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8 November 2021

Sarah Miggins, Deputy Director Off-Highway Motor Vehicle Recreation Division California Department of Parks and Recreation 1725 23rd Street, Suite 200 Sacramento, CA 95816

Dear Deputy Director Miggins,

Please find attached my report of findings regarding our spring 2021 sampling and analyses of airborne particulate matter (PM) collected at the location known as the CDF site on the Nipomo Mesa (Mesa) in south San Luis Obispo County, California. The CDF site is approximately two miles downwind of the Oceano Dunes State Vehicular Recreation Area (SVRA). The primary purpose of this investigation, which is part of a larger three-year study, is to quantify that portion of measured PM that consists of mineral dust. Mineral dust is generated from the windblown sand dune building process called saltation, and so quantifying the mineral dust portion of PM at the CDF site provides a conservative measure of that portion of PM on the Mesa that could possibly be from the Oceano Dunes SVRA. The mineral dust measure is conservative because saltation occurs in the dunes inside and outside the SVRA, and mineral dust is also derived from agricultural operations and vehicles driving on dirt roads—activities that occur in the region that lies between the SVRA and the Mesa.

Samples of PM10 and PM2.5 (PM that is aerodynamically ≤ 10 microns and ≤ 2.5 microns in diameter, respectively) were collected for 30 consecutive days, from late April to late May. May was targeted because May is typically the windiest month in the region. Each day, the air was sampled continuously for seven hours, from 11:00AM to 6:00PM (local time) because this is the timeframe when the seasonal westerly winds rise and fall, when saltation in the dunes is at its most active, and when some of the highest hourly PM10 and PM2.5 concentrations at the CDF site are recorded by the SLO County Air Pollution Control District (APCD).

Mineral dust content was determined using gravimetric and elemental analyses as detailed in the report. Key findings from the analyses show that on average, 14% of the BAM PM10 measured at the CDF site consists of mineral dust and 4% consists of sea salt. Specifically, for May 2021, the mineral dust fraction ranged from 2% to 32% on high-PM10 days. The remaining 82% of the PM10 is likely from atmospheric water, organic components, ammonium, nitrate, non-sea-salt sulfate, and other semi-volatile chemical species.



I would like to extend our appreciation to the California Geological Survey and to the California Department of Parks and Recreation for their assistance and access that has made our investigation possible.

Best regards,

MRussell Jynn /

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Scripps/UCSD Interim Report 2021:

Preliminary Results from May 2021 Aerosol Measurements

8 November 2021

Introduction

Building upon the results of the Scripps Institution of Oceanography (UCSD) Reports of 5 February 2020 and 20 September 2020, the Scripps team has undertaken additional quantitative chemical sampling to improve the understanding of the sources of airborne particles in the Oceano Dunes area. This interim report covers the gravimetric and elemental analyses of the teflon filters collected during the most recent sampling period from 27 April 2021 to 26 May 2021 (hereafter "Scripps May 2021" study). The objectives of this part of the research were to

- 1) Quantify the gravimetric mass and elemental component mass of PM10 aerosol particles at CDF.
- 2) Quantify the gravimetric mass and elemental component mass of PM2.5 aerosol particles at CDF;

It is important to note that some COVID-19 restrictions continued during this sampling period.

While prior work has focused on identifying sea spray components of PM2.5 at CDF (with a focus on PM with potential health effects) and of PM10 at a Beach site, the May 2021 sampling was designed to provide a quantitative assessment of the mineral dust fraction of the reported beta attenuation monitor (BAM) PM10 and PM2.5 concentrations during the conditions with the highest PM10 concentrations -- namely afternoons (the time of day with highest wind) in May (the month of the year with highest wind). For PM10 size cutoffs, we have used a standard method, and for PM2.5 we have used both a standard method (Very Sharp Cut Cyclone or VSCC) and an alternative method that was used previously to reduce costs (Sharp Cut Cyclone or SCC). In order to quantify the mineral dust contribution during the time with the highest PM10 concentrations, samples were collected for the afternoon hours of 1200 to 1900 local time (1100 to 1800 standard time). During spring in this area, westerly winds typically

have the highest speeds from late morning to early evening (see Appendix, Figure A3). These high wind speeds increase saltation of the dunes and coincide with elevated PM concentrations measured at CDF (Figure A3). Accordingly, it is during the afternoon hours that PM at CDF is expected to contain the largest concentration and the highest percentage of mineral dust. In this sense, the chemical identification of mineral dust in the afternoon provides an upper bound on the contribution of dust from Oceano Dunes, although a more extensive study could separate out the contributions of other sandy regions, agricultural zones, and road dust.

Background

The particle concentration in the Oceano Dunes region is expected to be a mixture of organic and inorganic components from natural and man-made sources. Its seaside location means that sea spray from breaking waves in the ocean will contribute particles with salt (NaCl as well as some trace additional salts) and organic components (from nutrients and exudates that are produced and consumed by marine biota) [Russell et al., 2010]. Another proximate natural source is mineral dust from sand-covered areas. which is generally associated with wind erosion [Li et al., 2013]. Contributions to dust emission by human activities has been estimated to be 10% or less in agricultural areas and as much as 50% for land use changes that remove vegetation [Shepherd et al., 2016; Tegen et al., 2004; Tegen and Fung, 1995]. However, the lack of difference between weekday and weekend coarse particle emissions supports natural rather than anthropogenic sources [Li et al., 2013]. Both sea spray and mineral dust emissions are increased by wind speed [Malm et al., 1994] as well as by source areas, both have substantial supermicron mass contributions with short atmospheric lifetimes, and neither is associated with evidence of chronic respiratory effects (since they are removed by impaction in the nasal passages and upper airways and since the salt and mineral components have not been associated with toxicity). In addition to these natural sources, local emissions associated with motor vehicles [Russell et al., 2011], residential and commercial activities (including use of personal care products [McDonald et al., 2018], food preparation [Chen et al., 2018], and heating), seasonal agricultural harvesting and fertilizing, wildfires, and long-range transport from high-population areas also contribute both organic and inorganic particle mass to PM2.5 and PM10, with the contribution from each varying with wind direction as well as other conditions.

