

# Quiescent Outgassing of Mauna Loa Volcano 1958-1994

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A continuous 37 year record of the quiescent CO<sub>2</sub> outgassing of Mauna Loa volcano was derived from atmospheric measurements made 6 km downslope of the summit caldera at Mauna Loa Observatory. The volcanic plume is sometimes trapped in the temperature inversion near the ground at night and transported downslope to the observatory. The amount of volcanic CO<sub>2</sub> was greatest shortly after the 1975 and 1984 eruptions and then decreased exponentially with decay constants of 6.5 and 1.6 years respectively. Between 1959 and 1973 the decay constant was 6.1 years. The total reservoir mass of CO<sub>2</sub> during each of the three quiescent periods was similar and estimated to be between  $2 \times 10^8$  kg and  $5 \times 10^8$  kg (0.2 Mt to 0.5 Mt). The 1975 eruption may have been preceded by a small increase in CO<sub>2</sub> emissions. A similar increase has occurred since early 1993. Condensation nuclei (CN), presumably consisting of sulfate aerosol, were measured in the volcanic plume throughout the 1974 to 1994 record. The post-1975 period had consistently high levels of CN. Between 1977 and 1980, light-scattering aerosols were detected, coincident with a period of visible fuming at the summit. CN levels after the 1984 eruption were greatly reduced. Two brief periods of low CN emissions during this time correlate with temporary halts or reductions in the rate of summit expansion. These temporary reversals in the inflation of the mountain did not affect the steady exponential decline of the CO<sub>2</sub> emissions rate. Upper limits were set on the amounts of H<sub>2</sub>O, O<sub>3</sub>, CH<sub>4</sub>, SO<sub>2</sub>, aerosol carbon, radon, CO, and H<sub>2</sub> present in the plume at various periods between 1974 and 1993. The ratio of SO<sub>2</sub> to CO<sub>2</sub> was less than  $1.8 \times 10^{-3}$  between 1988 and 1992.

## 1. INTRODUCTION

Mauna Loa Observatory (MLO) has been an important site for the continuous climatological monitoring of atmospheric CO<sub>2</sub> levels since 1958 [Pales and Keeling, 1965], and of a growing number of aerosol and trace gas species since 1974 [Ferguson and Rosson, 1991; Peterson and Rosson, 1993]. The observatory is at an elevation of 3400 m on the northern flank of 4169 m Mauna Loa Volcano, 6 km from the summit caldera.

Vented gas from the nearby Mauna Loa summit is sometimes transported downslope at night and detected by the CO<sub>2</sub>

analyzers [Pales and Keeling, 1965; Miller and Chin, 1978] and aerosol monitors [Bodhaine et al. 1980] at MLO. At a remote location such as MLO, the background air is normally well mixed and exhibits a steady hour-to-hour CO<sub>2</sub> concentration. Plumes from the summit caldera, a nearby source of CO<sub>2</sub>, are poorly mixed with the background air upon reaching MLO and can easily be identified by their highly variable CO<sub>2</sub> concentration. Previous studies have been concerned with identifying and eliminating this volcanic contamination from the climatological record [e.g. Keeling et al., 1976; Thoning et al., 1989]. The present study is the first to use the suite of MLO trace-gas data sets to monitor the long-term outgassing behavior of Mauna Loa volcano.

The history of published volcanic gas measurements on Mauna Loa is brief and intermittent. These have included fumarole SO<sub>2</sub> emission estimates for 1978-1979 [Casadevall and Hazlett, 1983], five months of continuous in-situ fumarole temperature and reducing gas activity measurements taken just

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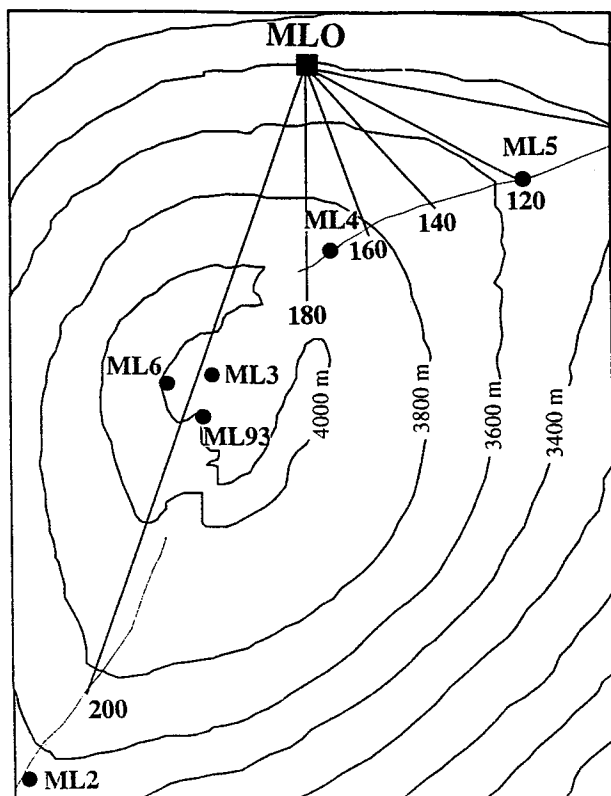


Fig. 1. Map of Mauna Loa volcano summit vicinity. Radial lines from the location of MLO give bearings in degrees from true north. The locations of identified thermal features are shown and described in the text.

before the 1984 eruption [Lockwood *et al.*, 1985; Sutton and McGee, 1989], a series of samples taken during and immediately after the 1984 eruption for eight gases including  $\text{CO}_2$  [Greenland, 1987], and satellite and aircraft measurements of the  $\text{SO}_2$  and  $\text{CO}_2$  emissions during the 1984 eruption [Casadevall *et al.*, 1984].

## 2. ENVIRONMENT

### 2.1 Site Description

MLO is located relative to the summit features in Figure 1. The summit caldera is 6 km from MLO at a bearing of  $190^\circ$ , with a floor elevation of 4000 meters. The caldera is 3 km by 5 km in diameter, elongated along two major rift zones extending to the northeast and southwest. The northeast rift lies at bearings of  $100^\circ$  to  $180^\circ$  from MLO, at a minimum distance of 4 km. The southwest rift lies at bearings between  $200^\circ$  and  $210^\circ$  at distances of 10 km and greater.

The height of the caldera rim varies from 180 meters on the

west side to near zero where it intersects the rifts to the NNE ("North Pit") and SSW ("South Pit"). This topography is a likely factor in the transport of volcanic fume from sources inside the caldera. Air trapped near the surface might "drain" out of the caldera at the locations of North Pit and South Pit. The observatory is almost directly downslope from North Pit, a favorable location for detecting air exiting the caldera at this point.

Outgassing sites in the summit region were visually identified by Casadevall and Hazlett [1983]. Five of these are located on Figure 1 and identified as ML2 - ML6. The primary source of outgassing before 1984 was at location ML3. This feature consisted of seven  $120^\circ$ - $362^\circ\text{C}$  active fumaroles located on the 1975 eruptive fissure, which produced 0.5 to 5 tons of  $\text{SO}_2$  per day [Casadevall and Hazlett, 1983]. This fissure was a source of reducing gas activity [Lockwood *et al.*, 1985] and visible fume which sometimes produced a dense blue haze on the mountain's upper flank [Lockwood *et al.*, 1987]. The remaining features in Figure 1 are comparatively minor gas sources and will not be discussed further.

The 1984 eruption covered a large portion of the caldera floor and formed new fissures. Visible fuming from ML3 ceased following this eruption [Lockwood *et al.*, 1987]. Visible fuming in the post-1984 era is greatly reduced and comes from a location marked ML93 in Figure 1 [J. Sutton, pers. communication, 1993]. No thermal inventories of Mauna Loa have been published since the 1984 eruption.

### 2.2 Site Meteorology

The volcanic plume only reaches MLO under certain meteorological conditions [Price and Pales, 1963; Garrett, 1980; Hahn *et al.*, 1993]. On clear nights radiative cooling produces a temperature inversion near the ground. Gravity pulls this cool, dense air down the mountain slope at speeds of several m/s in a thin layer tens of meters thick. If the free tropospheric winds are light, the volcanic plume remains trapped beneath the inversion layer to potentially be transported in the downslope wind to MLO. This condition is often disrupted by strong easterly or westerly tropospheric winds, which break up the surface temperature inversion and steer the plume away from the direct downslope path to MLO.

Meteorological variables have been measured at MLO since 1958 and include wind, temperature, humidity, and pressure. Before 1977, data were recorded on chart records and hand-scaled to obtain hourly averages with a 45-degree directional resolution. After this date, a computer data acquisition system was installed along with improved sensors, some of which have been subsequently upgraded. The wind direction data after 1977 has 1 degree resolution. Details of this program are given in Herbert *et al.* [1981].

### 3. CO<sub>2</sub> MEASUREMENTS

#### 3.1 Measurement Methodology

The original CO<sub>2</sub> monitoring program was started in 1958 by the Scripps Institute of Oceanography (SIO) and has produced the longest continuous record of atmospheric CO<sub>2</sub> available in the world. It has provided a textbook example of the effect of fossil-fuel burning on the global atmosphere. Complete details of this program are given in *Pales and Keeling* [1965] and *Keeling et al.* [1976, 1982, 1987]. Measurements were made using an Applied Physics Corporation (APC) dual detector non-dispersive infrared analyzer [Smith, 1953]. An air stream was sampled alternately from two separate intake lines for 10 minutes each followed by a 10 minute flow of reference gas. Water vapor was removed by passing the air through a freezer trap at -60 to -80 °C. The output of the analyzer was recorded on a chart record from which data was hand-scaled. If the variability of the trace during each 10-minute interval was visually judged to be significantly greater than that of the reference gas trace, the interval was flagged as "variable." These subjective flags were the basis for identifying the presence of volcanic plume in the SIO data set. Data used in the present study were obtained through the Carbon Dioxide Information Center [Keeling, 1986]. The precision of the SIO system in measuring reference gases was between 0.1 and 0.2 ppm. The precision of monthly baseline averages was approximately 0.5 ppm, increasing to as much as 1.0 ppm from mid-1964 to late 1968 [Keeling, 1986].

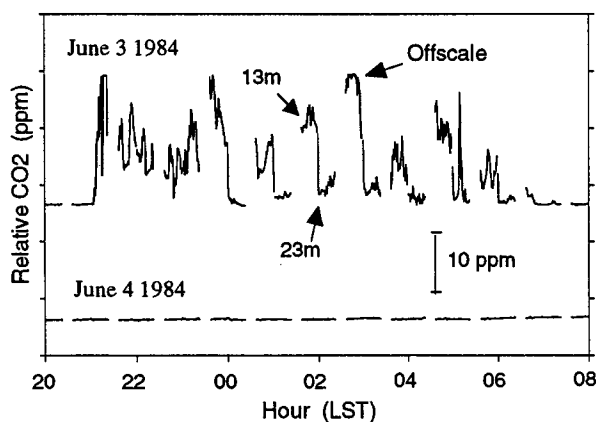


Fig. 2. Minute average atmospheric CO<sub>2</sub> concentrations for two consecutive nights in June 1984. The top trace illustrates the effects of the volcanic plume and the bottom trace shows the uncontaminated free tropospheric background. The two traces are offset by 20 ppm. Air was being sampled from heights of 13 meters and 23 meters respectively for 25 minutes each hour. A periodic 10 minute break occurs when the system is sampling reference gas. The data labeled "Offscale" are caused when atmospheric CO<sub>2</sub> concentrations exceed the range of the analyzer.

In May 1974, a second continuous CO<sub>2</sub> monitoring program was established by what is now the National Oceanic and Atmospheric Administration (NOAA). Details are given in *Komhyr et al.* [1983, 1989]. This program began using a Hartmann and Braun URAS-2 non-dispersive infrared analyzer until August 1987, when it was replaced by a Siemens Ultramat-3 analyzer. Two separate intake lines and two reference gases were sampled every hour. The air stream was dehumidified by passing it through a cold trap at -60 to -80 °C. The two reference gases were calibrated weekly by comparison with a suite of five standard gases. Beginning in 1976, 1-minute averages of the analyzer output voltage were recorded by a computerized data acquisition system [Herbert et al., 1986]. Variability in these data is flagged by computer.

These data were recently re-processed for this study to obtain 1-minute average concentrations following the calibration methodology of *Komhyr et al.* [1989]. The 1-minute data were then visually edited to remove periods when the system malfunctioned (brief power outages, freezer trap blockages, air pump failures, etc.)

