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Technical note

Technical note: A 23-year record of twice-weekly aerosol composition measurements at Mauna Loa Observatory

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ABSTRACT

This paper introduces a newly compiled data set of atmospheric particulate matter (PM) measurements from 1988 through 2010 at Mauna Loa Observatory (MLO), Hawaii, USA. The data are from two samplers: one running only during nighttime hours over multiple days and another running continuously over the same days. The objective of the night-only schedule is to capture samples from Pacific background air masses transported in the free troposphere with minimal contamination from local and marine emissions. Elements characteristic of soils generally exhibit similar concentrations between the continuous and night-only samples, which suggests Pacific background air masses are responsible for the majority of the fine soil aerosol observed at MLO. Sulfur concentrations in the continuous samples often substantially exceed those in night-only samples, suggesting that local sources contribute to the daytime S concentrations at MLO. Trends estimated from Thiel-Sen regression for all 23 years are 1.3% and −1.7% per year for S and Fe (significant at $p = 0.05$) in the night-only samples; S and Fe trends in the last 10 years are in the same directions and stronger (4.2% and −4.4% per year).

1. Introduction

The Mauna Loa observatory (MLO) is located on the slope of an active volcano at an elevation of 3.4 km above sea level. Mauna Loa most recently erupted in 1984 (USGS, 2012). The volcanic island topography and meteorology create a typical diurnal cycle of airflow regimes at MLO (Weber and McMurry, 1996). At night the observatory is above the inversion layer, in the free-tropospheric atmosphere with minimal influence from local emissions. Aerosol concentrations at night thus illuminate the free-tropospheric background air mass that is transported across the Pacific Ocean. During the day, solar heating of the volcano's slopes creates a surface layer of upslope flow. This surface layer contains aerosols from local sources at lower elevations on the island including agriculture, transportation, marine, and industrial activities. These local aerosols are added to the background aerosol concentrations and thus bring higher aerosol concentrations to the MLO observatory.

MLO's elevation and isolation in the mid-Pacific, make this an attractive site for tracking background atmospheric concentrations. Established in 1957 as an atmospheric research station (NOAA, 2012), MLO has generated continuing measurement series that are familiar to students of climate and atmospheric chemistry (e.g. Pales and Keeling, 1965). Routine atmospheric aerosol monitoring began at MLO in 1974 (Bodhaine, 1992), and the measurements reported here began in 1988.

The MLO measurements presented in this note were collected by two aerosol samplers that collect particulate matter with aerodynamic diameters less than 2.5 μm ($PM_{2.5}$). The samplers operated on different schedules in an attempt to exploit the location's typical diurnal airflow regime and segregate free-tropospheric background aerosol from locally-sourced aerosols. The first sampler runs only during the nighttime hours, when its predominant exposure is to free-tropospheric background aerosol. The second sampler runs around the clock (continuously), including daytime hours when the background aerosol is augmented by local and marine aerosols from lower elevations. Time alone is not an adequate criterion for determining the airflow regime, and as a result, some nighttime samples are expected to be contaminated by upslope flow and local aerosols (Huebert et al., 2001). In fact the start time for the night-only sampler was shifted from 20:00 to 22:00 on 25 January 1992 in response to concerns about upslope contamination in the early hours of the night-

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only samples. All the samples were analyzed for total aerosol mass and the masses of 24 elements.

This note introduces the 23-year data series resulting from measurements at MLO and invites its use by others. The sample analysis, documentation, and reporting of these measurements through the years has been incomplete and inconsistent. Missing sample analyses were recently completed, and the MLO data collected from 1988 through 2010 have now been compiled into a single data set for convenience and clarity. The following sections describe the measurements, summarize overall patterns in the data, and note some limitations of the data set.

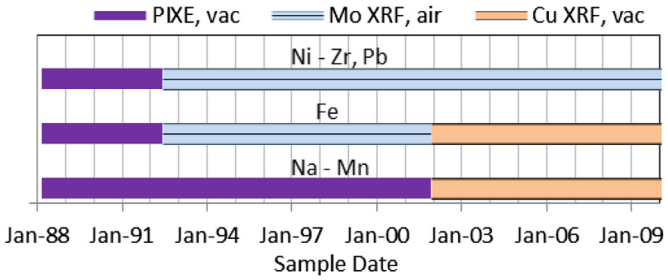

Fig. 2. Timeline of methods used to analyze the $PM_{2.5}$ filter samples from Mauna Loa.