PM2.5 and PM10 are regulated by U.S. and California clean air standards because of their known association with degraded visibility and detrimental health effects [US Clean Air Act (https://www.epa.gov/laws-regulations/summary-clean-air-act); Dockery et al., 1993; Pope et al., 2009; Apte et al., 2018]. PM10 exceedances of the 24-hr NAAQS (150 µg m⁻³) are infrequent, but the California 24-hr PM10 standard of 50 µg m⁻³ is exceeded 25% of the time [Motallebi et al., 2003]. These standards were developed based on measurements completed by federal reference methods (FRM) that relied on gravimetric measurements of filters that were equilibrated for 24 hr at 35% relative humidity (https://www.ecfr.gov/current/title-40/chapter-l/subchapter-C/part-50). Since then, BAM has been approved as a federal equivalent method (FEM) based on the similarity of hourly BAM, when averaged over 24 hr, to FRM methods for a set of test locations [Chow and Watson, 2008]. Those test locations typically included concentrations below 100 µg m⁻³ and frequently below 30 µg m⁻³ [Chung et al., 2001; Gobeli et al., 2008; Hafkenscheid and Vonk, 2014; Hart, 2009], as these conditions were more typical of areas of concern for PM2.5.

Apte et al. [2018], calculated the U.S. average life expectancy decrement to be 0.38 yr for PM2.5, which is 3 times lower than that of countries with higher PM2.5 (e.g. China, India). While the widespread availability of PM2.5 measurements often makes it the best proxy for epidemiological studies of populations, physiological studies of health effects have shown that the causes of cell degradation are most likely from specific toxic compounds, which are also regulated and include such compounds as polycyclic aromatic hydrocarbons that are associated with fossil fuel combustion and black carbon. Consequently PM1 has been recommended as a better cutoff for targeting health-related aerosol sizes [Lundgren and Burton, 2008]. Recent evidence also suggests that nanoparticles (less than 100 nm diameter) and transition metals, which are also associated with fossil fuel combustion, may also play an important role [Knol et al., 2009; Oberdorster et al., 2007; Gwinn and Vallyathan, 2006; Janssen et al., 2003; Hoek et al., 2002]. Since the association of PM2.5 with toxics is likely responsible for the association of PM2.5 with toxics is likely responsible for the association of PM2.5 with toxics.

There is no evidence that toxic compounds (such as heavy metals or polycyclic aromatic hydrocarbons) are associated with the two major PM2.5 sources (dune dust and sea spray) during windy conditions at Oceano Dunes, so association of PM2.5 with detrimental health effects may be without foundation. In urban locations that serve as the basis for epidemiological health studies, the large population density means that PM2.5 is largely associated with emissions from motor vehicles that include high amounts of toxics, nanoparticles, and transition metals. In areas where PM2.5 is

dominated by natural emission sources rather than man-made combustion activities, the causal link between toxics and health effects is unlikely to hold; exceptions could include severe dust storms [Krasnov et al., 2014], with concentrations exceeding 1000 μ g m⁻³ [Aghababaeian et al., 2021] or associated with Valley fever [Tong et al., 2017], which have not been identified in coastal California [Crooks et al., 2016]. For this reason, assessing whether health effects are associated with PM2.5 requires identifying what fraction of PM2.5 is from natural (non-toxic) sources and what fraction is from combustion emissions.

The chemical composition provides the first critical step to identifying how much of total particle mass is associated with different sources, each of which is associated with different health effects. In the 5 February 2020 UCSD/SIO Report, we used Fourier Transform Infrared (FTIR) spectroscopy and X-ray Fluorescence (XRF) to provide a first cut at the PM2.5 sources, using elemental composition to provide tracers for sea spray, mineral dust, and combustion emissions. This report builds on those results to quantify explicitly the substantial difference between the chemical measurements of dust components and the BAM PM2.5 and PM10 measurements regularly reported by the San Luis Obispo County Air Pollution Control District (APCD) at its CDF air monitoring station on the Nipomo Mesa, approximately 3.2 kilometers (2 miles) inland from Oceano Dunes. First, gravimetric measurements (at partially dried conditions of 35% relative humidity) are used to provide the analogous FRM method for particle mass for comparison to the FEM method hourly BAM. Then mineral dust components from XRF measurements are used to assess the fraction of the measured mass that is associated specifically with wind-blown mineral dust that likely originated from the Oceano Dunes region.

Methods

Aerosol particle sampling at CDF used two louvered PM10 sampling heads [Tolocka et al., 2001] on two separate lines at 16.67 L min⁻¹, followed by a PM10 filter (and bypass flow) on one line and a very sharp-cut cyclone with a calibrated cut at 2.5 μ m (VSCC operated at 16.67 L min⁻¹, BGI Inc., Waltham, MA) on the other line. The bypass flow on the first line included a sharp-cut cyclone operated with a calibrated cut at 2.5 μ m (SCC 2.229 operated at 7.5 L min⁻¹, BGI Inc., Waltham, MA). All flow rates were calibrated and recorded every ~10 s to verify cyclone performance. The VSCC has been EPA approved [Kenny et al., 2004], which allows for mass concentrations to perform at between -5% and +5% of the actual mass under testing conditions. Deviations from the expected cyclone performance have been shown to result for different reasons (see

Appendix): (1) differences between the actual measurement conditions and the testing conditions used for approval [Li et al., 2019], (2) degraded performance by dust accumulation [Lin et al., 2018], and (3) evaporation of liquid water and other semivolatile components by either the VSCC or SCC [Babila et al., 2020].

Teflon filters were used as substrates and have shown negligible adsorption of volatile organic compounds (VOCs) on duplicate back filters collected simultaneously with each sample [Maria et al., 2003; Gilardoni et al., 2007]. Filters for PM10 and PM2.5 were 1 µm pore size. Blank filters provided a measure of adsorption during sampling and contamination during handling (loading and unloading) and storage. Samples were quality-controlled with the following criteria: all filter and cyclone flow rates were within 5% for the duration of sampling, filter pressure increased by >0.01 psi per m³ air collected, and no anomalous readings in pressure, temperature, and relative humidity (as defined by the instrument specifications). These quality-control criteria were met for all 30 PM10 samples, 25 of 30 PM2.5 VSCC samples, and 28 of 30 PM2.5 SCC samples. Correlation coefficients are Pearson's R values for linear fits forced to 0, and percentages are based on the fitted lines of quality-controlled, above-detection samples.