#### 3.2 Variability in CO<sub>2</sub> Concentration

The presence of a volcanic plume caused an increase in the level of minute-scale variability in the CO<sub>2</sub> record. Hawaii is centrally located in the Pacific Ocean, far from continental CO<sub>2</sub> sources, so that background air at MLO is well mixed and has a steady hourly concentration. Since the Mauna Loa volcanic source is only a few km away, the plume gas is poorly mixed with background air upon reaching MLO, resulting in a large increase in the minute-scale variability of the CO<sub>2</sub> concentration. An illustrative example of background data and volcanically disturbed data taken shortly after the 1984 eruption is shown in Figure 2. Background CO<sub>2</sub> levels have risen from 315 ppm in 1958 [Keeling et al., 1976] to 358 ppm in 1993 with an annual cycle averaging 6-7 ppm and an average diurnal cycle of about one ppm [Thoning et al., 1989].

Minute-scale variability in the CO<sub>2</sub> record had other potential causes. These fall into two categories: sources of "noise" that caused both positive and negative changes in the background concentration and had a long-term sum of zero, and true CO<sub>2</sub> sources that caused only positive changes in the background concentration.

The identified or potential nearby, nighttime sources of CO<sub>2</sub>, in approximate order of their influence were:

1. Volcanic emissions from the Mauna Loa summit. These were the primary CO<sub>2</sub> sources, typically producing increases of several ppm.
2. Volcanic emissions from Kilauea volcano. CO<sub>2</sub>, SO<sub>2</sub>, and other volcanic emissions came from the nearby Kilauea region [Greenland et al., 1985; Connor et al., 1988] southeast of Mauna Loa at altitudes between sea level and 1200 m. This

source was active intermittently in the 1960s and 1970s, and was virtually continuous after 1982. The emissions usually remained trapped in the marine boundary layer, below 2000 m. In the afternoon, upslope winds commonly brought air from the marine boundary layer up to MLO. This air sometimes contained fume from Kilauea volcano. *Luria et al.* [1992] showed that this was the principal daytime source of SO<sub>2</sub> at MLO in 1989 (at concentrations of up to 50 ppb), and estimated a corresponding upper limit daytime CO<sub>2</sub> increase of 0.9 ppm. The possibility exists that some Kilauea-contaminated marine boundary layer air was occasionally caught up in a large-scale circulation pattern and became entrained in the downslope winds at night. Dilution would probably have reduced this nighttime excess CO<sub>2</sub> concentration to less than 0.1 ppm with variability less than that of the Mauna Loa plume because of greater travel times (about ten hours) and distances (at least 100 km).

3. Respired CO<sub>2</sub> from island ecosystems and island anthropogenic CO<sub>2</sub>. Most vegetation on the island of Hawaii is at elevations below 2000 m and most of the human population lives below 500 m. The daytime photosynthetic uptake of CO<sub>2</sub> by island vegetation at low altitudes caused decreases of up to several ppm when the air was blowing upslope in the afternoon [e.g. *Pales and Keeling*, 1965]. Because these sources were widely dispersed at distances of many tens of km, the CO<sub>2</sub> was more thoroughly mixed and had a correspondingly small minute-scale variability [*Thoning et al.*, 1989]. Nighttime contamination from these sources would have been minimal for the same reason as for the Kilauea plume. There is no vegetation on the barren lava at elevations above MLO.

4. Contamination from the vicinity of MLO. Events of this type were noted by *Keeling et al.* [1976] for certain daytime periods before mid-1971, and were attributed to local automobile traffic, which was absent at night. A diesel generator on the site provided station power and a local source of CO<sub>2</sub> from 1958 to early 1967. During this period, air was selected according to wind direction from two out of four orthogonal lines located on the corners of the site to maintain an upwind sampling of air. The steadiness of the nighttime downslope wind would have made inadvertent contamination from the generator a rare occurrence. Another potential problem was the leakage of room air through air lines or leaking diaphragm pumps. These episodes were presumed to be identified by the observers and flagged as instrument malfunctions.

The identified or potential sources of within-hour "noise" variability in the CO<sub>2</sub> record, in approximate order of their importance were;

1. Changes in the background concentration. Smooth within-hour variations (typically a few tenths of a ppm) occasionally occurred in the background CO<sub>2</sub> concentration. These could be caused by the synoptic movement of airmasses

having differing CO<sub>2</sub> concentrations, or result from a change in the vertical circulation of free tropospheric air near the mountain at times when a large vertical gradient of tropospheric CO<sub>2</sub> was present. For this study it was necessary to optimize the ability to distinguish changes in background concentration from volcanic plume events. The use of an hourly standard deviation as a measure of variability [e.g. *Thoning et al.*, 1989] was not satisfactory for this purpose because it often failed to discriminate between the high-frequency variability characteristic of plume events and the low-frequency changes in background concentration. An alternative measure was developed that more effectively separated out higher-frequency variability; the variability index (VI), defined as the average absolute difference between successive 1-minute average concentrations during each measurement interval.

2. Instrument noise. The SIO analyzer output was subject to occasional periods of excessive noise and drift primarily due to ageing and deterioration of vacuum tubes in the power supply, amplifier, and thermal regulation circuits. Locations of the analyzer and room temperature control apparatus were changed several times during the program to reduce the thermal drift of the analyzer. The decision to flag suspect periods as either an instrument malfunction or due to natural variability was made by the observer based on his experience and daily monitoring of the analyzer. The more modern NOAA analyzers had solid-state electronics and were much more stable. Two measures of the stability of the NOAA analyzers were obtained from analysis of the 1-minute data. First, the hourly standard deviation was calculated for the last two minutes of the two five-minute reference gas runs (n=4 each hour). The URAS-2 analyzer had an average reference gas standard deviation of 0.015 ppm from 1976 to 1980 and 0.03 ppm from 1981-1987. The Ultramat-3 analyzer had an average reference gas standard deviation of 0.009 ppm. Next, the drift in instrument output voltage between successive hourly calibration runs was calculated. The voltage drift in 30 minutes multiplied by the instrument scale factor ranged between 0.04 ppm and 0.1 ppm for the URAS-2 analyzer and between 0.01 ppm and 0.02 ppm for the Ultramat-3 analyzer.

3. Line voltage and frequency fluctuations. These caused a corresponding shift in the analyzer output that could appear as an abrupt or gradual drift, or a high frequency noise in the SIO data. Most events were presumed to be recognized by the observer and flagged as an instrument malfunction.

4. Radio frequency noise. In the 1960's, radio transmitters at the observatory site occasionally produced a high frequency noise on the CO<sub>2</sub> trace. These events were presumed to be flagged as an instrument malfunction by the observer and were so infrequent as to be of minor consequence.

5. Physical vibration of the analyzer. Vibration of either analyzer produced a brief "spike" in the instrument output.

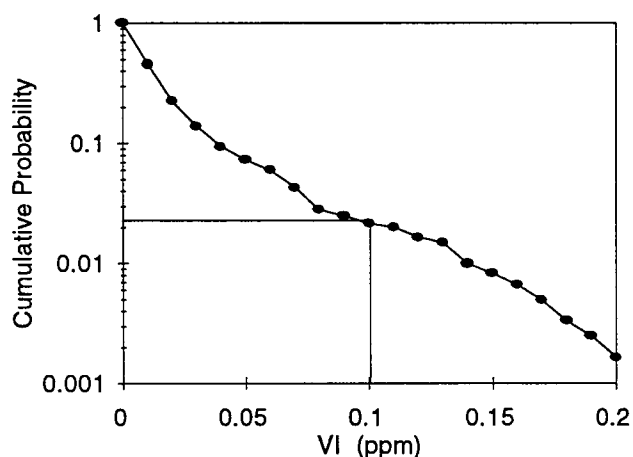


Fig. 3a. The cumulative probability of occurrence of hourly variability index values above a given threshold for presumably uncontaminated background air. Air was assumed to be uncontaminated between 1990 and 1992 when winds blew from 235 to 245 degrees. The sample size was 639 hours.

This was quite uncommon and is assumed to be of little consequence to this study.

### 3.3 Calculation of $\Delta\text{CO}_2$

$\Delta\text{CO}_2$  was defined as the difference between the measured concentration and the estimated background concentration during periods of high  $\text{CO}_2$  variability.  $\Delta\text{CO}_2$  was calculated as follows:

1. Only nighttime data between 2000 LST and 0759 LST (Local Standard Time) were analyzed. This was when the plume was most likely to be transported down the slope beneath the temperature inversion.

2. Every hour the average  $\text{CO}_2$  concentration measured from each of two intake lines, L1 and L2, was calculated. Each line was sampled for either 20 minutes (SIO data) or 25 minutes (NOAA data). The first three minutes of every sample was rejected to allow for a complete flushing of the lines. This produced two independent "measurements" per hour.

3. Each measurement was flagged as either variable or background.
  - a. For the SIO hand-scaled data, the variability flag in the original data set was used.
  - b. For the NOAA computerized data, an objective algorithm was used. Measurements in which the variability index (VI) exceeded a threshold value were flagged.

4. For each measurement flagged as variable, a corresponding background  $\text{CO}_2$  concentration was estimated by linear interpolation between the nearest non-flagged measurement before and after that hour.

5.  $\Delta\text{CO}_2$  was calculated as the difference between the average  $\text{CO}_2$  concentration and the estimated background.

As stated earlier, the NOAA data were flagged using a "variability index" (VI), which was the average absolute difference between successive 1-minute  $\text{CO}_2$  concentrations during a measurement interval. The choice of an optimum threshold value of VI involved a subjective compromise between including relatively small-amplitude, presumably volcanic events, and excluding relatively large amplitude noise as described earlier. In the SIO data, this decision had already been made by the observer in assigning the variability flags.

For the NOAA data, the distribution of hourly VI for presumed background air is shown in Figure 3a. Background air was presumed to be present when winds came from a  $10^\circ$  sector centered on  $240^\circ$  between 1990 and 1992. It will be shown later that volcanic  $\text{CO}_2$  was at a minimum in this sector, and that the level of  $\text{CO}_2$  outgassing was at a minimum during this period. Figure 3a shows that a VI threshold of 0.1 ppm excluded about 98% of the presumed background data.

The effect of varying the VI threshold on the distribution of  $\Delta\text{CO}_2$  for the entire NOAA record is shown in Figure 3b. The distributions were made up of the two components identified earlier; one arising from sources having only positive  $\Delta\text{CO}_2$ , and the other arising from "noise" which had  $\Delta\text{CO}_2$  of both signs and a net sum of zero. Reducing the VI threshold from 0.5 ppm to 0.05 ppm greatly increased the number of small-magnitude  $\Delta\text{CO}_2$  events detected from both components. At a VI threshold of 0.5 ppm, there was essentially no detectable noise component, but also a greatly reduced population of less than four ppm  $\Delta\text{CO}_2$  events.

The areas under the distributions shown in Figure 3b are plotted in Figure 3c as a function of VI. Since the noise component of the distribution had a net sum of zero, the area under the distribution gave the sum of the source component. Figure 3c suggests that a VI of 0.1 ppm detected 95% of the total source component, whereas a VI of 0.5 ppm detected only

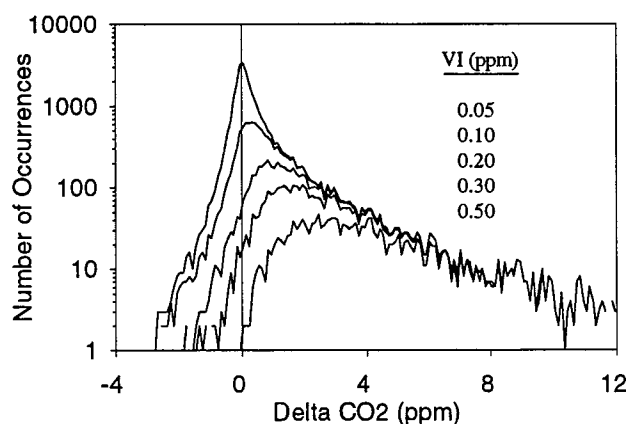


Fig. 3b. The effect of varying the variability index threshold on the distribution of hourly delta  $\text{CO}_2$ . The five labeled VI thresholds correspond vertically to the five distributions.

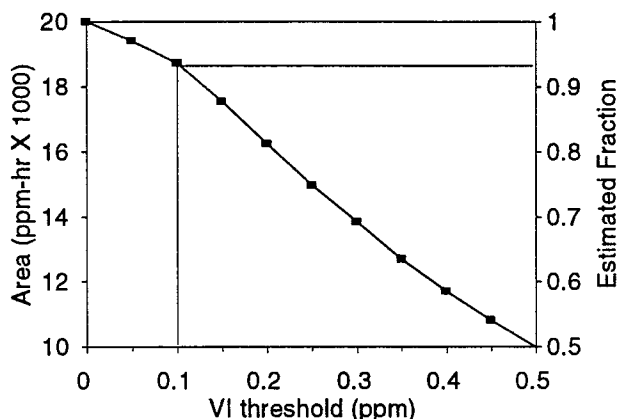


Fig. 3c. The areas under the distributions shown in Figure 3b. The "estimated fraction" gives the fraction of the total source component of  $\text{CO}_2$  that would be detected at the given VI threshold, assuming an extrapolated total component of  $2 \times 10^4$  ppm-hr.

