	0.022 ± 0.004	0.083 ± 0.011	0.183 ± 0.024
Plume of 25 May eruption							
38	28 May	0141	52.3, 129.0	15.2	0.278 ± 0.036	0.017 ± 0.004	0.383 ± 0.050
		0207	51.0, 127.6	16.8	0.189 ± 0.025	0.011 ± 0.004	0.684 ± 0.089
		0235	48.5, 125.4	18.3¶	0.044 ± 0.066	0.261 ± 0.033	0.211 ± 0.027
		0256	46.4, 124.0	18.3¶	0.283 ± 0.037	0.067 ± 0.020	0.350 ± 0.046
Plume of 13 June eruption‡							
39	14 June	2117	48.4, 112.1	13.1	0.073 ± 0.009	0.130 ± 0.023	
		2144	47.5, 112.0	13.7	0.334 ± 0.057	0.072 ± 0.012	
		2212	45.6, 114.6	14.6	0.049 ± 0.008	0.054 ± 0.010	0.286 ± 0.037
		2039	45.8, 113.1	18.9**	0.203 ± 0.026	2.26 ± 0.29‖	
40	17 June	1942	40.0, 104.6	18.3	0.239 ± 0.031	0.027 ± 0.004	
		2011	40.2, 104.7	18.9	0.231 ± 0.030	0.046 ± 0.006	0.378 ± 0.049
		2112	42.5, 107.4	18.9	0.101 ± 0.018	0.039 ± 0.007	0.300 ± 0.054
		2204	42.4, 114.3	18.9	0.245 ± 0.044	0.038 ± 0.007	0.540 ± 0.097

*Sampling time, in Universal Time, represents the midpoint of the acquisition time. †Coordinates represent midpoints of the aircraft's ground track. ‡Plume trajectory was at different levels for each flight. §Derived from first analysis; considered to be a lower limit. ‖Considered to be a lower limit; showed a marked decrease in SO_2 signal between first and second trials. ¶Sample taken outside the plume. **Sample taken in the plume trajectory of 18 May eruption.

Table 2. Mixing ratios by volume of anions from water-soluble gaseous constituents in the plume of Mount St. Helens determined by ion chromatography.

U-2 flight					Mixing ratio (ppb)		
No.	Date (1980)	Time*	Coordinates† (°N, °W)	Altitude (km)	Cl^-‡	SO_4^{2-}	NO_3^-
Plume of 18 May eruption							
36	19 May	1606	44.4, 108.6	14.0	1000 ± 10	174 ± 17	6.2 ± 0.6
		1539	45.2, 111.0	15.2		42 ± 4	222 ± 22
39	14 June	2039	45.8, 113.1	18.9	900 ± 90	5.7 ± 0.6	48 ± 5
Outside plume of 25 May eruption							
38	28 May	0235	48.5, 125.4	18.3	467 ± 47	2.7 ± 0.27	6.1 ± 0.6
Plume of 13 June eruption							
40	17 June	2204	42.4, 114.3	18.9	671 ± 100	4.0 ± 0.6	~3.5 ± 0.5§

*Sampling time, in Universal Time, represents the midpoint of the acquisition time. †Coordinates represent midpoints of the aircraft's ground track. ‡All chloride ion mixing ratios are upper limits; Cl^- signals were perturbed by the presence of unknown ionic constituents. §Limit of detection of NO_3^- signal.

36 at 15.2 km and 48 ppb in flight 39 at 18.9 km. These results imply HNO_3 plus NO_2 mixing ratios greatly exceeding those for the unperturbed stratosphere. Also, our results show higher mixing ratios for these nitrogen constituents at 15.2 km than at 14.0 km in flight 36. This is another indication of the nonuniform distribution in the plume.

Measurements were also made of ^{222}Rn from samples from flights 36 and 39 (*7*). The measured radioactivity for the 16.5-km sample from flight 36 was 0.13 ± 0.02 disintegration per minute per liter (at standard pressure and temperature), where the error limit is 3 standard deviations. The flight 39 sample from 18.9 km, which was collected 26 days later in the predicted trajectory of the plume sampled in flight 36, showed that the radioactivity was 0.018 ± 0.002 disintegration per minute per liter. From the ^{222}Rn time constant of 3.8 days, the radioactivity is calculated to have decayed to about 1.4×10^{-4}. The background level of ^{222}Rn activity of the unperturbed stratosphere must be better known before the difference between the measured and calculated results can be properly interpreted.