The gravimetric masses of reference filters were compared to the 7-hr average of co-located hourly BAM measurements. The hourly BAM concentrations (retrieved 7/1/21 from https://www.arb.ca.gov/aqmis2/aqdselect.php, where data after 2019 are noted as "preliminary") reported were averaged from the start time (1200 local, PDT) until the last measurement recorded at 1 hr before the stop time (1900 local, PDT), namely seven one-hr measurements reported for PST start times of 1100 through 1700 to provide comparison points (in accordance with the website information). At high relative humidity (>70%, such as those at CDF in May 2021, see Appendix, Figure A3), hourly measurements will report higher mass concentrations than multi-hour measurements [Schweizer et al., 2016]. Comparisons at other sites between gravimetric and BAM PM2.5 mass concentrations have shown correlation coefficients (R²) that varied between 0.65 and 0.99 and slopes that differed by as much as 30% depending on season and chemical composition [Hauck et al. 2004].

BAM uses a glass fiber filter for particle collection because of its high efficiency, but the glass fibers are known to have a positive sampling artifact (relative to Teflon) because they can adsorb gaseous SO_2 and HNO_3 into particulate sulfate and nitrate, respectively [Lipfert, 1994]. The amount of artificial nitrate taken up onto glass-fiber filters varies with both relative humidity and temperature changes [Appel et al., 1979].

All filters were weighed prior to sampling to provide filter-specific tare weights. After sampling, filters were weighed again, and the difference between the sampled weight and the tare was the reported gravimetric mass. The weighing procedure (Chester LabNet) for all samples used the PM2.5 reference method at 35±5% relative humidity for the 24 hr period (logged every 5 min), making the samples potentially drier or wetter than the ambient conditions in which they were collected. BAM measurements may also be drier than ambient humidity due to heating of the air when it is drawn into the instrument to an unknown temperature, but values of internal relative humidity are logged with the BAM measurements. Other differences may result from the hour-to-hour differences in the online BAM measurements compared to the offline filter storage at constant conditions.

All samples (and associated blank filters) were non-destructively analyzed by X-ray Fluorescence (XRF) measurements conducted by Chester LabNet (Tigard, OR) on the same filters used for gravimetric measurements. XRF analysis provided trace metal concentrations for elements Na and heavier [Maria et al., 2003].

Sea salt was measured above detection when Na and CI were above detection (defined as twice uncertainty), which was true for more than 92% of quality-controlled samples. Atmospheric ambient sea-salt concentrations were calculated using measured CI and 1.47*Na concentrations to account for the possible depletion of CI⁻ in the atmosphere, where 1.47 is the ratio of $(Na^++Mg^{2+}+Ca^{2+}+K^++SO_4^{2-}+HCO_3^-)/Na^+$ in seawater [Holland, 1978; Frossard et al., 2014]. This sea-salt calculation represents an upper limit for sea-salt mass because the HCO₃⁻ would have been titrated before CI⁻ was depleted significantly via acid displacement reactions. HCO₃⁻ is 0.3% of the total mass of sea salt. Excluding HCO₃⁻ from the ratio, as a lower limit, the ratio of $(Na^++Mg^{2+}+Ca^{2+}+K^++SO_4^{2-})/Na^+$ is 1.45, instead of 1.47, making the salt mass calculated <2% lower than calculated here.

Mineral dust was measured above detection if Al and Si were above detection (defined as twice uncertainty), which was true for more than 86% of quality-controlled samples. The mass of dust was calculated from XRF metal concentrations, assuming dust consists of MgCO₃, Al₂O₃ and SiO₂ (in the form of Al₂SiO₅), K₂O, CaCO₃, TiO₂, Fe₂O₃, MnO, and BaO [Liu et al., 2018; Gilardoni et al., 2007; Usher et al., 2003]. This calculation increases the mass by an average factor of 2.14 to account for the O and C associated with the measured elements for the PM10 samples. Because some elements are in both sea salt and mineral dust (K, Ca, Mg), the amount of those elements associated with the Na present was subtracted to avoid double-counting, resulting in ~2% less mass. Alternative approximations of the mineral dust contribution

based on other molecular forms of the same elements were also considered and are compared in the Appendix [Hains et al., 2007; Frank 2006; Malm et al. 1994].

Results

Samples were collected at CDF for the period of 27 April to 26 May 2021. The CDF site was co-located with the ongoing APCD sampling by BAM (beta attenuation monitor), which provides an hourly measurement of PM2.5 and PM10 concentration at near ambient conditions, which means that water and other semivolatile organic and inorganic components (notably ammonium nitrate) are included. The number of sampling days was maximized to document the day-to-day variability in the aerosol and to capture multiple days with high PM2.5 and PM10 concentration. Notably, the days with high PM at CDF were often predicted successfully from short-term forecasts of high-wind conditions, consistent with prior studies.

In order to optimize the sampling range for PM10 and PM2.5, flow rates were designed to not exceed the thin film assumption used for XRF. This condition was met for most samples as designed. However, the lower flow rate meant that some samples on low PM days were below detection limit for gravimetric mass (and some XRF elements). This limitation was by design, since the target of this study was high-PM10 days(defined to be those with 1-hr PM10 exceeding 140 μ g m⁻³), none of which exceeded the XRF thin film assumption and most of which were above detection limit (ADL).

The results addressing the objectives of the research are summarized below. We note that all of the results may differ by season, and their variability may be larger than could be captured in this short study.