2. Methods

The MLO measurements presented in this note were made with Interagency Monitoring of Protected Visual Environments (IMPROVE) samplers and analytical equipment. IMPROVE is a national aerosol-monitoring program that has tracked atmospheric visibility across the United States since 1988 (Malm et al., 1994). Although made with IMPROVE samplers and analytical systems, the MLO measurements are not standard IMPROVE data because the usual IMPROVE sampling strategy was not employed at MLO. There are two standard IMPROVE monitoring sites in Hawaii: one at Hawaii Volcanoes National Park (NP) on the big island and another at Haleakala NP on neighboring Maui. Data and documentation for these and other IMPROVE sites can be downloaded from http://views.cira.colostate.edu/fed/ and http://vista.cira.colostate.edu/improve/, respectively. As indicated in the introduction, two samplers are installed at MLO, operating in parallel on different schedules. The first sampler runs for multiple days during only the night hours, and the second sampler runs for multiple days continuously, as shown in Fig. 1. Samples are collected over three or four days to collect sufficient mass for satisfactory detection limits. There were some changes to the sampling schedule over the years, and some confusion remains about the exact sampling days prior to 24 February 2005. The raw data files have date stamps of Saturdays and Wednesdays, Perry et al. (1999) state that sample collection started on Sundays and Wednesdays in their paper summarizing the 1993–1996 data, and a readme document found with the older MLO data states that sample collection started on Mondays and Thursdays. We are unable to resolve these conflicts in the historical documentation, but have used our best judgment and set the sample start dates in the Supplemental data file to be Mondays and Thursdays prior to 24 February 2005. This date uncertainty limits comparisons with other measurements from MLO to time resolutions of about a month or longer. After 24 February 2005, sample collection began on Saturdays and Tuesdays. A smaller shift in the night-only sampler start times occurred on 25 January 1992; prior to that date, the night-only sample collection occurred from 20:00 to 06:00 Hawaii–Aleutian Standard Time (HAST) and after that date occurred from 22:00 to 08:00 HAST.

The samplers and sample analysis methods have changed some over the years also. The IMPROVE Version 1 samplers installed in 1988 were replaced on 24 February 2005 by IMPROVE Version 2 samplers. The Version 2 sampler is distinguished by electronic versus mechanical timing, electronic versus manual flow rate recording, and a different type of sample holders. The same cyclone separator design is used in both sampler versions to exclude particles with aerodynamic diameters greater than 2.5 μm from the sample stream; the fine particles ($PM_{2.5}$) that pass through the cyclone are deposited onto polytetrafluoroethylene (PTFE) filters. The filters have an overall diameter of 25 mm but at MLO are masked to concentrate the sample into the central portions of the filters; the masks reduce the effective sample deposit area by about 38% (from 3.53 cm^2 to 2.2 cm^2) to increase detection sensitivities.

The MLO samples were weighed to determine $PM_{2.5}$ mass and then analyzed for 24 elements (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Zr, and Pb). All the analyses were performed by Crocker Nuclear Laboratory (CNL) at the University of California in Davis (UCD) using the analytical systems shown in Fig. 2. Proton Induced X-ray Emission (PIXE) analysis with the CNL cyclotron was initially used to measure all 24 elements (Eldred et al., 1987). In 1992, an energy-dispersive x-ray fluorescence (EDXRF) system with a Mo-anode tube in air (Mo XRF) was introduced to obtain better sensitivity for the heavier elements, Fe–Pb (UCDavis, 1995). A second EDXRF system with a Cu-anode tube in

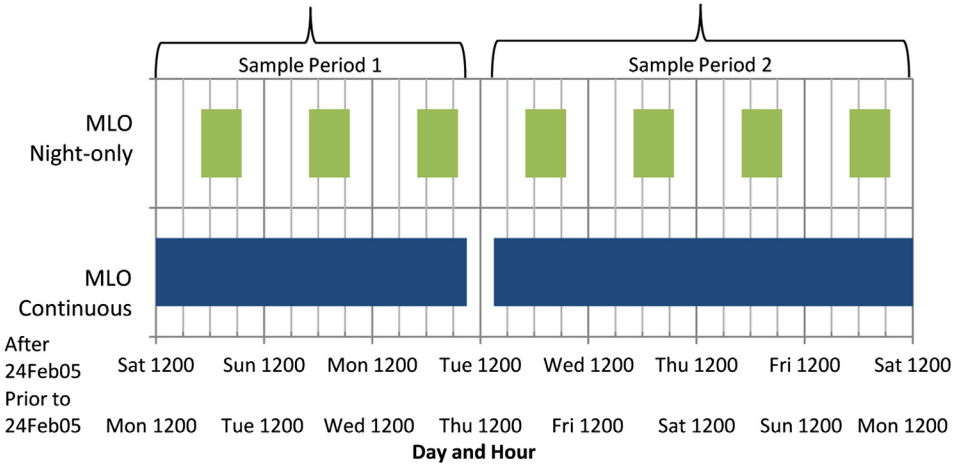

Fig. 1. Sampling schedules for the two IMPROVE-based samplers at Mauna Loa.

