Filter Measurements of Stratospheric Sulfate and Chloride in the Eruption Plume of Mount St. Helens

Abstract. *Five flights of the U-2 aircraft with a filter sampler aboard were flown in the Mount St. Helens debris from 19 May to 17 June 1980. Sulfate concentrations as large as 216 times the expected background were observed. The enhancements of acid chloride vapor were considerably smaller, suggesting an insignificant increase of background values of hydrogen chloride once the plume is well mixed throughout the lower stratosphere.*

During May and June 1980, a multifilter sampler (*1*) was flown aboard the NASA U-2 aircraft that sampled the debris in the atmosphere from the eruption of Mount St. Helens. Details of the sampling tracks relative to the plume are given in (*2*).

The filters used for sampling were IPC-1478 cellulose. The multifilter sampler, which accommodates filter packs with up to three filters in tandem, has a neutral IPC-1478 paper backed up by two filters impregnated with tetrabutylammonium hydroxide (TBAH) (*3*). The neutral IPC-1478 filter paper collects particles down to 0.03 μm in diameter (*4*). The TBAH-impregnated filter is effective for collecting acidic halogen vapors (*3*). In laboratory simulations, HCl and $ClONO_2$ (chlorine nitrate) have been shown to be efficiently scavenged (*5*). The collection efficiency of the TBAH-impregnated filters is assumed to be very low for organic halogen compounds. In the multifilter sampler, the particulates are measured on the neutral paper, and the acidic vapors are measured on the impregnated papers. Water-soluble components are removed from the filter with an aqueous wetting agent, and the aqueous solution is analyzed for the ion of interest (*6, 7*).

The accuracy of the data from the five sampling flights (Table 1) is in the range of ± 15 to 25 percent. Sampling in nonuniform distributions, such as those from a volcano, precludes having optimally accurate date. Average values of particulate sulfate and acidic chloride vapor (Table 1) were computed from seasonal profiles of these species during 1976 at Holloman Air Force Base, New Mexico (*8, 9*). These values are included as a reference for concentrations to be expected during times of relatively little volcanic activity and are referred to as the background level. Concentrations of particulate chloride during this earlier period were 0.002 to 0.2 ppb by mass in the appropriate altitude range. The sulfate values are higher than during earlier quiescent periods (*10, 11*).

The initial explosive eruption of 18 May was sampled on 19 May. The exposed filter papers, which normally appear white, were quite discolored, ranging from a brownish-gray at 17.7 km to a reddish-brown at 13.1 km. In other stratospheric filter sampling, we have never observed a discoloration of the filters. The particulate sulfate mixing ratios determined from this flight show that the cloud is not well mixed and is quite layered. The particulate sulfate is enhanced over the amount we would expect during times when the atmosphere is not perturbed by volcanic emissions (*7*). The particulate chloride observed is also enhanced (*3*). The acidic chloride vapor is enhanced on the sample taken at 14 km, but the sample from 15.2 km is about what we would expect for that altitude (*8*). The TBAH-impregnated filters were not exposed on the 17.7- and 13.1-km sampling altitudes.

Table 1. Concentrations (in parts per billion, by mass) of sulfate and chloride in the Mount St. Helens stratospheric plume and 1976 seasonal averages.

Date (1980)	Altitude (km)	Particulate SO_4^{2-}	Particulate Cl^-	Acidic Cl^- vapor	Seasonal average*	
					Particulate SO_4^{2-}†	Acidic Cl^- vapor‡
19 May	17.7	13.5	1.9		1.31	
	15.2	3.6	0.24	0.34	0.6	0.23 ± 0.21
	14.0	8.9	0.33	2.4	0.35	0.16 ± 0.02
	13.1	13.1	0.49			
22 May	18.6 to 20.1	21.2	0.07			
	20.1	263.0	0.83		1.22	
	20.7	3.1	0.02	0.51	1.12	0.73 ± 0.13
	20.1	82.0	0.37		1.22	
27 May	16.8	27.8	0.58	1.1	1.07	0.38 ± 0.22
14 June	18.9	1.4	0.73	0.36	1.4	0.64 ± 0.24
	14.6	0.21	< 0.1	0.15	0.5	0.20 ± 0.02
	13.7	0.40	< 0.1	0.18		13.0 ± 0.02
	12.8	0.89	< 0.1	0.08		
17 June	18.9	2.01	< 0.1		1.4	
	18.9	5.92	< 0.1		1.4	
	18.3	7.45	< 0.1		1.31	

*Measurements made at 33°N. †Measurements are from (*11*). ‡Measurements are from (*8*) and were converted from volume to mass terms; the value of 1 standard deviation is given.

The results from the 22 May flight indicate very large enhancements, up to 216 times background sulfate. The particulate chloride is enhanced at 20.1 km, but the other two altitudes show background values. The acidic chloride vapor observed at 20.7 km is at the background level.

During the 27 May flight only one sample was taken. This sample, from 16.8 km, shows enhanced particulate sulfate, particulate chloride, and acidic chloride vapor concentrations.

The concentrations observed from the 14 June flight are close to background values. Postflight meteorological analyses indicated that the samples, except the one taken at 18.9 km, came from outside of the plume from the eruption (*12*).

The flight on 17 June, which was designed to sample debris from the first eruption (18 May) after it had passed around the world once, showed that the particulate sulfate levels were still enhanced although not nearly as much as on the 22 May flight. The particulate chloride levels were quite reduced in comparison with the values before the world excursion. The acidic chloride vapors were not measured on the 17 June flight.