- 1. Quantify the gravimetric mass and elemental component mass of PM10 aerosol particles at CDF.
 - a. The time series of SIO gravimetric mass and APCD BAM PM10 concentration measurements tracked reasonably well (Figure 1). The offline gravimetric method is lower on average than the online BAM instrument for most samples at CDF (Figure 1). The difference is slightly larger on days with high PM10 (defined to be those with 1-hr PM10 exceeding 140 µg m⁻³). These observations hold when the below-detection samples are removed (see Appendix).
 - b. For the afternoons when hourly PM10 exceeded 140 µg m⁻³ for at least one hour, the gravimetric method PM10 concentration is on average 35% lower than BAM PM10 concentration. For all samples above detection

limit, the gravimetric method PM10 concentration is on average 29% lower than BAM PM10 concentration.

c. The mineral dust component of BAM PM10 ranged from 1% to 32% for ADL samples and from 2% to 32% for high-PM10 day samples. This amount represents an upper bound on the amount of PM10 that could be attributed to mineral dust from sand dune saltation. The average mineral dust amount of BAM PM10 was 14% with variability (standard deviation) of 17% for ADL samples and 14% with variability (standard deviation) of 14% for high-PM10 samples.



methods at CDF from 27 April to 26 May 2021, with XRF Mineral Dust and Sea Salt concentrations (all samples). Error bars represent twice the method uncertainty.

- 2. Quantify the gravimetric mass and elemental component mass of PM2.5 aerosol particles at CDF.
 - a. The time series of SIO gravimetric mass and APCD BAM PM2.5 concentration measurements tracked reasonably well (Figure 2). The offline gravimetric method is lower on average than the online BAM instrument for most samples at CDF for both VSCC and SCC cyclones (Figure 2). The difference is slightly larger on days with high PM10. These observations hold when the below-detection samples are removed (see Appendix).
 - b. For the afternoons when hourly PM10 exceeded 140 μg m⁻³ for at least one hour, the gravimetric method PM2.5 is on average 18% for VSCC and 39% for SCC lower than BAM PM2.5. For all samples above detection

limit, the gravimetric method PM2.5 is on average 13% for VSCC and 32% for SCC lower than BAM PM2.5.

- c. The mineral dust component of BAM PM2.5 by VSCC ranged from 1% to 42% for ADL samples and from 11% to 42% for high-PM10 day samples. The mineral dust component of BAM PM2.5 by SCC ranged from 1% to 34% for ADL samples and from 2% to 31% for high-PM10 day samples. The average mineral dust amount by VSCC of BAM PM2.5 was 20±20% for ADL samples and 27±10% for high-PM10 day samples. The average mineral dust amount by SCC of BAM PM2.5 was 15±14% for ADL samples and 19±19% for high-PM10 day samples.
- d. Organic mass concentration was quantified by FTIR for 13 PM2.5 SCC filters at mass concentrations of 0.8-3.7 μg m⁻³ for ADL samples, accounting for 1-18% of BAM PM2.5 concentrations.





Discussion

BAM has been employed to provide hourly PM10 and PM2.5 concentrations across much of California since the approval of 24-hr average BAM as a federal equivalent method (FEM) in 2008 [USEPA, 2013]. Comparisons of BAM and filter-based reference methods have shown that BAM values are often higher than filter-based methods

because of the loss of the more volatile, or semivolatile, components during collection and equilibration on Teflon filters [Tao and Harley, 2015; Takahashi et al., 2008; Chow et al., 2006]. This has been especially true in regions like California, in which a substantial amount of PM2.5 is contributed by ammonium nitrate, causing the South Coast Air Quality Management District to apply to exclude BAM PM2.5 measurements from determination of attainment [Tao and Harley, 2015], since the standards are based on equilibrated filters by the federal reference method (FRM) rather than BAM. Corrections for BAM to gravimetric have been developed for some regions in order to use BAM to determine if air quality standards are exceeded [Le et al., 2020]

One reason for higher BAM concentrations in coastal areas with high ambient relative humidity is that the BAM may not have sufficient residence time to allow for full equilibration of particles to ~35% relative humidity, making the effective relative humidity of the measurement higher than the 35% required by the FRM. The role of sea salts and other minerals in delaying the loss of water from particles because of hydrate formation is well known [Frossard et al., 2012; Cziczo and Abbatt, 2000; Harvie et al., 1980]. One coastal study in Greece has shown that the amount that BAM exceeds gravimetric is correlated to the normalized water vapor pressure in the air and that the positive bias is highest for relative humidity 40-80% and temperature 11-22°C [Triantafyllou et al., 2016]. Another study showed a 30% positive bias of BAM to gravimetric for temperatures above 16°C and above 80% relative humidity at concentrations of 30-60 µg m⁻³ [Takahashi et al. 2008]. The PM2.5 sampling reference method (https://www3.epa.gov/ttn/amtic/files/ambient/pm25/ga/m212.pdf) requires that samples be stored at 35% relative humidity for a minimum of 24 hr in order to dry the particles to what is assumed to be equilibrium. In contrast, BAM and EBAM measurements are collected at ambient relative humidity and then heated during flowing through the instrument to bring the relative humidity to 35%, allowing only minutes for equilibration on the glass-fiber filter. At CDF ambient relative humidity exceeded 35% for 27 April through 26 May 2021 (Figure A3), meaning that the BAM measurements needed to be dried in order to remove particle-bound water that was present at ambient conditions. Even at relative humidity as low as 50%, the amount of particle-bound water in PM10 has been shown to be as high as 33% by mass compared to filters below 30% relative humidity [Imre et al., 2014]. Some water can even remain after 24 hr equilibration, contributing to reference filter mass concentrations [Rees et al., 2004]. These results make it likely that the difference in mass on high-PM10 days is due to adsorbed water and other semivolatile components (ammonium nitrate and organic mass) evaporating less in the BAM method and more in the gravimetric method [Le et al., 2020; Tao and Harley, 2015]. The lower gravimetric than BAM mass concentrations are consistent with the expectation that the BAM method includes more water and other

semivolatiles that can evaporate during the gravimetric reference method. The increase in the difference between BAM and gravimetric mass concentration on days with high PM10 (35% compared to 29%) is consistent with higher particle loadings giving less complete evaporation in BAM. The water contribution could be assessed by repeating the gravimetric method at higher relative humidities.