50% of the total source component. Based on these considerations, the VI threshold was chosen to be 0.1 ppm.

The next step in calculating  $\Delta\text{CO}_2$  was to apply a correction to those periods in the NOAA 1-minute data when the analyzer signal went off-scale, as illustrated in the top trace of Fig. 2. The NOAA analyzers had a range of about 50 ppm, and a manual offset adjustment was periodically made to keep the output voltage approximately centered in this range during background  $\text{CO}_2$  conditions. A strong volcanic plume having excess  $\text{CO}_2$  greater than 25 ppm above background caused the analyzer output to saturate at a constant maximum voltage. This occurred during 72 measurements in 1984, 23 in 1985, 17 in 1986, 5 in 1987, and one each in 1976 through 1981. The curve in figure 4 was used to extrapolate for  $\Delta\text{CO}_2$  at these times. This curve was obtained from over 3000 within-range measurements in 1985 when  $\Delta\text{CO}_2$  was greater than zero. It gives the average fraction of the total  $\Delta\text{CO}_2$  represented by a cumulative number of ascending-ordered 1-minute values. The extrapolation was applied according to the following example. Suppose that only 15 minutes of a measurement interval had within-range  $\Delta\text{CO}_2$ , and that the average  $\Delta\text{CO}_2$  of these was 10 ppm. From Figure 4, this represents 0.5 of the extrapolated 22-minute average  $\Delta\text{CO}_2$ , which would therefore be 20 ppm. Of the 121 measurements in which one or more minutes were over-range, nine had an extrapolated average  $\Delta\text{CO}_2$  of 100 ppm or greater. The maximum extrapolated 22-minute average  $\Delta\text{CO}_2$  was 690 ppm.

### 3.4 Vertical $\Delta\text{CO}_2$ Gradient

The height above the ground from which  $\text{CO}_2$  was sampled varied between 7 meters and 40 meters [Keeling *et al.*, 1982; Komhyr *et al.*, 1989]. Both the SIO and NOAA programs

sampled air from two separate lines each hour. The average hourly  $\Delta\text{CO}_2$  ratio between these lines was calculated (Table 1). When the lines were at the same height, this ratio was within a few percent of 1.00. Ratios from lines at different heights were used to derive the average vertical  $\Delta\text{CO}_2$  profile (Figure 5). This shows that the volcanic plume near MLO was trapped beneath the temperature inversion near the ground [e.g. Hahn *et al.*, 1992; Lee *et al.*, 1993]. The evolution of this phenomena throughout the night is shown in Figure 6. From 2000 LST to about 0100 LST the concentration of the volcanic plume measured at MLO gradually increased. This was likely caused by the strengthening of the surface temperature inversion and downslope wind as the sun-warmed lava slope underwent radiative cooling throughout the evening. Meteorological conditions stabilized after 0100 LST, and the average concentration of the plume was steady until the breakup of the temperature inversion after sunrise.

### 3.5 Long-term $\Delta\text{CO}_2$ Record

The long-term  $\Delta\text{CO}_2$  record is shown in Figure 7. It was derived from SIO data between 1958 and 1975 and NOAA data from 1976 to 1994. Each  $\Delta\text{CO}_2$  measurement (two per hour from separate intake lines) was normalized to a standard sampling height of 23 meters using the ratios given in Table 1 and was used to calculate monthly averages. Hours in which the plume was absent ( $\Delta\text{CO}_2 = \text{zero}$ ) were included in the averages.

The period between August 1968 and April 1971 had

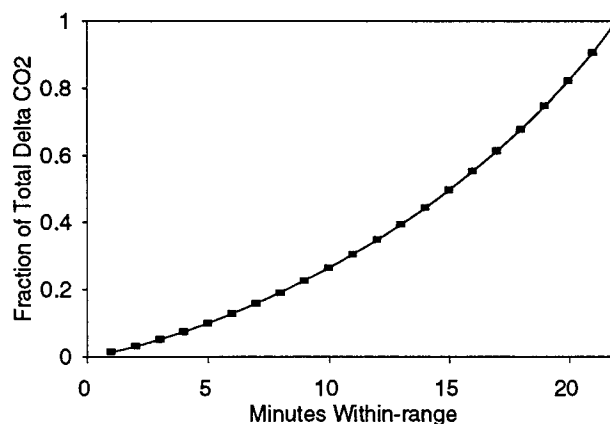


Fig. 4. For each measurement interval, the 1-minute-averaged delta  $\text{CO}_2$  values were arranged in 22 ascending order bins by concentration. The average concentration of each bin was calculated for over 3000 within-range measurement intervals in 1985. This figure shows the cumulative fraction of the total delta  $\text{CO}_2$  represented by a cumulative number of ascending order bins. This relationship was used to estimate delta  $\text{CO}_2$  for those measurement intervals in which one or more minutes had  $\text{CO}_2$  concentrations above the range of the analyzer.

anomalously high nighttime  $\Delta\text{CO}_2$  concentrations. *Keeling et al.* [1982] report that the sampling lines were found broken near the ground several times during this period, possibly contributing to a dramatic increase in daytime  $\text{CO}_2$  "peaks." In the present study, it was assumed that air was sampled near ground level throughout this period, and a 23 meter normalization factor of 3.0 (extrapolated from Figure 5) was applied.

Figure 7 shows a strong association between  $\Delta\text{CO}_2$  and the volcanic activity of Mauna Loa volcano. Eruptions of Mauna Loa occurred in 1950, 1975, and 1984.  $\Delta\text{CO}_2$  increased abruptly shortly after the 1975 and 1984 eruptions and decreased systematically after that.

The month-to-month variability in  $\Delta\text{CO}_2$  was primarily caused by variations in the frequency and efficiency of plume transport to MLO, as suggested by Figure 8. An annual cycle was seen in the monthly frequency of volcanic plume episodes at MLO, with the minimum occurring in winter/spring. Strong free tropospheric winds occurred more frequently during these seasons [e.g. *Harris and Kahl*, 1990] which tended to prevent the plume from reaching MLO, as discussed in section 2.2.

The distribution of  $\Delta\text{CO}_2$  with wind direction is shown in Figure 9. The distribution peaked in the  $180^\circ$  to  $190^\circ$  direction.

TABLE 1.  $\Delta\text{CO}_2$  Ratios at Various Sample Heights

	L1 (m)	L2 (m)	Period	Months	$\Delta\text{CO}_2$ L1/L2
SIO	7	7	05/58 - 02/71	143	0.97
	23	23	04/71 - 09/73	16	1.09
	23	16	10/73 - 12/86	140	<u>0.69</u>
NOAA	13	13	06/77 - 01/80	31	0.98
	23	13	02/80 - 11/84	55	<u>0.58</u>
	23	23	12/84 - 04/88	38	0.97
	40	23	05/88 - 10/93	65	<u>0.87</u>

Ratios Normalized to 23m	
Height	$\Delta\text{CO}_2$ Ratio
40	0.87
23	1.00
16	1.45
13	1.72
7	2.0 (est)
1	3.0 (est)

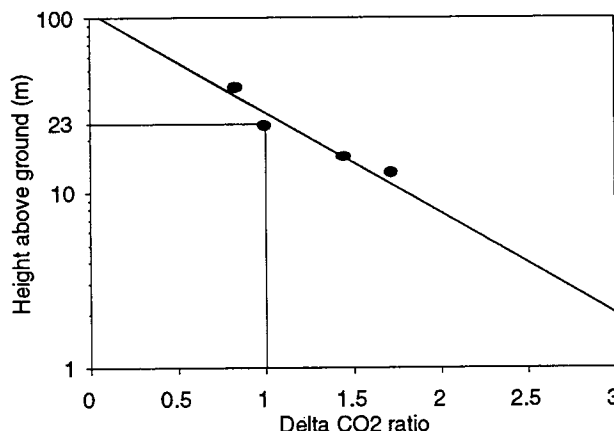


Fig. 5. The vertical profile of delta  $\text{CO}_2$  based on the results in Table 1, and normalized to a standard sampling height of 23 meters. The fit is a logarithmic regression.

This is the bearing to North Pit, identified in section 2.1 as the most likely location for volcanic plume trapped in the surface inversion layer to emerge from the caldera at night. The distribution peak had a full width at half-maximum of about  $40^\circ$ . Nighttime wind directions east of  $110^\circ$  or west of  $260^\circ$  occurred less than 20 hours per year.

#### 4. AEROSOL MEASUREMENTS

##### 4.1 Measurement Methodology

Continuous measurements of atmospheric aerosol particles were begun in January, 1974 when a Meteorology Research Inc. four-wavelength nephelometer was installed to monitor the aerosol light scattering extinction coefficient,  $\sigma_{sp}$ , at wavelengths of 450, 550, 700, and 850 nm [*Bodhaine*, 1978]. The

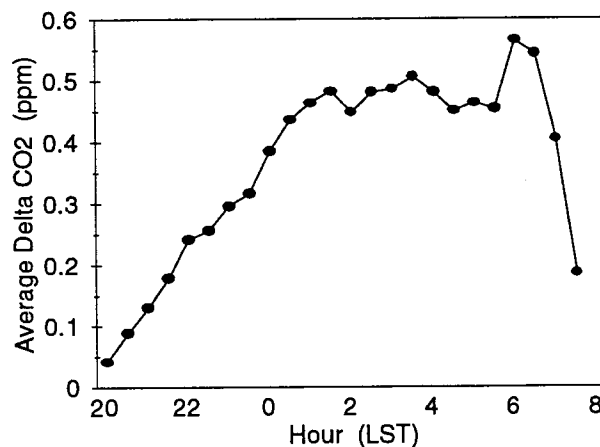


Fig. 6. The average delta  $\text{CO}_2$  as a function of local time between 1977 and 1980. All sampling was done from a height of 13 meters during this period.

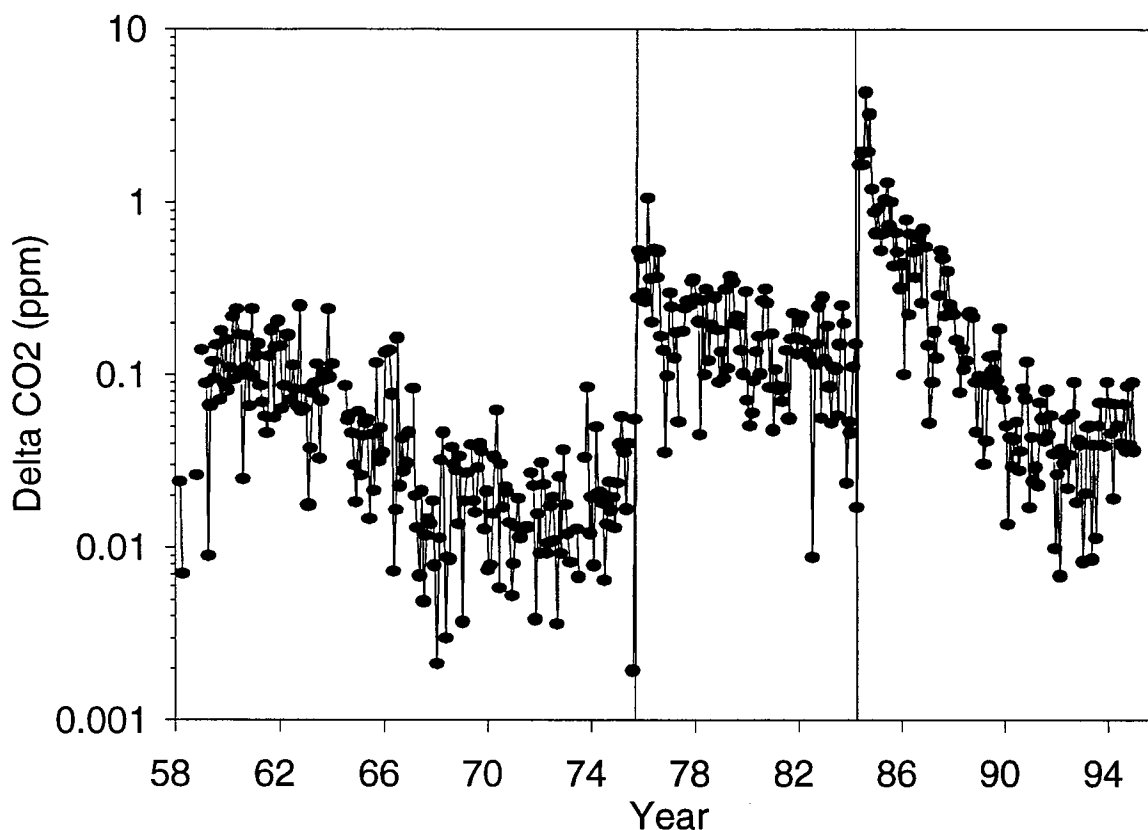


Fig. 7. Monthly average delta CO<sub>2</sub> between 2000 LST and 0759 LST, normalized to a standard sampling height of 23 meters. The 1975 and 1984 eruptions are denoted by vertical lines. Data before 1976 were derived from hand-scaled data obtained by the Scripps Institute of Oceanography and the rest were derived from computer digitized NOAA data.

molecular component of light scattering is typically one to one hundred times greater than the background aerosol component of light scattering. The aerosol component is isolated by real-time subtraction of the signal measured from a filtered air sample, using a 45 minute averaging time constant to obtain a suitable signal to noise ratio. Details of the nephelometer program are given by *Bodhaine* [1983] and *Massey et al.* [1987]. The nephelometer measures particles in the size range of 0.1 to 1.0  $\mu\text{m}$ . In sufficiently large numbers these appear as visible haze.