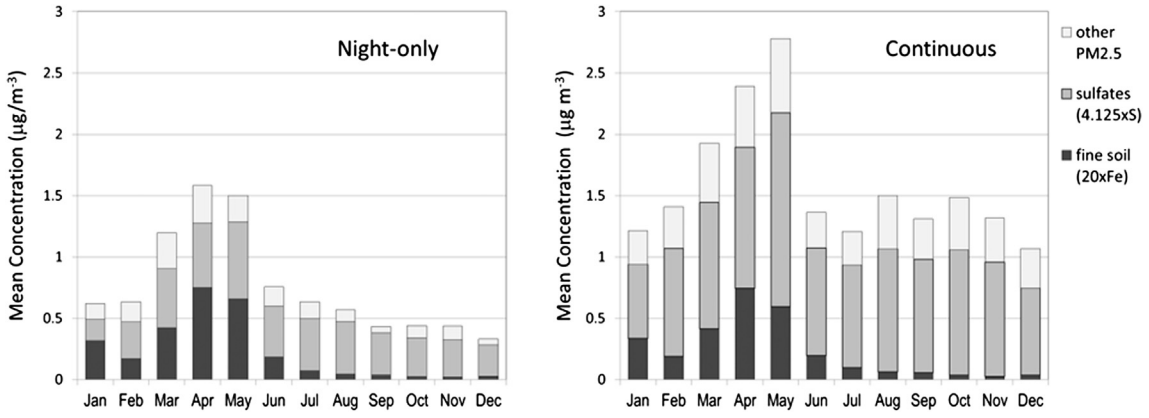

Fig. 3. Monthly contributions of sulfates, fine soil, and other species to total $PM_{2.5}$ mass measured by the night-only and continuous samplers at Mauna Loa.

vacuum replaced PIXE for the lighter elements Na–Fe in December 2001. These analytical instruments were also used in the routine IMPROVE network.

The gravimetric analyses (weighings) were always performed within four weeks after sample collection. From 1988 through November 2001, the XRF analyses were completed within approximately one year of sample collection. Samples collected after November 2001 were put into storage after being weighed and did not undergo elemental analysis until 2011. The samples were stored in cardboard boxes in a temperature-controlled office. The samples collected from December 2001 through December 2010 were analyzed by XRF as a single batch in December 2011. This delay in analysis raises some concerns about sample stability, but previous work found losses from similarly long-archived samples only for Br (Hyslop et al., 2012). A compensating advantage of the delayed analysis is that the entire 10-year sample series was analyzed in a single batch over a short period of time, eliminating any concerns about possible instrument drift.

3. Results

The two IMPROVE samplers at MLO exhibit some interesting patterns that will be noted briefly. Both the night-only and continuous $PM_{2.5}$ samples from MLO are dominated by soil and sulfates as shown in Fig. 3, which summarizes data from 2006 through 2010. Contributions from sulfate are estimated by assuming that all measured sulfur is in the form of ammonium sulfate $(NH_4)_2SO_4$; S is multiplied by a factor of 132/32 to account for the non-sulfur mass. Contributions from fine soil are estimated by assuming that all measured iron is derived from soil with a 5% Fe content (Mason and Moore, 1982). The "other $PM_{2.5}$" category is total measured $PM_{2.5}$ mass minus the sulfate and soil mass as calculated above. Total $PM_{2.5}$ mass concentrations are higher in the continuous samples, which capture daytime contributions from the marine and local aerosols, than in the night-only samples, which are dominated by free tropospheric air masses. In contrast, the similarity of soil concentrations in the continuous and night-only samples suggests that most of the soil arrives in the free-tropospheric background. A spring pulse of soil dust transported from Asia has long been recognized at MLO (Duce et al., 1980; Perry et al., 1999; VanCuren and Cahill, 2002) and is evident in Fig. 3. Sulfate concentrations are higher in the continuous samples throughout the year, accounting for most of the observed day–night difference in total $PM_{2.5}$. Sulfate concentrations measured by both samplers peak in spring; similar seasonal patterns in sulfate have been observed by Huebert et al. (2001) and Zieman et al. (1995).