Another possibility is that the BAM calibration does not apply well to the composition and concentration conditions that are relevant to this site. EPA approval of BAM relied on testing conditions that were typically limited to concentrations lower than 100 μ g m⁻³ and that were 24-hr average measurements [Chung et al., 2001; Gobeli et al., 2008; Hafkenscheid and Vonk, 2014; Hart, 2009]. At PM10 concentrations exceeding 30 µg m⁻³, BAM and gravimetric methods were not found to be equivalent using consistency criteria [Gebicki and Szymanska, 2012]. BAM PM2.5 performance relative to reference methods has been shown to vary seasonally and to include an uncertainty of 16% [Hafkenscheid and Vonk, 2014]. A large fraction of PM2.5 can be volatile, and comparisons to reference filters typically show a high bias for the BAM [Hart, 2009], especially for PM2.5 concentrations exceeding 40 µg m⁻³ [Le et al., 2020]. This difference varies with relative humidity, often reducing the correlation between BAM and filters [Chow et al., 2005; Hains et al., 2007]. Since relative humidity often varies with a daily cycle (as it does at CDF in May 2021, Figure A3), comparisons of BAM and gravimetric may tend to have a larger bias for comparing partial days (e.g. afternoon only) than for a 24-hr measurement.

Central California studies have shown that 80% of nitrate in PM2.5 can volatilize in spring and summer conditions [Chow et al., 2005]. Particulate nitrate is higher when ambient relative humidity is high [Dassios and Pandis, 1999]. There is also evidence that the positive bias of BAM relative to gravimetric increases for ambient temperatures below 25°C, when the amount of particulate nitrate may be high [Le et al., 2020]. These errors often vary with time of day, with water adsorption in the BAM affecting afternoon readings and desorption affecting readings after midnight, so that hourly BAM concentrations may have biases of ~20 μ g m⁻³ even when 24 hr averages include cancelling errors [Kiss et al., 2017].

In summary, there are two types of reasons for the differences between BAM and gravimetric filter measurements here. The first and very well-known reason is the contribution of semivolatile components. These are components that evaporate from particles when temperature increases, including water, ammonium nitrate, and other semivolatiles. Sampling for 24 hr means that some particles on an FRM filter will lose mass when these components evaporate. Sampling periods shorter than 24 hr can

reduce this evaporation if they reduce the amount of temperature change during sample collection [Mader et al., 2001]. This effect means that the online BAM measurement may be closer to ambient particle mass concentrations (i.e. more similar to the atmosphere) but the longer filter measurement is closer to federal and state standard methods (i.e. more similar to the regulated quantity). For this reason, the gravimetric mass concentrations should be used to assess PM10 and PM2.5 exceedances. Since BAM is used to provide more frequent and routine measurements, here we report the fractions of components relative to BAM.

The second reason is different performance of the samplers because of size cut design or flow rate issues. For PM10, both BAM and gravimetric samplers used nominally the same size cut design at the same flow rate [Tolocka et al., 2001]. The performance of the samplers may be affected by the accumulation of particles on the walls of the sampling head (which may entrain large solid particles above the size cut, as has been observed in testing in agricultural regions [Faulkner et al., 2014; Le et al., 2019]). However, the difference between BAM and gravimetric concentrations persisted from the beginning (with a clean sampling head for gravimetric filters) to end (after 30 days without cleaning) of the sampling with similar magnitude (Figure 1), making it difficult to show any effect from either recent cleaning or accumulated particles. This makes it likely that the 35% (56.8 μ g m⁻³) difference on high-PM10 days is attributable to the first reason (semivolatile components) rather than to size cut performance issues [Triantafyllou et al., 2016]. For PM2.5, the same reasoning applies for the 18% (6.3 µg m⁻³) difference between the VSCC filters and the BAM. The correlation coefficients (see Appendix) are lower than the range found in other studies $(0.72 < R^2 < 0.90)$ [Triantafyllou et al., 2016], which is not surprising given the less than 24-hr averaging times (7 hr), the variable conditions of the short (30-day) study, and the limited number of high-PM10 days (10).

The PM2.5 and PM10 apportionments by component of the BAM concentrations measured at CDF are summarized in Figure 3, where we have labeled the difference between BAM and gravimetric mass as the "Semivolatile" fraction. This fraction is likely from atmospheric water associated with the high ambient relative humidity. Ammonium nitrate and semivolatile organic components may also contribute. Figure 3 also illustrates the measured mass component contributions: mineral dust accounts for 14% of BAM PM10 at CDF on high-PM10 afternoons, ranging from 2% to a single-day high of 32%. This means that on average less than one fifth of the BAM-based PM10 at CDF can be attributed to mineral dust during the 10 high-PM10 days sampled in April-May 2021. The average PM10 concentration on high-PM10 afternoons was 161.2 μ g m⁻³, of which only 23.2 μ g m⁻³ was dust. PM2.5 on high-PM10 days had an average afternoon

BAM concentration of 33.9 μ g m⁻³, of which mineral dust accounted for 27% of BAM PM2.5 at CDF (ranging from a low of 11% to a high of 42%).



Figure 3. Summary of apportionment of BAM mass concentrations by component for High-PM10 days for (a) PM10 and (b) PM2.5 by VSCC. High-PM10 day samples are those with 1-hr PM10 exceeding 140 µg m⁻³. "Mineral Dust" provides the upper bound on the amount of PM that could be associated with the sand dune source. The "Semivolatile" is the difference between BAM and gravimetric mass concentration, which may be a combination of incomplete drying of water in BAM and loss of semivolatile components by the filter reference method. The category labeled "Other" (green) includes water and other semivolatile components (ammonium, nitrate, sulfate and organic components), and small amounts of trace metals.

Conclusions

Filter-based chemical mass concentration measurements show that on average 14% of PM10 and 27% (VSCC) of PM2.5 can be attributed to mineral dust on high-PM10 days. Sea salt contributed roughly 4% for PM10 and 9% (VSCC) for PM2.5 on high-PM10 days. The remaining 64% of BAM PM2.5 and 82% of BAM PM10 is likely from water, organic components, ammonium, nitrate, non-sea salt-sulfate, and other semivolatile chemical species. While prior results did not report the mineral dust fraction of BAM or gravimetric PM10 [SLOAPCD, 2007], the reported mineral dust (crustal) fraction of gravimetric PM2.5 reported by the San Luis Obispo Air Pollution Control District for its Nipomo Mesa Particulate Study (Phase 1) for the Mesa2 annual 24-hr average was 20% [SLOAPCD, 2007]. This value is similar to the 7-hr afternoon average in May 2021 for above detection samples reported here (23% of gravimetric), with the higher value for the afternoons in May being consistent with the timing and season providing a conservative upper bound.