In May 1975, continuous measurements of condensation nuclei (CN) were begun using a General Electric CN counter. In 1991, this was replaced by an alcohol-based instrument manufactured by Thermo Systems, Inc. (TSI). Details of the CN program are given by *Bodhaine* [1983] and *Massey et al.* [1987]. In the General Electric CN counter, humidified air undergoes a rapid adiabatic expansion, which creates a supersaturation of water vapor. The water vapor condenses around aerosol nuclei, forming a cloud that diminishes the amount of light reaching a photodetector. The attenuated signal minus a dark background signal is used to calculate the number

density of CN. In the modern TSI instrument, alcohol droplets are formed around each CN and are counted individually as they interrupt a laser beam. The condensation nuclei counter responds to particles in the 0.002 to 0.1  $\mu\text{m}$  range. Oxidation of SO<sub>2</sub> forms sulfate aerosols in this size range. There have been no previous studies of Mauna Loa volcanic aerosols. The Mauna Loa volcanic aerosol measured at MLO is young (typically 0.5 hours) and is transported in dry air (relative humidity typically less than 20%).

All aerosol sampling was done from a height of 13 meters. Data were recorded by a computer and on a chart record. The chart record data were visually checked to remove periods of instrument malfunction and local contamination from the final digital data record.

#### 4.2 Nearby Aerosol Sources and Variability

Variations in background aerosols were large compared to variations in background CO<sub>2</sub>. The annual cycle in CN varied by 50% from monthly averages of 218 cm<sup>-3</sup> to 326 cm<sup>-3</sup>. The 550 nm  $\sigma_p$  varied annually by a factor of five, from an average



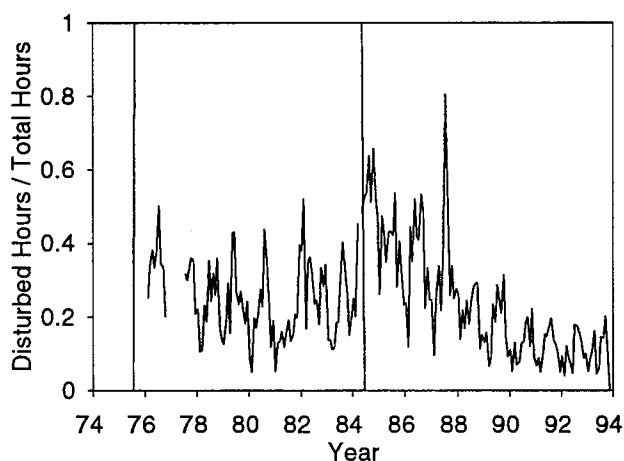


Fig. 8. Monthly fraction of hours between 2000 LST and 0759 LST in which the variability index was greater than 0.1.

November low of  $3.1 \times 10^{-7} \text{ m}^{-1}$  to an April high of  $1.7 \times 10^{-6} \text{ m}^{-1}$  [Massey *et al.*, 1987].

Sources of aerosols on Hawaii were identified by Pueschel and Mendonca [1972]. These sources can be divided into two categories: those at lower altitudes (in the marine boundary layer), and those at or above MLO.

Aerosols from sources in the marine boundary layer were frequently transported to MLO by the daytime upslope winds,

but were mostly absent in the nighttime downslope wind. These included Kilauea volcano (the largest source of condensation nuclei, frequently accompanied by visible haze), combustion from forest fires and sugar cane fires, combustion from anthropogenic activity in coastal towns, and sea salt aerosols. Pueschel and Mendonca [1973] combined visual observations, aerosol measurements at MLO, and thermal energy calculations to show that Kilauea aerosols could penetrate the trade wind inversion (at an altitude of 1700 m) during an episode of active fountaining, but not during a subsequent period of flowing surface lava. This implied that direct injection of Kilauea aerosols above the inversion into the free troposphere was only possible on those rare occasions of active fountaining.

Aerosols from the vicinity of MLO came primarily from infrequent automobile traffic, which occurred almost entirely during the day. The only identified nearby source of aerosols from altitudes above MLO was Mauna Loa volcano itself [Bodhaine *et al.*, 1980].

#### 4.3 $\Delta \text{CN}$ and $\Delta \sigma_p$ Records

Most of the aerosol data were recorded by computer as 10 minute averages and processed as hourly averages. It was therefore impossible to identify aerosol plume events on the basis of minute-scale variability in aerosol data. Because of this, variability in  $\text{CO}_2$  (as described earlier) was used to

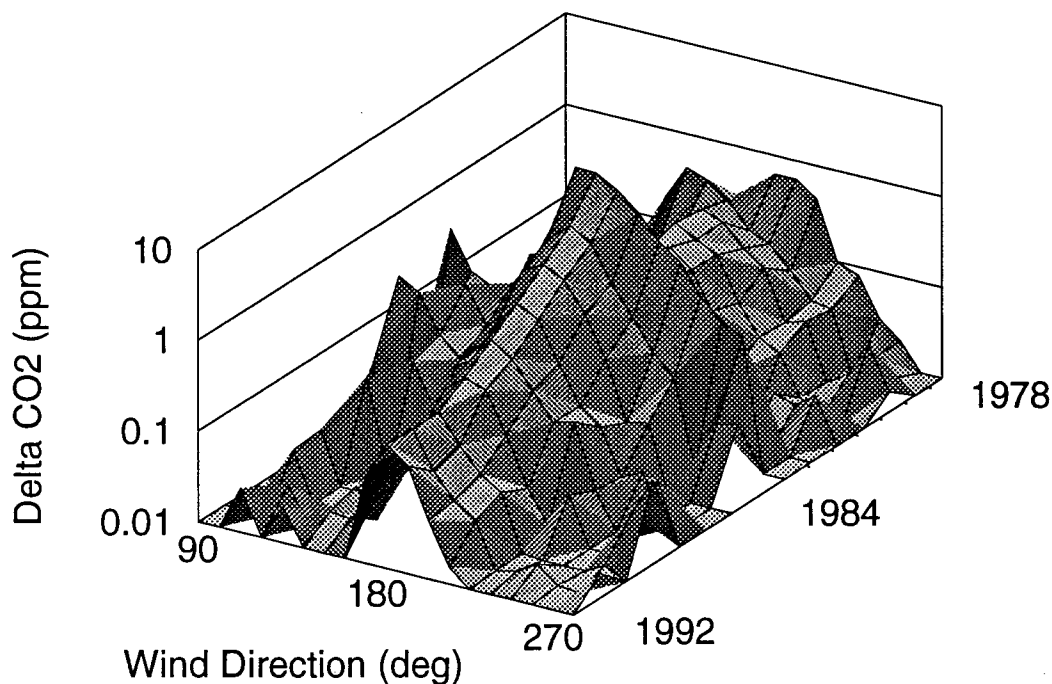


Fig. 9. Yearly average delta  $\text{CO}_2$  between 2000 LST and 0759 LST in 10 degree wind direction bins from 1978 to 1992. Delta  $\text{CO}_2$  was normalized to a standard sampling height of 23 meters. Winds outside of 110 to 260 degrees blew too infrequently to yield statistically significant delta  $\text{CO}_2$  averages.

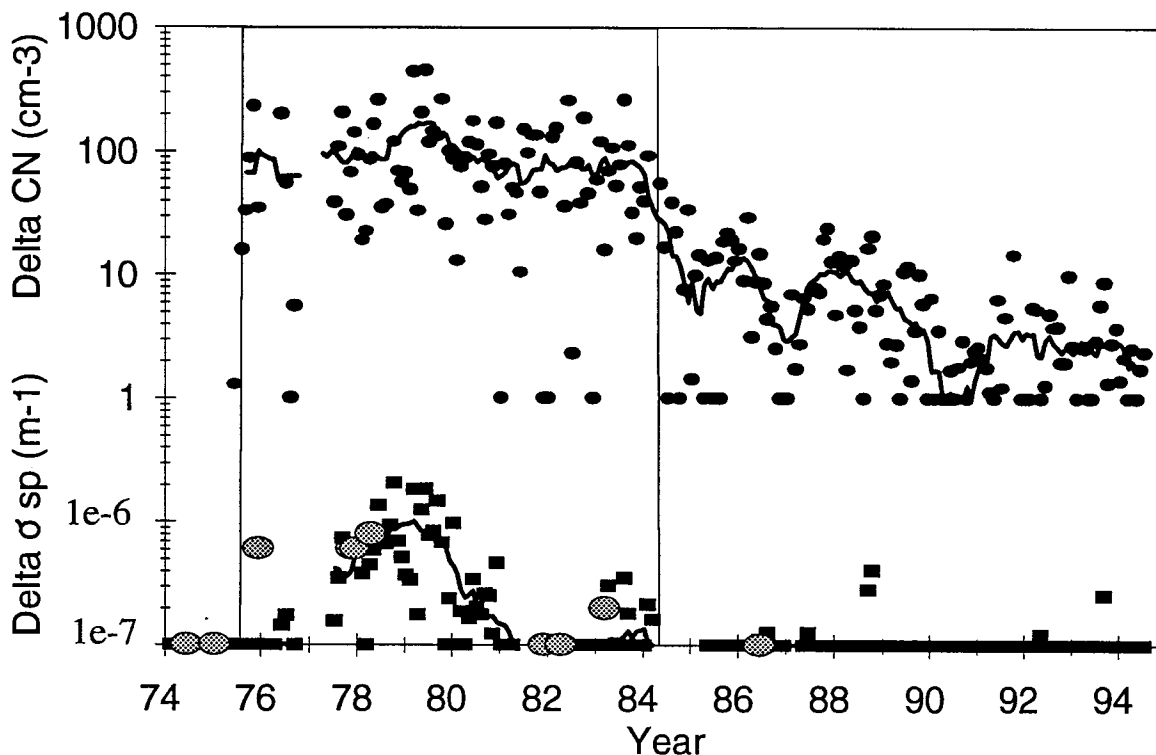


Fig. 10. Monthly average delta aerosols between 0000 LST and 0759 LST measured from a sampling height of 13 meters. Vertical lines denote the 1975 and 1984 eruptions. The fits are 12 month running means. Delta CN less than  $1 \text{ cm}^{-3}$  is plotted as  $1 \text{ cm}^{-3}$ . Delta 550nm light scattering less than  $1 \times 10^{-7} \text{ m}^{-1}$  is plotted as  $1 \times 10^{-7} \text{ m}^{-1}$ . The solid circles with the light scattering data indicate the visual thickness of fume at the caldera vents estimated from aerial photographs on a scale of zero to five and then linearly scaled between  $1 \times 10^{-7} \text{ m}^{-1}$  and  $1 \times 10^{-6} \text{ m}^{-1}$ .

identify the presence of volcanic plume or the presence of background conditions. Calculations of  $\Delta \text{CN}$  and  $\Delta \sigma_{\text{sp}}$  were then made in the same way as for  $\Delta \text{CO}_2$ .

Bodhaine [1978] noted that the best time for sampling background aerosols was between 0100-0700 LST. On average, the downslope wind pattern did not become fully developed until after midnight (as suggested by Figure 6). Unlike  $\text{CO}_2$ , the background aerosol concentration at MLO typically had a factor of 10 diurnal variation, which was due to the upslope transport of aerosol-rich marine boundary layer air in the afternoon. Evening hours between 2000 LST and 0000 LST commonly had steady background levels of  $\text{CO}_2$  while the corresponding aerosol concentrations were still decreasing from high afternoon levels [Clarke and Bodhaine, 1993]. This was more evident in the nephelometer data (which had a 45 minute averaging time constant) than the CN data (which had a 0.2 second response time). When contaminated evening hours were misidentified as having background aerosol levels, the interpolated background later in the night was over-estimated, frequently resulting in negative  $\Delta \text{CN}$  and  $\Delta \sigma_{\text{sp}}$  values. Inadvertent background contamination was minimized

by restricting delta aerosol calculations to the stable period between 0000 LST and 0759 LST.