Fig. 4 directly compares concentrations of Fe and S measured by the two samplers in the same multi-day period. As foreshadowed

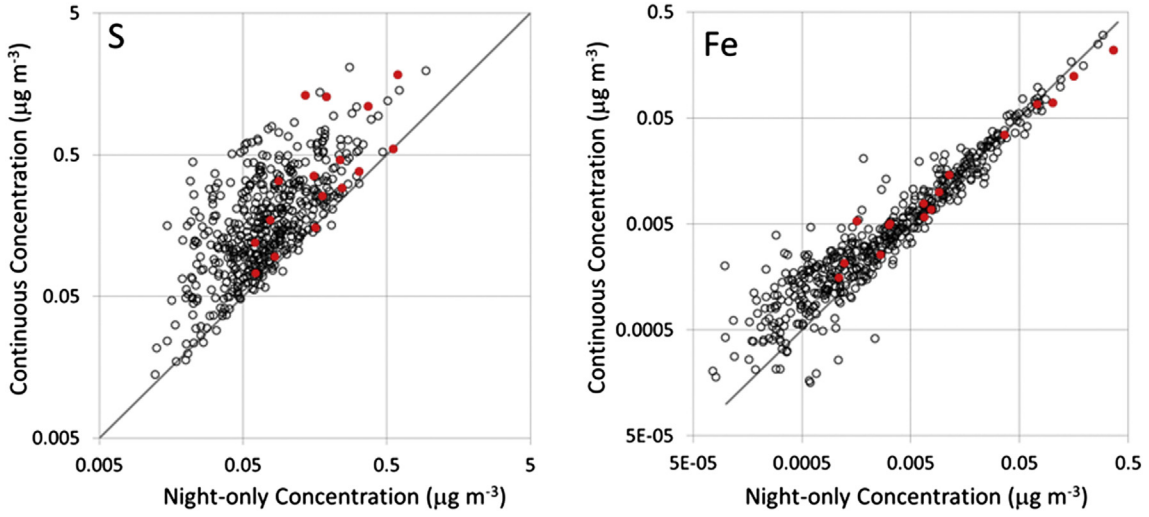

Fig. 4. Continuous versus night-only concentrations of $PM_{2.5}$ iron and sulfur in multi-day samples from 2006 through 2010. Filled red symbols distinguish the eight-week period immediately following an eruption on neighboring Kilauea. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

by the averages shown in Fig. 3, the night-only and continuous Fe concentrations are also quite similar during individual periods. Consistent with the earlier inference that Pacific background air is the dominant source of Fe, Fig. 4 suggests that the increment added locally is distinguishable (on the logarithmic scale) only when this background is very low. A quite different pattern is observed in the data for S. S concentrations from the continuous sampler are often many-fold higher than those measured in night-only samples, which supply a lower bound for the continuous S measurements. The distinct lower edge imposed by the night-only measurements suggests that the contribution of Pacific background S is present at all hours. It seems worth noting that the observed patterns of diurnal variability persisted through an explosive eruption that started on 19 March 2008 at the smaller Kilauea volcano on Mauna Loa's flank (NASA, 2008); samples from the eight weeks following this eruption are plotted with filled symbols in Fig. 4. Both samplers measured above-average concentrations of Fe and S during this period – suggesting the potential for local volcanic activity to influence the measurements.

Fig. 5 shows time-series plots along with regression curves for several species measured on the night-only samples from 1988 through 2010. Detection limits were substituted for zero concentration values in these graphs, and some changes in detection limit reporting are noticeable in the graphs (e.g., values were rounded prior to March 2000). All the series share a strong seasonal cycle that presumably reflects large-scale airflow patterns. The dramatic shifts in Se and Pb concentrations in early 1992 resulted from changes in analytical methods discussed in the Methods section. Systematic reanalyses of previously-analyzed samples from other sites (Hyslop et al., 2012) show S, K, and Fe measurements to have been relatively unaffected by such methods changes, and the mass measurement has been consistent throughout the program.