These results show that on average less than one-fifth of the BAM PM10 at CDF can be attributed to dust during the high-PM10 days sampled in April-May 2021. Rarely (one in 10 high-PM10 days sampled) mineral dust accounted for almost one-third of the BAM PM10. There is no evidence of mineral dust contributing all or even the majority of BAM PM10, as has apparently been assumed in past reporting [SLOAPCD, 2007].

The association of high PM10 and PM2.5 with high wind conditions, even when recreational vehicles were limited at Oceano Dunes compared to prior years, indicates that dune-derived mineral dust is more likely to be primarily caused by natural forces (*i.e.* wind) rather than human activities. The attribution of mineral dust to natural wind is a common feature of air quality in the western U.S. [Malm et al., 1994; Noll et al. 1985]. While the short duration of this study provides only limited statistics in support of this result, the longer records provided by APCD provide additional confirmation [Li et al., 2013]. For this reason, the contribution of mineral dust to high PM10 concentrations measured on high wind days in and downwind of Oceano Dunes are likely dominated by natural saltation processes associated with the indigenous geomorphological dune structure rather than by recreational activities, as negligible differences were observed between weekday and weekend concentrations [Li et al., 2013].

PM2.5 and PM10 mass concentrations at CDF show contributions of sea spray and mineral dust during high wind episodes. This result means that a substantial fraction of PM2.5 was not associated with fossil-fuel combustion emissions, so that PM2.5 is not a good predictor of toxic emissions or health effects for this location in high wind conditions. For this reason, direct measurements of toxics would be needed in order to associate PM2.5 (or PM10) with health effects at this location.

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For completeness, the measured composition of all CDF PM10 and PM2.5 measurements are shown in Figure A1. These include PM10 and VSCC and SCC PM2.5 for High-PM10 days and for all days that were above detection. The mineral dust contribution is 14% for PM10 on both High-PM10 days and all days above detection. For PM2.5, the High-PM10 days have a higher contribution of 27% for VSCC (19% for SCC) compared to 20% for VSCC (15% for SCC) on all days above detection.



Figure A1. Summary of apportionment of BAM mass concentrations by Component for (a,b,c) Hi-PM10 days and (d,e,f) all samples that were above the detection limits. High PM10 day samples are those with 1-hr PM10 exceeding 140 µg m⁻³. "Mineral Dust" provides the upper bound on the amount of PM that could be associated with the sand dune source. The "Semivolatile" is the difference between BAM and gravimetric mass concentration based on incomplete drying in BAM, and it is likely to include water, ammonium nitrate, and other semivolatile components. The category labeled "Other" (green) may include water and other semivolatile components (ammonium, nitrate, sulfate and organic components) as well as non-volatile components that remain at 35% relative humidity and were not measured by this project.

There were 14 measurements that were above detection limits for VSCC and SCC; 11 of these were at mass concentrations below 20 μ g m⁻³ which meant an uncertainty of 25-50% for a gravimetric measurement error of 10 μ g, resulting in only a moderate correlation (R=0.51). This lack of sufficient data for a comparison is the result of targeting higher concentrations and a short time period in order to quantify the maximum mineral dust contribution. Nevertheless, on average, the SCC measurements were consistently lower than the VSCC 27%. As noted above, the less-sharp SCC

cutoff can only explain this if ~30% of PM2.5 mass concentration lies directly below the PM2.5 cutoff with very little mass above the PM2.5 cutoff. While this is possible, it is an unusual particle size distribution for mineral dust and should be confirmed with size-resolved composition measurements.



The SCC method has demonstrated size cut sharpness of 1.25 [Cauda et al., 2014]. The VSCC method has a reported sharpness of 1.16 under clean conditions [Kenny and Thorpe, 2000], although that sharpness is expected to increase (i.e. become less sharp) as particles accumulate in the cyclone between cleaning [Kenny et al., 2004]. There is also evidence that performance of similar cyclones degrades at increasing relative humidity due to wall effects [Chen and Huang, 1999]. Desorption or adsorption of semivolatile components can occur during sampling and during storage, tending to increase with higher flow rates, longer sampling times, changing temperatures, and changing ambient conditions [Lipfert, 1994; Appel et al., 1979; Mader et al., 2001].

We can further investigate the PM2.5 differences by comparing the VSCC and the SCC mass concentrations. On the 7 high-PM10 days when both VSCC and SCC sampled, the average gravimetric mass concentration was 27.6 μ g m⁻³ for VSCC and 19.5 μ g m⁻³ for SCC. Of the difference of 8.1 μ g m⁻³, the concentration that is attributable to salt is 1.2 μ g m⁻³ and to mineral dust is 3.6 μ g m⁻³ leaving 3.2 μ g m⁻³ attributable to differences in semivolatile or unmeasured components. This result indicates that 60% of the difference was due to size cut performance with the VSCC collecting more mass than the SCC, and that up to 40% of the difference may have been due to differences in adsorption and desorption associated with the difference between VSCC filters and BAM PM2.5 on high-PM10 days, since both filter methods will have more net desorption of semivolatiles than BAM. The difference in size cut performance of 4.8 μ g m⁻³ (18%) between VSCC and SCC is higher than has been reported for other intercomparisons in

the literature [Kenny et al., 2017; Peters et al., 2001]. The low bias of SCC relative to VSCC could only be explained by the larger sharpness value of 1.25 compared to 1.16 if there are higher mass concentrations just below 2.5 µm than above the 2.5 µm, as that would be the condition under which the higher sharpness of VSCC collection exceeds SCC collection [Li et al., 2019]. Further size-resolved chemical measurements could be used to confirm this assertion. This explanation seems unlikely given that SCC penetration curves often show a bias toward larger sizes [Peters et al., 2001]. This result is consistent with previous reports of high PM2.5 relative to PM10 near CDF [Craig, 2011; SLOAPCD, 2007].