The complete  $\Delta \text{CN}$  and  $\Delta \sigma_{\text{sp}}$  (550 nm) record is shown in Figure 10. Volcanic aerosols behaved differently from volcanic  $\text{CO}_2$ . The post-1975 quiescent period had higher levels of  $\Delta \text{CN}$  and  $\Delta \sigma_{\text{sp}}$  than the post-1984 period. Since all aerosol data were measured from the same height above the ground, the vertical distribution of the aerosol plume could not be derived.

To find out if  $\Delta \sigma_{\text{sp}}$  was a measure of the intensity of visible fume from the volcano, a comparison was made with a series of aerial photographs taken of the summit caldera area (J. Lockwood, pers. com., 1993). In each photograph the relative size and opacity of the visible plumes, which emanated from location ML3 (Figure 1), were estimated on a scale of zero to five, with five being the most intense. The estimates were not corrected for the effects of wind speed and relative humidity on the opacity of the visible fume. These estimates were compared with the  $\Delta \sigma_{\text{sp}}$  data in Figure 10 (where a value of zero was scaled to  $1 \times 10^{-7} \text{ m}^{-1}$  and a value of five was scaled to  $1 \times 10^{-6} \text{ m}^{-1}$ ). The subjective photographic data gave supporting evidence that  $\Delta \sigma_{\text{sp}}$  was a measure of the visible fume from

Mauna Loa. It showed the high levels of 1978, the cessation of visible fuming in 1981-82, and a return to low levels of visible fuming in 1983. The two records only disagreed once out of ten times, in late 1976, when the photographic evidence suggested a greater degree of fuming than the light scattering data.

At those times when measurable fume was present,  $\Delta\sigma_{sp}$  measured by the four channels was systematically greater at shorter wavelengths. This showed that the peak of the aerosol size distribution occurred at a particle size smaller than about 0.3  $\mu\text{m}$ .

## 5 TRACE SPECIES MEASUREMENTS

### 5.1 Measurement Methodology

The following species were analyzed using the method outlined in the preceding sections:  $\text{H}_2\text{O}$ ,  $\text{CO}$ ,  $\text{H}_2$ ,  $\text{SO}_2$ ,  $\text{O}_3$ ,  $\text{CH}_4$ , Radon<sub>222</sub>, and aerosol Black Carbon.

Water vapor was measured from a height of 2 m using a dew cell from 1974 to 1981, and a dew point hygrometer after 1981. Temperature was measured by a thermograph before 1975, and after that by an aspirated, shielded thermocouple at a height of 2 m [Herbert *et al.*, 1987]. Hourly water vapor mixing ratios were calculated from measured dew point, temperature, and pressure observations.

Carbon monoxide and hydrogen were sampled from a height of 40 m using a Trace Analytical Reduction Gas Analyzer gas chromatograph [Novelli *et al.*, 1991]. The instrument precision for CO was approximately 0.5 ppb [Ferguson and Rosson, 1991; Novelli *et al.*, 1991]. The data used here were unedited preliminary results from 1992 and 1993 [P. Novelli, pers. com., 1994]. The chromatograms have a hydrogen peak that was not analyzed as part of the climatological monitoring program (the concentration of hydrogen in the reference tank was not measured). Hourly hydrogen concentrations provided for the present study were based on an arbitrary assignment of 100 ppb to the reference tank  $\text{H}_2$  concentrations, and may have been systematically low by a factor of five.

Sulfur dioxide was measured by a Thermo Environmental Instruments (TEI) model 43S pulsed fluorescence analyzer. From December 1988 to November 1989 an instrument was operated by the NOAA Air Resources Laboratory from a sampling height of 13 m, with a 1-hour detection limit of 41 ppt [Luria *et al.*, 1992]. From September 1991 to August 1992, an identical instrument was operated intermittently as part of the MLOPEX-II experiment from a sampling height of 7 m [Hubler, 1993, Hubler pers. com., 1993]. A program designed specifically to detect  $\text{SO}_2$  in the Mauna Loa plume was started in June 1994 and continues to the present. It also uses a TEI model 43S analyzer, sampling alternatively from heights of 4 m and 34 m. Zero- $\text{SO}_2$  measurements are made twice per hour

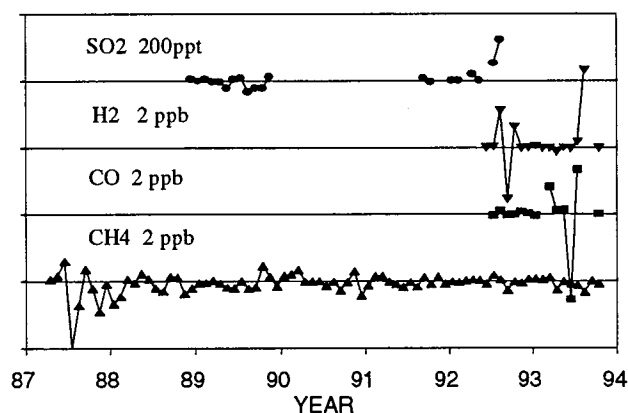


Fig. 11a. Monthly average delta values of four trace gas species between 0000 LST and 0759 LST from 1987 and 1993. The scale interval for the upper trace ( $\text{SO}_2$ ) is 200 ppt. The scale interval for the lower three traces is 2 ppb.

for 10 minutes each. A 10 ppm reference gas is injected into the high-volume sampling line to obtain a 1.2 ppb calibration twice daily with a 120 ppt to 5 ppb six-point calibration made every 10 days. The 95% confidence detection limit for a 20 minute measurement is 30 ppt.

Radon ( $\text{Rn}_{222}$ ) was measured from a height of 40 m by an instrument built by the DOE Environmental Research Labs [Thomas and LeClare, 1970; Negro, 1979]. The half-hour detection limit was 70  $\text{mBq m}^{-3}$  in 1991 and 1992, and was 30  $\text{mBq m}^{-3}$  in 1993. Radon measurements at MLO are discussed by Whittlestone *et al.* [1992].

Ozone was measured from a height of 13 m by an electrochemical concentration cell [Komhyr, 1969] from 1974 to 1976, and by a Dasibi ultraviolet photometer from 1976 to 1993 [Oltmans, 1981; Oltmans and Komhyr, 1986].

Methane was measured from a height of 23 m between 1987 and 1991 and from 40 m after that using a Carle Series 400 gas chromatograph with flame ionization detection [Ferguson and Rosson, 1992; Masarie *et al.*, 1991].

Aerosol black carbon was measured from a height of 13 m starting in 1990 using an aethalometer [Hansen *et al.*, 1984; Gundel *et al.*, 1984].

### 5.2 Delta Analysis for Trace Species

Hourly delta values were calculated for the eight trace species listed using the method described in section 4.3 for aerosols. Calculations were restricted to the period between 0000 LST and 0759 LST to reduce the possibility of inadvertent contamination from residual marine boundary layer air which occasionally persisted into the late evening hours. Results are shown in Figure 11 and Table 2. The long-term average monthly delta values for seven of the species

TABLE 2. Monthly Average Delta Trace Species

Species	Period	Months	Avg. $\Delta$ Species	$2\sigma$
H <sub>2</sub> O	1974-1993	196	-7 ppm	32 ppm
CO	1992-1993	14	4 ppt	1.6 ppb
H <sub>2</sub>	1992-1993	16	0.2 ppb	1.5 ppb
SO <sub>2</sub>	1988-1992	20	6 ppt	64 ppt
SO <sub>2</sub>	1994-1995	8	2.8 ppt	4.4 ppt
O <sub>3</sub>	1974-1993	204	-0.3 ppt	215 ppt
CH <sub>4</sub>	1987-1993	79	70 ppt	640 ppt
Carbon	1990-1993	33	-0.3 ng m <sup>-3</sup>	3.5 ng m <sup>-3</sup>
Radon	1991-1993	27	1.8 mBq m <sup>-3</sup>	3.5 mBq m <sup>-3</sup>

(excluding radon) were not significantly different from zero. Three species with long data records, H<sub>2</sub>O, O<sub>3</sub>, and CH<sub>4</sub>, showed no trends or systematic changes associated with the eruptive cycle of Mauna Loa.

The detection limit at the 95% confidence level for each species was taken as two standard deviations about the mean, and is given in Table 2. This represented an upper limit to the volcanic contamination potentially present in an unedited, monthly averaged climatological baseline data set.

Delta radon averaged 1.8 mBq m<sup>-3</sup> (with a monthly standard deviation of 1.7 mBq m<sup>-3</sup>) between 1991 and 1993. Since radon is known to emanate from Mauna Loa lavas [Wilkening, 1974], a rough calculation was made to determine if the upper slopes of Mauna Loa could have been the source of this excess radon rather than the volcanic plume. Wilkening [1974] reported an average radon flux of 0.012 atoms cm<sup>-2</sup> sec<sup>-1</sup> for Mauna Loa and Cape Kumukahi lavas. If all the radon emanating from the slope above MLO was trapped in the nighttime inversion layer and uniformly mixed to a height of 50 m at an average downslope wind speed of 3.4 m s<sup>-1</sup>, the resultant radon activity at MLO (6 km from the summit) would be 30 mBq m<sup>-3</sup>. This is significantly greater than 1.8 mBq m<sup>-3</sup>, the average delta radon activity. Conditions that favored the transport of volcanic plume (i.e. light winds and a strong surface temperature inversion) would have also created the greatest atmospheric concentrations of ground-emanated radon at MLO [Whittlestone *et al.*, 1993]. This effect could easily account for the small positive delta radon observed. It is therefore concluded that no volcanic radon was present in the plume at a detection limit of 3.5 mBq m<sup>-3</sup>.

## 6. INTERPRETATION OF RESULTS

### 6.1 Short-term Variations in $\Delta$ CO<sub>2</sub>

Variations in  $\Delta$ CO<sub>2</sub> on short time-scales (hours-to-weeks) before and after the 1975 and 1984 eruptions were examined. The amount of CO<sub>2</sub> reaching MLO depended on two factors; the volcanic emissions rate and the airflow pattern between the point(s) of emission and the observatory. To reduce the effects of airflow variations, hourly data were selected in which the observatory wind direction was within a 45° sector centered on 180° and the wind speed was between 2 and 5 m s<sup>-1</sup>. These conditions were most favorable for plume transport to MLO (Figure 9). These data are shown for 2-year periods centered on the 1975 and 1984 eruptions (Figure 12). Data was missing for 35 days following the start of the 1984 eruption because the lava flow cut the power to MLO.

No significant increase in hourly  $\Delta$ CO<sub>2</sub> averages occurred in the twelve months preceding either the 1975 or 1984 eruption. The probability that a random, short-duration outgassing event would have been detected at MLO depends upon the frequency of wind conditions favorable for plume transport. Detection probabilities were calculated for a 1-week period prior to each eruption under the assumption that a random event would be detected only if it occurred between 2000 LST and 0659 LST when the hourly average wind direction was within a 45-degree sector centered on 180°. No events would have been detected for 24 hours before the 1975 eruption, which started at 2342 LST on July 5 [Lockwood *et al.*, 1987]. In the seven days preceding this eruption, the probabilities of detecting events with durations of 1 hour, 10 hours, and 24 hours were 21%, 63%, and 89% respectively. No events would have been detected for 90 hours prior to the 1984 eruption, which began at 0125 LST on March 25 [Lockwood *et al.*,

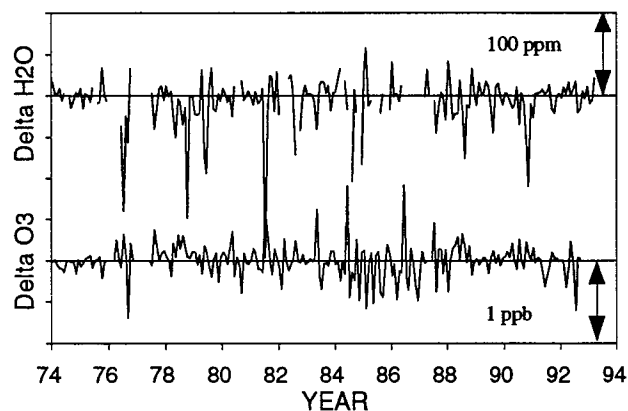


Fig. 11b. Monthly average delta values for water vapor (top, scale interval of 100 ppm) and ozone (bottom, scale interval of 1 ppb) between 0000 LST and 0759 LST from 1974 to 1993.

1987]. The probabilities of detecting events with durations of 1 hour, 10 hours, and 24 hours in the week before this eruption were 15%, 32%, and 46% respectively.