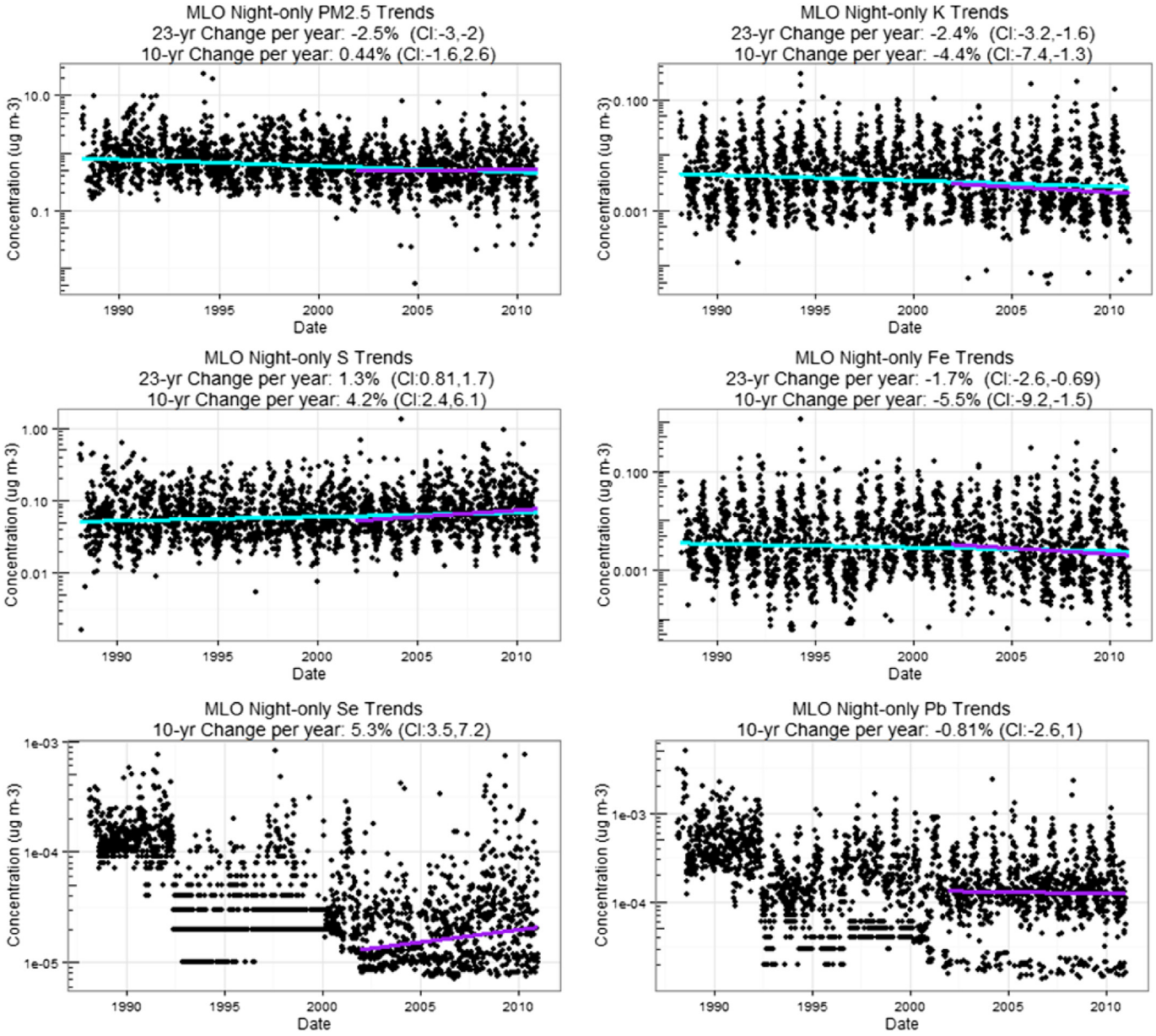

Fig. 5. $PM_{2.5}$ total mass, potassium, sulfur, iron, selenium, and lead concentrations measured from 1988 through 2010 on samples collected only during nighttime hours at MLO. Trend estimates determined from Thiel-Sen regression are plotted for the full 23-year period (cyan) and the last 10-year period (purple). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Changes in analytical methods caused shifts in measured concentrations for several other elements. Potential trends analysts are cautioned to be mindful, as recently modeled by Collaud Coen et al. (2012), of the various analytical changes that took place during this long measurement period.

Regression curves are displayed in Fig. 5 for the most recent 10-year period for all species and for the entire 23-year period for species that were well-measured throughout the history. The curves are based on Thiel-Sen regression as calculated by the ZYP package in R (Bronaugh and Werner, 2009). The resulting slope estimate is the median of the slopes calculated from all the possible pairs of measurements in the data set. The confidence intervals listed above each graph represent the 95th percentile range of slopes. With the exception of the 10-year $PM_{2.5}$ mass and Pb slopes, all the slopes are significant (confidence intervals do not cross zero). The estimated trends in Fe and K, indicative of soil, are negative in both the 10-year and 23-year periods, whereas the estimated trends in S and Se, indicative of coal-burning, are positive in both the 10-year and 23-year periods.

These MLO samplers were shut down in January 2013.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2013.07.038.

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