There are a number of other reasons that VSCC and SCC differ, including performance degradation caused by changes in loading and humidity that can change VSCC or SCC cutoff performance or sharpness [Chen and Huang, 1999; Lin et al., 2018; Kenny et al., 2004]. For example, changes in VSCC sharpness from 1.16 to 1.19 have been observed after multiple days of high concentrations (150 µg m⁻³), which resulted in a small positive bias by the VSCC when tested on coarse aerosol [Kenny et al., 2004]. The high bias of VSCC was also present in field tests with high ratios of coarse to fine aerosols, as in Phoenix, Arizona, although observations at high concentrations were not available [Kenny et al., 2004]. SCC differences from the EPA method of record (Well Impactor Ninety-Six, WINS, described in the US Federal Register 40 CFR Part 50, Appendix L, https://www.ecfr.gov/current/title-40/chapter-l/subchapter-C/part-50) for PM2.5 have typically been reported <5% [Lin et al., 2018], with a lower decrease in efficiency from high loading and higher differences for coarse aerosol [Kenny et al. 2000]. It is also possible that the lower flow rate used for the SCC could enhance particle losses in the cyclone [Mader et al., 2001; Appel et al. 1979]. While lower SCC sharpness could account for some of the mass difference between SCC and BAM PM2.5, the remaining difference of 18% for VSCC would still only be explained by evaporation of some components or BAM calibration issues. Moreover, it does not explain the 35% difference between gravimetric and BAM PM10. Records of the BAM internal temperature and relative humidity could show the water content in the BAM, which could have a strong effect on the comparison [Huang and Tai, 2007]. For consistency with the BAM (with VSCC size cut), the VSCC filter results are used for PM2.5 apportionment.

Ambient relative humidity varies during the course of a typical day at CDF, with a minimum of 60-80% at approximately noon (Figure A3). This means the relative humidity in the afternoon is typically increasing to the night time value of 60-80%. When ambient relative humidity is increasing, BAM measurements may tend to be higher than gravimetric even though the 24 hr average may be similar.



Figure A3. Daily time series of wind speed (top), BAM PM10 (middle), and ambient relative humidity (bottom) from 27 April to 26 May 2021 at CDF. The green box shows the filter sampling time to capture the highest wind speeds with the highest mineral dust contributions. This time period includes increasing ambient relative humidity.

There are several estimates for crustal material from elemental composition that have been introduced. A classic estimate for the western U.S. [Malm et al., 1994; Motallebi et al., 2003] is based on five of the most prevalent elements (Al, Si, Ca, Fe, Ti) and was also used by San Luis Obispo Air Pollution Control District for its Nipomo Mesa Particulate Study (Phase 1) [SLOAPCD, 2007]. A more comprehensive estimate was proposed to account for additional minerals from nine elements (Mg, Al, Si, K, Ca, Ti, Fe, Mn, Ba) [Usher et al., 2003], but needed to be corrected to avoid double counting of sea salt components (Mg, Ca, K) [Gilardoni et al, 2007]. Figure A4 shows that these three estimates are within ±3% of each other.



exclude sea salt, and Malm et al. (1994), both without sea salt correction.

To compare these estimates of mineral dust to the specific composition of Oceano Dunes, we also collected samples of sand from Oceano Dunes to be resuspended and measured gravimetrically for PM10 concentration. The resuspension was completed at 35% relative humidity. It shows that at this low relative humidity there is still approximately 27% water present.

Appendix B

B.1 Sampling Flow Configuration Design

The configuration of the sampling flow used by Scripps was designed by calculating the minimum losses using current state-of-the-art calculations. To optimize the sampling for high-wind, high-PM10 conditions, the collection systems used were not based entirely on federal reference methods (FRM), since those methods were not designed for the relevant conditions. Nonetheless, the PM10 sampling inlet and the gravimetric analysis and conditioning were based on FRM.

The PM10 sampling inlet used was the same as that used for BAM. This inlet is designed to be approximately "isokinetic" in many wind conditions, where isokinetic means that the ratio of the wind speed to the velocity in the sampler is equal. In this sense, all sampling for BAM and filters, and by Scripps and SLOAPCD, had the same wind speed to flow conditions, pulling 16.7 Ipm through the sampling head.

In order to allow for 7-hr samples with the XRF method that was recommended as most accurate by Chester Labs, the flow after the inlet was split so that only part of the 16.7 Ipm was collected on the filters. This plan was discussed with Parks and DRI. The design for a flow splitter varies based on size range and flow ratio, and these factors were considered using a peer-reviewed model of particle losses (Leiden et al., 2009). Scripps calculated the effects of non-isokinetic sampling, non-isoaxial sampling, diffusion losses, sedimentation losses (and gains), turbulent inertial deposition, inertial deposition in a bend, and inertial deposition in a contraction (Figure B1). Because the target of the project was PM10, we optimized the flow sampling to prevent PM10 losses. To do this, for the air flow carrying the sampled PM10, we maintained isoaxial flow in a downward direction, with no bends and laminar conditions. This means that coarse particles are efficiently captured on the filter, and, if anything, the sample provides an upper bound on the coarse particle mass. Specifically we calculated that the supermicron mass could be enhanced 2-40%, with an expected enhancement of 20% for a mean mass diameter of 6 µm. While a custom designed splitter would have allowed fewer losses in the bypass flow removed, it would still have incurred either losses or gains based on the angle of the flow to the filter. For this reason, the potential 20% enhancement was considered acceptable. We note that while a minority of PM10 filter gravimetric samples did exceed BAM concentrations, the majority did not, indicating that the difference between BAM and gravimetric is not from the sampling configuration.

A similar design of flow splitting to the PM10 was used for PM2.5 collection with the VSCC filter, but for fine particles the expected enhancement was only +2%. Since the SCC was used as a backup and comparison to the VSCC, to conserve resources and available equipment, it was collected downstream of two 90-degree sampling bends in the PM10 setup. Such bends cause large losses of coarse particles, but the combined effect of the two bend-splits was -1% for PM2.5. For this reason, the 90-degree bends available with off-the-shelf plumbing was considered sufficient. These -1% to +2% differences are too small to explain the observed differences between PM2.5 VSCC and SCC. They are also too small to explain the differences are most likely due to variability in ambient relative humidity and upwind particle source types that result in differing contributions from semi-volatile particles.