After the 1975 eruption, there was a period of 65 days in which every wind-selected hour had  $\Delta\text{CO}_2 = \text{zero}$ . On day 65, there was an hour in which  $\Delta\text{CO}_2$  was 1.7 times greater than any hourly value that occurred in the year before the eruption. This shows that enhanced outgassing was delayed by about 65 days following the end of the 1975 eruption. The eruption ended with magma venting at an elevation of 3700 m [Lockwood *et al.*, 1987]. If the primary source of  $\text{CO}_2$  was a recently recharged magma reservoir at 3 km depth [Decker *et al.*, 1983] (equivalent to an elevation of 1000 meters above sea level), it would follow that the newly exsolved bubbles would have to rise through a 2700 m column to reach the surface. A bubble rising 2700 m in 65 days would have an average ascent rate of  $1.7 \text{ m hr}^{-1}$ .

Following the end of the 1984 eruption, MLO was without power for 14 days. For 6 days after this, every wind selected hour had  $\Delta\text{CO}_2 = \text{zero}$ . Then on May 6, there were several hours with an elevated  $\Delta\text{CO}_2$ , the highest being 1.7 times greater than any hourly value that occurred in the year preceding the 1984 eruption. This shows that enhanced outgassing was first observed 21 days after the end of the 1984 eruption, although the power outage caused a data black-out for the first 14 days. During this time, atmospheric air samples were collected almost daily in glass flasks for later analysis. Most were exposed during periods when the winds brought clean, baseline air to MLO. Fortunately, four flask samples were collected while MLO was in "heavy fumes" (according to the observers logbook) on the morning of April 24. These flasks had  $\text{CO}_2$  concentrations averaging 4.7 ppm above a baseline concentration estimated from clean air samples taken on April 20 and April 25. This is 1.2 times greater than the maximum hourly  $\Delta\text{CO}_2$  measured in the year preceding the eruption. It suggests that enhanced outgassing of  $\text{CO}_2$  was present 9 days after the end of the 1984 eruption. Direct measurements of vented gas by Greenland [1987] show that  $\text{CO}_2$  was becoming enriched relative to  $\text{SO}_2$  on April 18, three days after the end of the eruption.

## 6.2 Pre-Eruption Trends in $\Delta\text{CO}_2$

Variations in  $\Delta\text{CO}_2$  on time-scales of months-to-years were examined before the 1975 and 1984 eruptions. Gerlach [1986] suggested that, for Kilauea volcano, monitoring summit emissions might show variations in the rate of supply of parental magma to the summit magma chamber and provide a tool for eruption forecasting. This idea was tested for Mauna Loa using the  $\text{CO}_2$  outgassing record.

Examination of Figure 7 shows that the exponential decrease of  $\Delta\text{CO}_2$  that occurred throughout the 1960's leveled off

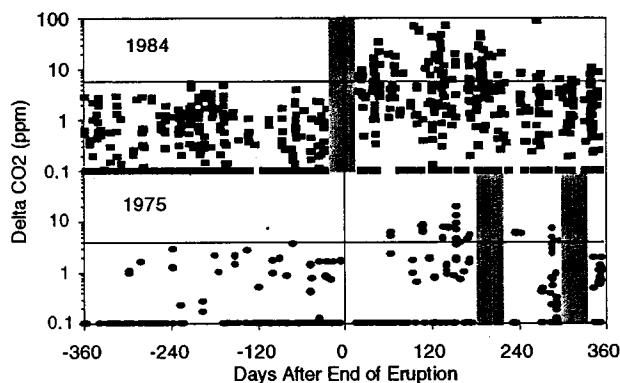


Fig. 12. Hourly  $\Delta\text{CO}_2$  between 0000 LST and 0659 LST selected for winds between 158 and 202 degrees with wind speeds between 2 and 5 m/s. Hours with  $\Delta\text{CO}_2$  less than 0.1 ppm (primarily including  $\Delta\text{CO}_2 = 0$  ppm) are plotted as 0.1 ppm. Periods with missing  $\text{CO}_2$  or wind data are left blank. The horizontal lines give the maximum hourly  $\Delta\text{CO}_2$  which occurred during the 360 days before the start of each eruption.

sometime after 1970. There may have been a slight increase of about 0.015 ppm in the trend of  $\Delta\text{CO}_2$ , beginning two to three years before the 1975 eruption. As mentioned in section 3, the data taken before 1976 were recorded on a first-generation analyzer, were hand scaled, and were subjectively selected for variability. These and other factors may have contributed to drifts in  $\Delta\text{CO}_2$  that were not related to changes in volcanic emissions, so caution must be exercised in drawing conclusions from the pre-1976 data. There was no apparent increase before the 1984 eruption, but  $\Delta\text{CO}_2$  at this time was about a factor of 10 greater than in 1972-73. An increase of 0.015 ppm would represent a 10% change in pre-1984 levels and may not have been detectable.

An increasing trend in  $\Delta\text{CO}_2$  began in early 1993 and continued up through the most recent data available for this paper, January 1995 (Figure 7). Based on a 1-year running mean,  $\Delta\text{CO}_2$  increased by almost 0.02 ppm, from 0.034 ppm to 0.053 ppm. The distribution of  $\Delta\text{CO}_2$  with wind direction (Figure 13) changed dramatically between 1992 and 1993-1994. The height of the peak in the distribution near  $180^\circ$  decreased by a factor of two while there was a large increase in  $\Delta\text{CO}_2$  from both the southeast and southwest directions, being greatest at  $230^\circ$ . The broadening of the  $\Delta\text{CO}_2$  distribution observed in 1994 was unprecedented in the 37-year record. Annual average ratios of  $\Delta\text{CO}_2$  were calculated between the  $135^\circ \pm 22.5^\circ$  (southeast) and  $180^\circ \pm 22.5^\circ$  (south) sectors, and between the  $225^\circ \pm 22.5^\circ$  (southwest) and  $180^\circ \pm 22.5^\circ$  (south) sectors. A flat distribution would have a ratio near 1.0 and a distribution sharply peaked near  $180^\circ$  would have a ratio approaching 0.0. In every year from 1958 to 1992, the calculated ratios were all less than 0.35, with an average of

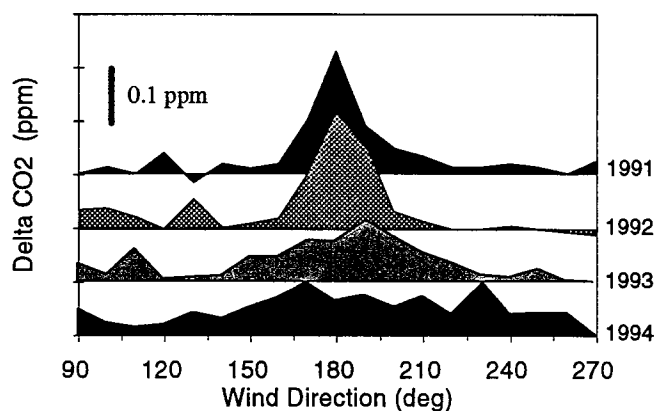


Fig. 13. Average delta  $\text{CO}_2$  as a function of wind direction in 10 degree bins for 1991-1994. The distributions are each displaced by 0.1 ppm for clarity.

0.15. In 1994, the southeast to south ratio was 0.7 and the southwest to south ratio was 0.9.

The changes in  $\Delta\text{CO}_2$  observed in 1993-94 were not due to changes in wind patterns or the performance of the  $\text{CO}_2$  analyzer. There were no significant changes in the annual MLO wind direction frequency distributions, the average MLO wind speeds partitioned by wind direction, or the noise level of the analyzer reference gas signal between 1991 and 1994. Increases in  $\Delta\text{CO}_2$  from the southeast and southwest could have potentially come from a source other than Mauna Loa volcano, but this is considered unlikely as described in section 3.2. Kilauea volcano emissions reaching MLO, which typically have  $\text{SO}_2$  to  $\text{CO}_2$  ratios greater than 0.1, would have been accompanied by a large increase in  $\text{SO}_2$ , which was not observed.

There have been no detailed studies of the airflow patterns around the summit of Mauna Loa that would allow the location of a new source(s) to be identified based on the  $\Delta\text{CO}_2$  distribution. The most likely location(s) for a volcanic source outside the caldera are one or both of the rifts [Casadevall and Hazlett, 1983]. The simplest interpretation is that the northeast rift was the source of increased  $\Delta\text{CO}_2$  from the southeast and the southwest rift was the source of  $\Delta\text{CO}_2$  from the southwest. From a historical perspective, this is perhaps unlikely, since one or the other, but not both, rifts tend to be active at one time [Lockwood and Lipman, 1987]. A second possibility is that there is a single source on the southwest rift. When the free-tropospheric winds blow from the southwest, MLO is on the leeward side of the mountain. Under these conditions, a plume originating on the southwest rift would travel equal distances around the mountain to arrive at MLO from either the southwest or the southeast (Figure 1). The northeast rift is unlikely to be the only source since the plume would have to travel clockwise about 330 degrees to arrive at MLO from the southwest.

In summary, it appears that the outgassing behavior of Mauna Loa has undergone an unprecedented transition during the last two years. The  $\text{CO}_2$  emissions coming from the summit have continued to decline, while  $\text{CO}_2$  emissions coming from a source or sources located high on the southeast rift (or possibly both rifts) have apparently increased. This has resulted in a net increase in  $\Delta\text{CO}_2$  measured at MLO. Although the size of this increase has thus far been small (0.02 ppm), it is similar in size to an increase that may have preceded the 1975 eruption. This activity could be an early precursor to the next eruption. The magma responsible for the increase in  $\text{CO}_2$  must be at a depth great enough not to cause increases in either  $\text{SO}_2$  or sulfate (CN), which have not been observed.

### 6.3 Mass Estimate of $\text{CO}_2$ Emissions

The annual  $\text{CO}_2$  mass emission rate of Mauna Loa volcano was estimated based on the observatory measurements of  $\Delta\text{CO}_2$  as a function of wind direction (Figure 9) and height above the ground (Figure 5) shown earlier. The following assumptions were made:

1. The plume measured at MLO was fully trapped in the surface temperature inversion between the hours of 0000 LST and 0759 LST (Figure 6).
2. Variations in  $\Delta\text{CO}_2$  caused by changing meteorological transport conditions could be eliminated by taking yearly averages.
3. At night, all of the  $\text{CO}_2$  in the plume was trapped in the surface temperature inversion and transported down the slope. This assumption had no supporting evidence. The degree to which the plume was trapped in the inversion layer has never been measured. To the extent that part of the plume may have escaped directly into the free troposphere, the  $\text{CO}_2$  emissions estimate based on this assumption would represent a lower limit.
4. The average normalized vertical profile of the plume  $\text{CO}_2$  6 km downslope from the summit was given by Figure 5. The integrated area under this curve is equivalent to a 79 meter column having a uniform ratio of 1.0.
5. The distribution of  $\Delta\text{CO}_2$  with wind direction was observed to have a full width at half-maximum of 40 degrees (section 3.5). This was assumed to be the azimuthal extent ("width") of the plume 6 km downslope from the summit.
6. The average speed of the plume 6 km downslope from the summit was 3.4 m/s. This was the climatological average of the nighttime downslope component of wind velocity measured at a height of 8.5 meters.

$\text{CO}_2$  mass emissions were calculated as follows. The plume was contained in a three-dimensional pie-shaped segment originating at the summit with a radius of 6 km, an angle of 40 degrees (from assumption 5), and a scale height of 79 meters (from assumption 4). The downslope vertical face of the

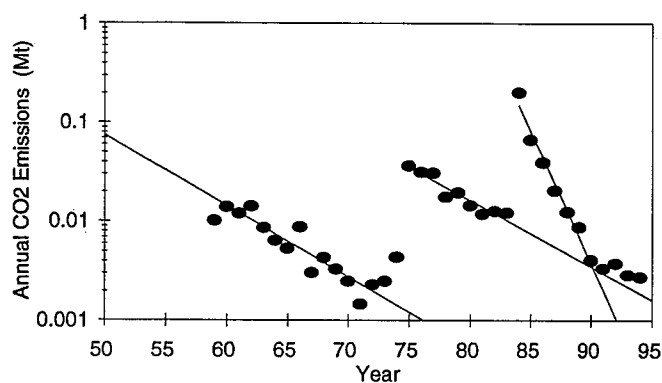


Fig. 14. Estimated annual output of CO<sub>2</sub> from the summit area of Mauna Loa volcano using the transport model described in the text. Yearly averages are taken for calendar years except for the years occurring on either side of an eruption. These are the 365 day intervals before and after the date of the start of the eruption. The fits are logarithmic regressions to the 1960-1973, 1975-1983, and 1984-1989 points respectively. One Mt equals 10<sup>9</sup> kg.

segment had an area of 3.3 X 10<sup>5</sup> m<sup>2</sup>. The volume of air moving at 3.4 m s<sup>-1</sup> (from assumption 6) through this face was 1.1 X 10<sup>6</sup> m<sup>3</sup> s<sup>-1</sup>. At the 680 mb average atmospheric pressure of MLO, one ppm of CO<sub>2</sub> is equivalent to 1.06 X 10<sup>-6</sup> kg m<sup>-3</sup> CO<sub>2</sub>. The total mass of CO<sub>2</sub> emerging from the segment face, equivalent to the emission rate of the source, is therefore 1.2 kg s<sup>-1</sup> ppm<sup>-1</sup>. Over one year, an average MLO plume concentration of one ppm is equivalent to an emission of 3.7 X 10<sup>7</sup> kg CO<sub>2</sub>. The plume concentration was taken as the annual average ΔCO<sub>2</sub> between 0000 LST and 0759 LST (assumption 1) when the wind was in a 45° sector centered on 180°.