The particulate sulfate values reflect great inhomogeneity in the plume. Despite the ambiguity posed by a lack of good mixing, it appears that the formation of sulfate aerosol in the early stages was very rapid. The particulate chloride is enhanced on all of the samples taken within a few days of the eruption, but enhancement is not apparent after the plume has circumnavigated the world.

Only two measurements of acidic chloride vapor among five taken in the eruption plume show enhancements over the expected background. These measurements at 14 km on 19 May and 16.8 km on 27 May are higher than the 1976 seasonal composite profile (*8*) for the given altitudes by factors of 15.0 and 2.9, respectively.

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Lazrus *et al.* (*11*) addressed the problem of the possible impact of volcanoes on stratospheric ozone concentrations. Volcanic hydrochloric acid vapor injected above the tropopause can react with the hydroxyl radical to yield atomic chlorine, which is capable of catalytically depleting ozone.

Measurements of stratospheric acid chloride before the major eruption of Volcan de Fuego in Guatemala in October 1974 indicated no significant enhancement of chloride (*12*). On the other hand, measurements of the ratios of HCl to SO_2 in tropospheric explosive eruption plumes of Volcan de Fuego, in conjunction with the observed tenfold enhancement of stratospheric sulfate throughout the Northern Hemisphere after the major Fuego eruption, suggested that a significant increase of HCl should also have occurred. We did not observe any preferential removal of HCl relative to SO_2 as a function of the age of the tropospheric Fuego plumes. The failure to observe significant enhancements of stratospheric acid chloride was attributed to the solubility of HCl, which is 300 times greater than the solubility of SO_2 in water at 0°C. If the copious quantities of water typically condensing from volcanic plumes as they cool become appreciably acidic, the solubility of SO_2 is even further depressed. Most of the ash particles, which are likely to be made more massive by coatings of ice, were found to leave the stratospheric plume of Mount St. Helens within several days (*13*), probably also causing a selective depletion of chloride relative to sulfur. Though the particulate chloride appears to be consistently enhanced during the earliest stages, the resulting enhancement of stratospheric chloride concentrations after extensive mixing of the plume throughout the stratosphere should be very small. This also applies to the acid chloride vapor concentrations in the plume. We do not know the extent to which the eruption plume was initially enriched in HCl, but observations continue to suggest that major eruptions do not significantly enhance stratospheric acid chloride levels. Measurements of HCl and SO_2 in the tropospheric plumes of Mount St. Helens are under way. Our observations do not preclude the possibility of significant enhancement of stratospheric chlorine by organic halogen compounds enriched in the volcanic plume.

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References and Notes

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13. N. Farlow (*ibid.*) reported that the particles sampled on 19 May 1980 contained very little H_2SO_4 liquid on them when examined under an electron microscope. Also, the number of ash particles appeared to diminish greatly in subsequent flights.
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Trace Element Composition of the Mount St. Helens Plume: Stratospheric Samples from the 18 May Eruption

Abstract. *Atmospheric particulate material collected from the stratosphere in the plume of the 18 May 1980 eruption of the Mount St. Helens volcano was quite similar in composition to that of ash that fell to the ground in western Washington. However, there were small but significant differences in concentrations of some elements with altitude, indicating that the stratospheric material was primarily produced from fresh magma, not fragments of the mountain.*

The effects of aerosols in the earth's atmosphere on climate are the object of constant study and interest, especially the effects of sudden changes in the aerosol composition such as those produced by a large-scale volcanic eruption (*1*). Most studies of volcanoes have involved only the measurement of the number particles or the total mass or particle size distributions in plumes (*2*). Studies of the chemical compositions of particles from volcanic plumes have used aircraft sampling systems to collect tropospheric samples (*3, 4*). However, none of these projects included samples from a large-scale primary eruption, nor did they include samples from the stratosphere.

Mount St. Helens erupted catastrophically on 18 May 1980, sending clouds of ash and debris into the stratosphere to an altitude in excess of 18 km. The first sampling of the volcanic plume in the stratosphere took place on 19 May 1980, less than 24 hours after the major eruption. The sample collection flight covered areas over Oregon, Idaho, Montana, and Wyoming; samples were taken from the plume at various altitudes between 13 and 18 km. On 22 May, samples from a similar geographic area were collected at altitudes of about 20 km. These samples were taken to monitor chemical changes with time as the volcanic cloud dispersed. On 27 May, after the 25 May eruption, samples were collected along the Canadian coastline at an altitude of about 17 km.

A multifilter sampling device mounted in a wing tank of a NASA U-2 aircraft was used (*5*). Samples were collected on IPC cellulose filter papers and had a collection time of about 20 minutes each. Blanks were also taken in between each pair of samples (1 minute or less collection time) to correct for elements contained in the filter papers. Blanks collected immediately after the first and biggest eruption became heavily loaded with particles after just 1 minute of collection and were thus useless as blanks; the abundant elements suggest extremely high levels of contaminants even at these high sampling altitudes. In these cases, blanks collected on days when the clouds were not as thick were used to make the corrections.

One-half of each filter was sent to us, and it was pressed into a pellet and sealed in a clean polyethylene bag before being counted for natural radioactivity. The other half of the filter was analyzed by Gandrud and Lazrus (*5*) for water-soluble species. The pellets were analyzed by prompt γ-ray activation analysis (PGAA) (*6*) and instrumental neutron activation analysis (INAA) (*7*). Both procedures were carried out at the National Bureau of Standards reactor. The PGAA was done first and used a neutron-beam facility developed specifically for the rapid analysis of samples by prompt γ-rays emitted while samples were being irradiated (*6*). For INAA, samples were irradiated along with the appropriate standards in a flux of 6×10^{13} neutrons per square centimeter per second for a