Figure B1. Particle sampling efficiency associated with the flow sampling design for each of the collectors used in the Scripps study. Note that sampling efficiency above 100% indicates increases in concentrations whereas sampling efficiency below 100% indicates decreases in particle concentrations (losses). The PM2.5 SCC flow included two bends with splits, and those are shown separately and as the product of both. The black vertical line indicates the PM2.5 cutoff and the right end shows the PM10 cutoff.

B.2 Evidence of Semivolatile Contribution to Differences between BAM and Gravimetric

Because temperature controls whether particles are in the gas phase or the particle phase for semivolatile components, showing the role of semivolatiles is clear from a consideration of temperature on the differences between the BAM and Gravimetric methods. To do this, we note that the Scripps sampler was suspended on a building and the filters remained on the sampler for only the 7 hr of sampling in the afternoon. In this sense, the sampling and the filters were at ambient temperature. In contrast, the BAM was located inside the APCD shelter at CDF, which is temperature controlled to maintain 20-30°C continuously. This temperature was typically warmer than ambient during May 2021, resulting in a heating of air as it was sampled and then a further heating inside the instrument for the purpose of reducing the relative humidity to below 30%. While the temperature inside the instrument is not recorded, the temperature inside the instrument room is recorded and has been provided by APCD.

If there were no contributions from semivolatile components, then there would be no effect of temperature on either the BAM or Gravimetric results. However, as shown in Figure B2, there is a moderate correlation between the ratio of BAM to Gravimetric and the ambient temperature. This indicates that the warmer the outside temperature, the more BAM exceeded gravimetric. This is consistent with the fact that the saturation pressure of water and other semivolatile components increase with temperature, allowing air to "hold" more in the vapor phase that is then available to condense onto particles (and filter substrates, especially for glass and quartz filters typically used in the BAM). This effect is especially important downwind of the ocean, where air is often near 100% relative humidity.



Figure B2. Relationship between the ratio of PM10 APCD BAM to Scripps Gravimetric mass concentrations with the average ambient temperature at CDF during 7-hr afternoon samples in May 2021. The correlation indicates the larger role of gas uptake and evaporation in causing the larger difference between the two PM10 methods at higher temperatures.

To illustrate that there is more water available at higher ambient temperatures for the same relative humidity, it is important to consider how different water amounts represent the same relative humidity for different temperatures. For the May 2021 sampling, the average relative humidity in the afternoon was 71% with a standard deviation of 6%. Figure B3 illustrates the absolute amount of water present for a constant relative humidity of 71% at a series of different ambient temperatures observed during May 2021 (12-17°C). For this temperature range, at the same relative humidity of 71%, the water vapor pressure ranges from 10 to 14 mbar (or equivalently the mass fraction or specific humidity varies from 0.006 to 0.009 g/m³). These data illustrate the water amount changes even more than the temperature even if relative humidity is nearly constant.



for a constant relative humidity (RH) of 71% as a function of ambient temperature. During May 2021 the average relative humidity for the afternoon sampling period was 71%, but the ambient temperature varied from 12 to 17°C so that the amount of water vapor also changed as a strong function of temperature.

This result is also similar to the results from another near-coastal site (in suburban Athens) during a 4-year study (Triantafyallou et al., 2016). It is worth noting that this study found that the BAM and gravimetric results were most similar when the same type of filter was used for gravimetric as was present in the BAM, suggesting that if both filters adsorbed the same amount of semivolatile then the results agreed better. However, Scripps used a Teflon filter, which is known to take up fewer semivolatile components from the gas phase (Mader et al., 2001). Generally this means that the Scripps Teflon filters would be expected to be lower in concentration because they had a smaller artifact from the uptake of gases.

There were some Scripps Teflon filters that were higher than BAM, and to understand this effect we consider the difference between the ambient and room temperatures, namely how much the air was heated when entering the room, before it even got to the BAM instrument. This relationship is shown in Figure B4, where the weak correlation indicates a smaller effect, but nonetheless an important relationship. The BAM is lower than the Gravimetric only when the difference between the ambient and room



temperature is highest. Specifically, the trendline for the BAM to Gravimetric ratio falls below the equivalence at 1 when the temperature difference is greater than 11°C.

Figure B4. Dependence of the ratio of PM10 APCD BAM to Scripps Gravimetric mass concentrations with the difference between the instrument room temperature and the average ambient temperature at CDF during 7-hr afternoon samples in May 2021. The correlation indicates the role of heating the instrument room relative to the outside temperature in causing the smaller difference between the two PM10 methods.

In addition to temperature, the effect of semivolatile components can be related to the amount of semivolatile components present in the air being sampled. While the relative humidity is a "relative" measure of that amount of water vapor, the absolute humidity (usually called the specific humidity) or the water vapor pressure are metrics used to quantify the amount of water actually present in the air. As suggested by Triantafyallou et al. (2016), this quantity needs to be normalized to the amount of particles in the air, so that the relative effect on the mass concentration will be scaled appropriately. This comparison of the ratio of BAM to Gravimetric mass concentration to the normalized water vapor pressure is shown in Figure B5. Again the correlation is weak though quite evident. The weakness of the correlation is consistent with the expectation that water vapor is not the only semivolatile component contributing to the difference between BAM and Gravimetric, as nitrate and organic components likely also play a role.



B.3 Implications of Evidence for Gas Uptake and Evaporation for Mineral Dust

There is no reason to believe that the Scripps measurements of mineral dust mass concentration would be affected by gas uptake and evaporation. The temperature dependence of the ratio of the BAM and Gravimetric methods shows that gas uptake and evaporation play a major role in the difference between the methods, but the mineral dust does not change with temperature. It is worth noting that this report does not address the question of whether BAM or gravimetric for the 7-hr afternoon sampling is considered "right" -- either atmospherically most accurate or legally most relevant -- as that was not the objective of the Scripps study. However, since BAM has been put forth by APCD as the standard by which exceedances should be determined, the measured mineral dust fraction should be reported on the basis of that same standard. This means that the ratio of mineral dust to BAM mass concentration is completely unaffected by the differences in gas uptake and evaporation between the two methods.

The results of this study do suggest that further consideration of the effects of temperature conditioning on PM10 measurements of the BAM and filter sampling at CDF is merited, even though the mineral dust concentration is not dependent on those results.