Annual CO<sub>2</sub> emission estimates from the Mauna Loa summit between 1959 and 1994 are shown in Figure 14. Logarithmic regressions were calculated for the three post-eruptive periods. The fit to the 1960-1973 period was extended back in time to obtain an estimated emissions of 7.4 X 10<sup>7</sup> kg for 1950, the year of the previous eruption. The area under each fit, integrated from the year of the eruption to T = infinity, was

taken as an estimate of the total mass of CO<sub>2</sub> in each quiescent reservoir. These results are listed in Table 3 along with the eruptive volume of the preceding eruption, taken from *Lockwood and Lipman* [1987].

The emissions estimated in Table 3 can be compared with measurements of the CO<sub>2</sub> emission rate during the 1984 eruption [*Casadevall et al.*, 1984], which ranged between 2.4 X 10<sup>5</sup> kg day<sup>-1</sup> and 1.4 X 10<sup>6</sup> kg day<sup>-1</sup>. If the average emission rate was the mean of these extreme values, the total mass of CO<sub>2</sub> produced during the 21 days of the 1984 eruption would have been 1.7 X 10<sup>7</sup> kg. This represents about 5% of the average quiescent reservoir mass of CO<sub>2</sub> from Table 3, suggesting that much more CO<sub>2</sub> is degassed during quiescent periods than during eruptions.

The volume of magma required to supply a given reservoir quantity of CO<sub>2</sub> can be estimated using the CO<sub>2</sub> barometer of *Harris* [1981] and the model of *Gerlach* [1986]. The dissolved component of CO<sub>2</sub> as a function of pressure is taken to be 5.9 X 10<sup>-4</sup> wt % MPa<sup>-1</sup> and the magma density is assumed to be 2.6 X 10<sup>3</sup> kg m<sup>-3</sup>. The 1984 eruption produced 2.2 X 10<sup>8</sup> m<sup>3</sup> of lava [*Lockwood et al.*, 1987], equivalent to 5.7 X 10<sup>11</sup> kg of magma. The average quiescent reservoir mass of CO<sub>2</sub> (from Table 3) was 3.5 X 10<sup>8</sup> kg. A mass of magma equivalent to that erupted in 1984 would lose 0.061 wt % CO<sub>2</sub> in outgassing the mass of CO<sub>2</sub> lost during quiescence. This represents a magma decompression of 103 MPa, equivalent to an ascent of 4.1 km, which is comparable to the vertical scale size of the magma system beneath Mauna Loa based on seismic evidence [e.g. *Lockwood et al.*, 1987]. The mass estimates of quiescent CO<sub>2</sub> emissions reported here are therefore consistent with the view that bodies of magma degas in a shallow summit chamber before being erupted.

The quiescent reservoir mass of CO<sub>2</sub> was similar for all three periods, yet the volume of the 1975 eruption was much less than the volumes of the 1950 and 1984 eruptions (Table 3). This suggests that a large fraction of the 1975 magma did not erupt, consistent with seismic evidence of magma intrusion into the northeast rift during and following that eruption [*Lockwood et al.*, 1987].

TABLE 3. Estimated CO<sub>2</sub> Emissions From Mauna Loa Summit

Period Fit	r <sup>2</sup>	1/e (years)	Σ Mass (10 <sup>8</sup> kg CO <sub>2</sub> )	Previous Eruption	Initial Rate (10 <sup>7</sup> kg CO <sub>2</sub> yr <sup>-1</sup> )	Lava Volume (10 <sup>6</sup> m <sup>3</sup> )
1960-73	0.86	6.1	4.8 (est) ??	1950	7.4 (est) ??	376
1975-83	0.89	6.5	2.4	1975	3.5	30
1984-89	0.97	1.6	3.3	1984	15.0	220

TABLE 4. Ratio of Gas Species to CO<sub>2</sub> in the Plume

Period	H <sub>2</sub> O	CO	H <sub>2</sub>	SO <sub>2</sub>
01/74 - 12/74	< 390			
01/78 - 12/78	< 350			
06/84 - 05/85	< 47			
12/88 - 11/89	< 270			< 1.0 X 10 <sup>-4</sup>
09/91 - 08/92	< 540			< 1.8 X 10 <sup>-3</sup>
01/92 - 12/93	< 470	< 3.1 X 10 <sup>-2</sup>	< 3.0 X 10 <sup>-2</sup>	
06/94 - 01/95				7 X 10 <sup>-5</sup>
4/18/84 vent sample [Greenland, 1987]	21.4	1 X 10 <sup>-3</sup>	1.6 X 10 <sup>-2</sup>	1.65

An exponential regression provided an excellent fit ( $r^2 > 0.85$ ) to the CO<sub>2</sub> emissions data for all three quiescent periods (Figure 14). This characteristic is predicted by *Johnson* [this volume], who suggests that Mauna Loa's summit reservoir is rapidly resupplied with a large influx of fresh magma from a deeper source while an eruption is in progress. The new magma enters the reservoir from below but does not mix quickly enough to be part of the eruption. If the rate of magma resupply to the summit reservoir during the subsequent repose is low, this fresh body of magma would be the primary source of quiescent CO<sub>2</sub> emissions. It would degas as a single batch with a characteristic exponentially decaying rate.

Following both the 1975 and 1984 eruptions, there were periods of several months when  $\Delta$ CO<sub>2</sub> was greater than the subsequent exponential decay rate would predict (Figure 7). This could mean that the period of rapid refilling of the summit reservoir proposed by *Johnson* [this volume] continued for several months beyond the end of the eruption.

Between 1984 and 1989, CO<sub>2</sub> emissions decreased at a rate that should have resulted in an estimated output of  $3 \times 10^5$  kg CO<sub>2</sub> by 1994. The observed emissions in 1994 were almost 10 times greater than this, so an additional source must have been present. It is interesting that the fit to the 1975-1983 data comes close to fitting the 1990-1994 data points as well (Figure 14). This is unlikely to be a coincidence. It suggests that the excess emissions observed after 1990 came from the same source that was outgassing between 1975 and 1984, and that the 1984 eruption did not affect the exponentially decaying CO<sub>2</sub> emissions rate of this source. This implies that the post-1975 magma body remained physically separate from and was not disrupted by the emergence of the post-1984 magma body. Therefore, the post-1975 magma was not the source of the 1984 eruption, in agreement with the conclusions of *Lockwood et al.* [1987] and *Rhodes* [1988] based on lava chemistry evidence. After 1984, there were two independent magma bodies degassing CO<sub>2</sub> from the vicinity of the summit caldera.

#### 6.4 Gas Ratios in the Plume

For gas species that do not react or fractionate during atmospheric transport in the plume, the ratio of the delta values as measured at MLO is equivalent to the emission ratio at the source. Changes in this ratio over time may be directly related to the volcanic processes that produce the gases.

Four of the trace gases examined in section 5 were measured in vent samples taken by *Greenland* [1987] four days after the end of the 1984 eruption. In Table 4, the mole percent ratios for four gases measured in a vent sample taken on April 18, 1984 are compared to the delta ratios obtained at MLO for various periods between 1974 and 1993. The detection limit ratios of  $\Delta$ H<sub>2</sub>O,  $\Delta$ CO, and  $\Delta$ H<sub>2</sub> to  $\Delta$ CO<sub>2</sub> were all significantly greater than ratios of these gases measured in the post-eruption vent sample. Although the relative abundances of these gases could not be measured in the MLO data, the upper limits show that they did not increase greatly between 1984 and 1992.

The detection limited  $\Delta$ SO<sub>2</sub> to  $\Delta$ CO<sub>2</sub> ratio between 1991 and 1993 was over three orders of magnitude less than the post-eruptive vent sample ratio, suggesting that volcanic SO<sub>2</sub> should have been easily detected in the MLO measurements. *Gerlach* [1986] predicted a total S to CO<sub>2</sub> mole fraction exsolution ratio near 0.2 for reservoir-equilibrated magma ascending through a depth of one to three thousand meters (the presumed depth of the top of the Mauna Loa summit magma chamber from *Decker et al.*, [1983]). Airborne measurements of non-eruptive degassing at the Kilauea summit caldera gave SO<sub>2</sub> to CO<sub>2</sub> ratios of about 0.1 [*Greenland et al.*, 1985]. From this evidence, the quiescent Mauna Loa SO<sub>2</sub> to CO<sub>2</sub> ratio might be expected to be on the order of 0.1. This is over 100 times greater than the detection limit of the MLO measurements, yet essentially no SO<sub>2</sub> was present in the plume.

The loss of a large fraction of SO<sub>2</sub> during transport between



the vent(s) and the observatory could potentially account for the discrepancy, so this was investigated. The two principal processes in atmospheric  $\text{SO}_2$  removal expected for the nighttime summit environment are liquid phase oxidation, and dry deposition to the ground. Moller [1980] gave a typical  $\text{SO}_2$  liquid-phase mean residence time in dry air (characteristic of the Mauna Loa summit environment) of 30 hours. Dry deposition velocities reported in the literature for  $\text{SO}_2$  range from  $0.04$  to  $7.5 \text{ cm s}^{-1}$  [Sehmel, 1980]. The dry deposition velocity depends on the surface moisture content and surface roughness. Lee *et al.* [1993] reported dry deposition velocities for  $\text{HNO}_3$  at MLO of  $0.27$  to  $4 \text{ cm s}^{-1}$ . A reasonable, conservative estimate of the  $\text{SO}_2$  dry deposition velocity at MLO is therefore  $1 \text{ cm s}^{-1}$ . Using this value and assuming a uniform downslope mixing depth of  $74 \text{ m}$  (obtained in section 6.3), the dry deposition mean residence time would be two hours, making this the predominant loss term. The average plume transit time between the vent(s) and the observatory (at a distance of  $6 \text{ km}$  and speed of  $3.4 \text{ m s}^{-1}$ ) is only  $0.5$  hours. This suggests that less than  $20\%$  of the vented  $\text{SO}_2$  was lost during transit to MLO. It is thus likely that there was no appreciable atmospheric loss of  $\text{SO}_2$  and that the  $\Delta\text{SO}_2$  to  $\Delta\text{CO}_2$  ratios in Table 3 represent the emissions at the vent(s).

In 1978 Mauna Loa was visibly fuming.  $\Delta\text{CN}$  was  $10$  to  $50$  times greater than during the 1988 to 1993 period (Figure 10).  $\text{SO}_2$  measurements were made at MLO in 1978 using a chemical method [Bodhaine *et al.*, 1980; Komhyr, pers. com., 1993]. The data were recorded on chart records that were never reduced. It was found that nighttime episodes of  $0.5$  to  $>10 \text{ ppb SO}_2$  (above a  $< 0.1 \text{ ppb}$  background) often occurred, usually coinciding with periods of high CN associated with the presence of volcanic plume. Hourly  $\Delta\text{CO}_2$  in 1978 was typically in the range of  $0.5$  to  $10 \text{ ppm}$ , suggesting that the  $\Delta\text{SO}_2$  to  $\Delta\text{CO}_2$  ratio during this period was about  $1 \times 10^{-3}$ .

The fact that there is over  $100$  times less  $\text{SO}_2$  relative to  $\text{CO}_2$  in the quiescent Mauna Loa plume compared to the quiescent Kilauea plume shows that there must be a major difference between these two systems in the chain of events from exsolution at depth to plume dispersal. A continuous monitoring program for  $\text{SO}_2$  was established in early 1994 at MLO to look more closely at this problem. Initial results for the first eight months of this program show that the average  $\text{SO}_2$  to  $\text{CO}_2$  ratio was approximately  $7 \times 10^{-5}$ .