Measurements of N_2O, $CFCl_3$, CF_2Cl_2, and CO_2 showed that the concentrations were within the range of mixing ratios previously measured in unperturbed stratospheric air in locations at similar latitudes (*8*).

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Changes in Stratospheric Water Vapor Associated with the Mount St. Helens Eruption

Abstract. *A frost point hygrometer designed for aircraft operation was included in the complement of instruments assembled for the NASA U-2 flights through the plume of Mount St. Helens. Measurements made on the 22 May flight showed the water vapor to be closely associated with the aerosol plume. The water vapor mixing ratio by mass in the plume was as high as 40 × 10^{-6}. This compares with values of 2 × 10^{-6} to 3 × 10^{-6} outside of the plume.*

Stratospheric water vapor—its concentration, variability, sources, and sinks—has been the subject of considerable interest and controversy ever since Brewer and co-workers (*1*) made measurements in the late 1940's. To obtain new data on this water vapor, we assembled a frost point hygrometer for use on the U-2 aircraft.

Table 1. Stratospheric water vapor mixing ratios in parts per million (ppm) measured over Moffett Field, California, 15 May 1980.

Altitude (km)	Mixing ratio (ppm)	
	Average	Range
15	1.5	1.1 to 2.0
16.5	1.4	1.0 to 1.9
18	1.4	1.0 to 1.6
19.5	1.9	1.7 to 2.1

The instrument, based on the design used by Mastenbrook (*2*) in his balloon program, consists of a small mirror that is controlled by temperature at the frost point. The mirror is connected through a moderate thermal resistance to a liquid nitrogen reservoir and has an electrical heater attached to it. The temperature is controlled by balancing the electrical heat input with the thermal conduction to the cold reservoir. The presence of frost on the mirror is measured optically and is used to servo control the temperature. A knowledge of the frost point yields the absolute humidity and the water vapor mixing ratio.

The instrument was installed in the wing tank of the U-2. Ambient air was taken in through a Rosemont probe mounted on the skin of the wing tank; it flowed across the mirror surface and was exhausted at the back of the tank. The major concern in any water vapor measurement is that the ambient air is not contaminated in the sampling process. The flow through our system is fairly high (1.6 liters per minute), and metal tubing is used throughout.

After fabrication and testing of the unit in late April and flight testing on the U-2 during May, the first flight with the unit was made on 15 May. When Mount St. Helens erupted on 18 May provision was made to fly the frost point unit on several flights into the volcanic cloud. Data were obtained on 22 and 27 May and 14 and 17 June 1980.

The water vapor mixing ratios, measured during the 15 May flight over NASA's research center at Moffett Field, California, are given in Table 1. Both average mixing ratios and the ranges for each altitude are shown. At this time, because of the limited data base with the instrument, we are not able to separate the fluctuations due to measurement precision from those due to water vapor variability. The figures are included for comparison with data obtained during penetration of the volcanic cloud on 22 May (Table 2). The time range for the measurements is included so that the water vapor data can be compared with measurements made by other sensors aboard the U-2 and decribed in accompanying reports.

Our data indicate that the aircraft was in the cloud at 1845 Universal Time (*3*). The water vapor data show a marked decrease in mixing ratio associated with the increase in aircraft altitude at 1925 and a sharp increase in mixing ratio when the aircraft descended again at 2000. The mixing ratio by mass decreases significantly after 2015 and appears to reach a background level of 3 × 10^{-6} at an altitude of 20.2 km by 2030. A background of 2.6 × 10^{-6} at 19.8 km was measured on the 15 May flight. These data confirm that significant amounts of water vapor were injected into the stratosphere by the 18 May eruption. On the flight of 22

Table 2. Stratospheric water vapor mixing ratios in parts per million (ppm) measured in the plume of Mount St. Helens on 22 May 1980.

Time	Altitude (km)	Mixing ratio range (ppm)
1845 to 1920	18.6 to 20.1	15 to 40
1930 to 1955	20.7	2.5 to 5.0
2000 to 2015	20.1	3.0 to 25
2030 to 2115*	20.1	2.0 to 3.5

*These data were obtained well away from the plume and represent unperturbed background mixing ratios.

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