### 6.5 Ratios of Aerosols to $\text{CO}_2$

Besides  $\text{CO}_2$ , the only observatory-monitored species detected in measurable quantities in the Mauna Loa plume were CN ( $0.002$  to  $0.1 \mu\text{m}$  particles) and light scattering ( $0.1$  to  $1 \mu\text{m}$  particles). The CN in the volcanic plume presumably consisted primarily of sulfate aerosol produced by gas-to-particle conversion of  $\text{SO}_2$ . Sub-micron sulfate particles have

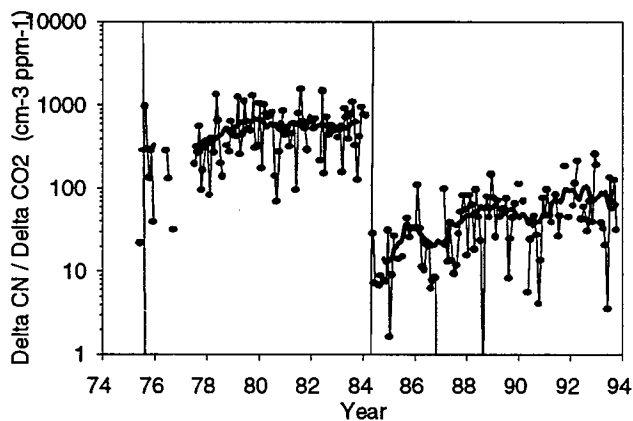


Fig. 15 The ratio of monthly average delta CN and delta  $\text{CO}_2$  between 0000 LST and 0759 LST. Vertical lines denote the 1975 and 1984 eruptions. The fit is a 12 month running mean.

a much smaller deposition velocity than does  $\text{SO}_2$  [Fisher, 1978], suggesting that losses of volcanic CN during atmospheric transit between the vent and observatory were negligible (i.e. much less than  $20\%$ ). Therefore, ratios of  $\Delta\text{CN}$  to  $\Delta\text{CO}_2$  measured at MLO are most likely the same as those present at the vent(s).

The monthly average  $\Delta\text{CN}$  to  $\Delta\text{CO}_2$  ratio is shown in Figure 15 along with a 12-month running mean. In units of  $\text{cm}^{-3} \text{ ppm}^{-1}$  the ratio increased from about  $300$  to  $600$  between 1974 and 1979 and remained near  $600$  until the 1984 eruption. Following the 1984 eruption, the ratio gradually climbed from  $15$  to  $100$ , with two notable dips in 1986-87 and 1991. Gerlach [1986] has shown that the S to  $\text{CO}_2$  ratio of exsolved gas increases as the depth of the source magma decreases. The high  $\Delta\text{CN}$  to  $\Delta\text{CO}_2$  outgassing ratio during the post-1975 period compared to the post-1984 period would be expected if magma were emplaced at relatively shallow depths following the 1975 eruption, as suggested by Lockwood *et al.*, [1987].

### 6.6 Relationship of Emissions to Summit Inflation

Geodetic monitoring of Mauna Loa has shown that the summit has been gradually inflating since the 1984 eruption. There was one reported period of non-inflation in 1990 [Okamura *et al.*, 1991; Miklius *et al.*, 1993] which correlated with a large decrease in  $\Delta\text{CN}$  and the  $\Delta\text{CN}$  to  $\Delta\text{CO}_2$  ratio (Figures 10 and 15). Semi-annual EDM measurements of the distance across the summit caldera made by the Hawaii Volcanoes Observatory [Miklius, pers. com., 1994] showed a second period in 1986-1987 in which the rate of summit expansion was slowed or briefly reversed. This also correlated with a temporary decrease in both  $\Delta\text{CN}$  and the  $\Delta\text{CN}$  to  $\Delta\text{CO}_2$  ratio. These observations suggest that the short-term changes observed in the rate of CN (sulfate) production are related to changes in summit inflation.

The two brief halts in the rate of summit expansion in 1986-1987 and 1990 did not measurably affect the rate of CO<sub>2</sub> outgassing (Figures 7 and 14), which underwent steady exponential decay. If inflation of the summit is caused by refilling of the summit reservoir [Decker *et al.*, 1983] with CO<sub>2</sub>-rich parental magma [Gerlach, 1986], it follows that changes in the rate of inflation should be accompanied by changes in CO<sub>2</sub> emissions. Two presumed temporary halts in the magma supply rate did not produce measurable changes in the CO<sub>2</sub> emissions measured at MLO. Either (1) the new magma responsible for inflation was already depleted in CO<sub>2</sub>, or (2) the quantity of new magma was so small that the CO<sub>2</sub> emissions from it were insignificant compared to those from the existing reservoir. This second possibility was not supported by the results of a comparison between the calculated volume of magma supplied to the reservoir and concurrent estimates of CO<sub>2</sub> emissions. Okamura *et al.* [1991] used geodetic measurements to calculate that  $1.1 \times 10^7 \text{ m}^3$  of magma was added to the summit reservoir in 1991. This is equivalent to  $2.9 \times 10^{10} \text{ kg}$  of magma having a density of  $2.6 \times 10^3 \text{ kg m}^{-3}$ . Exsolution of CO<sub>2</sub> at the 0.06 wt % ratio of the existing quiescent reservoir (from section 6.3) would have produced  $1.7 \times 10^7 \text{ kg CO}_2$ . Subsequent outgassing with a 1.6 year exponential decay rate (characteristic of the post-1984 reservoir) would have resulted in CO<sub>2</sub> emissions of  $8 \times 10^6 \text{ kg}$  during the first year (1991). The observed CO<sub>2</sub> emissions in 1991 were only  $3.3 \times 10^6 \text{ kg}$  (Figure 14). Most of the 1991 emissions presumably came from the gradual degassing of the pre-existing reservoir; therefore, the incremental CO<sub>2</sub> added by recently injected magma should have been much less than  $3.3 \times 10^6 \text{ kg}$ . This raises the possibility that, by 1991, the new magma responsible for summit inflation may have already been depleted in CO<sub>2</sub> by the time it reached the reservoir.

### 6.7 Eruptive Degassing

The 1975 eruption lasted less than 19 hours during a period of unfavorable winds, and no trace of the eruptive plume was present in the data.

The 1984 eruption began at 0125 LST on March 25. Observatory winds throughout the night were from 140° to 160° at over  $10 \text{ m s}^{-1}$  and the plume was not detected. By 0600 LST, the wind speed fell below  $6 \text{ m s}^{-1}$  and the CO<sub>2</sub>, CN, and  $\sigma_{sp}$  concentrations began to rise above background levels. Between 0700 and 0800 LST, the plume was most intense, with  $\Delta\text{CO}_2 = 1.80 \text{ ppm}$ ,  $\Delta\text{CN} = 136,000 \text{ cm}^{-3}$ , and  $\Delta\sigma_{sp} = 6.5 \times 10^{-6} \text{ m}^{-1}$ . The  $\Delta\text{CN}$  to  $\Delta\text{CO}_2$  ratio was  $75,600 \text{ cm}^{-3} \text{ ppm}^{-1}$ . The CN levels recorded during this hour were the highest ever measured at MLO.

Compared to average quiescent conditions just before the eruption, the period in which the eruptive plume was most intense had similar amounts of CO<sub>2</sub>, fifty times more light

scattering particles, and over one thousand times more CN. At this time, the eruption was emanating from the north-east rift zone near the caldera at 3700 meters elevation [Lockwood *et al.*, 1987].

By 1300 LST on March 25,  $\Delta\text{CO}_2$  had returned to zero and  $\Delta\text{CN}$  was down to  $1300 \text{ cm}^{-3}$ , presumably due to a shift to more northerly winds. The nephelometer had been turned off at 0800 LST, and MLO was completely shut down by a power failure the next morning. The analyzers were without power for the rest of the eruption. Manual CN readings taken at MLO between April 4 and April 16 (when lava was flowing from vents on the northeast rift between 2770 m and 2930 m) ranged between  $1400 \text{ cm}^{-3}$  and  $31,000 \text{ cm}^{-3}$ .

These observations show that the early eruptive magma was mostly depleted of CO<sub>2</sub>, in agreement with Gerlach [1986] (for Kilauea), Greenland [1987], and Johnson [this volume]. The early eruptive plume was very rich in small particles (sulfate), and moderately enriched in large (0.1 to 1.0  $\mu\text{m}$ ) particles.

## 7. CONCLUSIONS

Atmospheric trace gas and aerosol measurements made at Mauna Loa Observatory were used to characterize the quiescent volcanic plume coming from the 6 km distant summit of Mauna Loa volcano. Minute-scale variability in the atmospheric CO<sub>2</sub> concentration was used to identify the presence of the plume at night in the downslope wind. The excess concentration of CO<sub>2</sub> above background levels was calculated for each hour in which the plume was present.

Excess CO<sub>2</sub> was greatest when winds blew from the direction of the summit caldera (180° to 190°). The distribution of excess CO<sub>2</sub> with wind direction had a full-width at half-maximum of about 40°. The plume was trapped in the nighttime surface temperature inversion layer with an average scale height of tens of meters. The strength of the plume at MLO followed the evolution of the temperature inversion, forming after sunset, gradually intensifying, and reaching a stable maximum between 0100 LST and 0600 LST.

Excess CO<sub>2</sub> was measured in the plume throughout the 1958 to 1994 period of record. The amount of volcanic CO<sub>2</sub> was greatest shortly after the 1975 and 1984 eruptions and decreased exponentially in the following years. Enhanced outgassing was delayed by 65 days following the 1975 eruption, and by less than 9 days following the 1984 eruption. The 1975 delay time implies a bubble ascent rate through a presumed 2700 m magma column of approximately 2 meters per hour.

From 1959 to 1994 the total annual mass of vented CO<sub>2</sub> was estimated, based on a simple model of plume dispersal. The total mass of the post-1950, post-1975, and post-1984 CO<sub>2</sub> reservoirs was estimated at  $4.8 \times 10^8 \text{ kg}$ ,  $2.4 \times 10^8 \text{ kg}$ , and  $3.3 \times 10^8 \text{ kg}$  respectively. This mass of CO<sub>2</sub> would require

eruptive-scale volumes of magma (on the order of  $10^8 \text{ m}^3$ ) to ascend several km. The three reservoirs had exponential decay constants of 6.1 years, 6.5 years, and 1.3 years respectively. The 1984 eruption apparently did not affect the outgassing rate of the post-1975 reservoir. After 1984,  $\text{CO}_2$  was presumably being produced by both the post-1975 and post-1984 reservoirs.

The 1975 eruption was preceded by a three-year period in which the average excess  $\text{CO}_2$  in the plume at MLO increased by 0.015 ppm. There was no measurable increase preceding the 1984 eruption, although an increase of this size would not have been observable due to higher average plume concentrations at this time. An increase of 0.02 ppm occurred from early 1993 to late 1994. During this time, excess  $\text{CO}_2$  continued to decrease when the winds blew from the direction of the summit, while there was an unprecedented increase in excess  $\text{CO}_2$  when winds blew from the southeast and southwest. This was most likely caused by a new source, possibly located on the southwest rift. This activity may be an early precursor to the next eruption.

Excess aerosol particles were measured in the plume through-out the record between 1974 and 1994. Condensation nuclei (particle size of  $0.002 \mu\text{m}$  to  $0.1 \mu\text{m}$ , presumably sulfate aerosol) were present in large numbers throughout the post-1975 period, decreased by a factor of five soon after the 1984 eruption, and gradually decreased by a further factor of five between 1984 and 1994. The post-1984 decrease was punctuated by two brief dips in 1986-87 and 1990-91 which correlate with temporary halts or reductions in the rate of summit expansion measured by Hawaii Volcanoes Observatory. These changes in the rate of summit expansion did not measurably affect the steady exponential decrease of  $\text{CO}_2$  emissions. Particles that scatter light ( $0.1 \mu\text{m}$  to  $1 \mu\text{m}$ ) were present in detectable quantities only between 1977 and 1980, and to a lesser degree in 1983. These data were consistent with estimates of the visual thickness of fume at the vents obtained from photographs.

Eight additional observatory data sets were examined for a volcanic plume component. These were  $\text{H}_2\text{O}$  (1974-93),  $\text{O}_3$  (1974-93),  $\text{CH}_4$  (1987-93),  $\text{SO}_2$  (1988-92), aerosol carbon (1990-93), radon (1991-93),  $\text{CO}$  (1992-93), and  $\text{H}_2$  (1992-93). None of these species were present in the plume to the detection limits of the analysis technique. The upper limit of the ratios of  $\text{H}_2\text{O}$ ,  $\text{CO}$ , and  $\text{H}_2$  to  $\text{CO}_2$  was much greater than the ratios of these gases measured at the vent shortly after the 1984 eruption. The upper limit to the  $\text{SO}_2$  to  $\text{CO}_2$  ratio was  $10^{-3}$ , approximately two orders of magnitude less than that reported for the quiescent Kilauea plume. Recent measurements show a ratio of  $7 \times 10^{-5}$ .

The 1984 eruptive plume was sampled at MLO early in the first day of the eruption. Compared to levels measured during the quiescent period before the eruption, the eruptive plume

had similar concentrations of  $\text{CO}_2$  and a thousand times greater number density of condensation nuclei.

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