21 September 2020

The Off-Highway Motor Vehicle Recreation Commission
c/o
Off-Highway Motor Vehicle Recreation Division
California Department of Parks and Recreation
1725 23rd Street, Suite 200
Sacramento, CA 95816

Dear Commissioners,

Please find attached my supplemental report of findings regarding gravimetric and elemental analyses of airborne particle samples collected at the Oceano Dunes State Vehicular Recreation Area and on the Nipomo Mesa. My colleagues and I are in the second year of a three-year investigation to determine marine and terrestrial sources contributing to airborne particulate matter (PM) detected seasonally on Nipomo Mesa (Mesa). The San Luis Obispo County Air Pollution Control District (APCD) operates equipment on the Mesa at a location called CDF that monitors PM10 and PM2.5 (PM that is 10 microns or less in diameter and 2.5 microns or less in diameter, respectively) with an instrument called a beta attenuation monitor (BAM).

This supplemental report was prepared in response to your request made at your August 6, 2020 meeting. As I understand it, your request was prompted by our February 20, 2020 report, which detailed a difference between the PM2.5 mass of the chemical components that we measured and the PM2.5 mass measured by the APCD BAM. Those findings prompted us to use additional techniques to more accurately determine what fraction of airborne particles are dust. As detailed in this report, I have found that mineral dust, on average on high PM days, accounts for 20% of the overall mass of the PM2.5 measured by the APCD BAM at CDF. On lower PM days, the mineral dust mass is lower still. This shows that it is incorrect to assume that all PM2.5 measured at CDF monitors is mineral dust.

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. I look forward to continued collaboration as this project continues.

Sincerely,

Lynn M. Russell
Professor of Atmospheric Chemistry
Introduction

Building upon the results of the UCSD Report of 5 February 2020, this project has undertaken additional quantitative chemical sampling to improve the understanding of the sources of airborne particles in the Oceano Dunes area. This supplemental report covers the gravimetric and elemental analyses of the teflon filters collected during the most recent sampling period from 27 April 2020 to 17 May 2020. The objectives of this part of the research were to
1) Quantify the gravimetric mass and elemental component mass of PM2.5 aerosol particles at CDF;
2) Quantify the gravimetric mass and elemental component mass of PM10 aerosol particles at a near-beach site just beyond high tide, designated as the “Beach” site.

It is important to note that recreational vehicles were not allowed during this period because of COVID-19 restrictions that had been in place since March 2020. Vehicles for park services including habitat restoration continued essential activities.

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. Both sea spray and sand (or mineral) dust are increased by wind speed as well as coverage and proximity, 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), and 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. 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]. Recently Apte et al., 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. 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 health effects, the use of PM2.5 as a health indicator assumes it co-occurs with toxics.

However, it is worth noting that there is no evidence that toxic compounds 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 would not hold. 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 each of these different sources. In the 5 February 2020 UCSD Report, we used Fourier Transform Infrared (FTIR) spectroscopy and X-ray Fluorescence (XRF) to provide a first cut at these sources, using elemental composition to provide tracers for sea spray, mineral dust, and combustion emissions. This report builds on those results to examine the substantial difference between the chemical measurements of dust components and the BAM PM2.5 measurements regularly measured 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 (RH)) are used to provide a lower bound on the water fraction of the particle mass. Then dust components from XRF measurements are used to assess the fraction of the remaining mass that is associated with dust.

Results

Samples were collected at CDF site and the Beach site for the period of 27 April to 17 May 2020. The CDF site was co-located with the ongoing APCD sampling by BAM, which provides a metric representing the PM2.5 (and PM10) concentration at modified ambient conditions, which means that water and other semi-volatile 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. The Beach site was sampled from 28 April to 16 May 2020, with more limited samples targeting only high wind (high PM) afternoons. The number of samples at this site was limited by the lack of sufficient power for 24-hr operation and the lack of support personnel due to access restrictions (and COVID-19). The Beach site was selected to provide a benchmark for non-dune ocean sources, since it is estimated to be approximately 100 meters from the mean high tide line. Notably, the days with high PM at CDF were often predicted successfully from short-term forecasts of high-wind conditions, consistent with prior studies.

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 PM2.5 aerosol particles at CDF.
   a. The time series of SIO gravimetric mass, EBAM, and APCD BAM PM2.5 concentration measurements tracked reasonably well (Figure 1) and
showed a moderate correlation ($R^2 \sim 0.7$). The offline gravimetric method is 26% lower on average than the online BAM instrument for all 26 afternoon and overnight samples at CDF (Figure 2). If only the 10 afternoons with 24-hr PM10 exceeding 140 $\mu g \, m^{-3}$ are averaged (https://ww3.arb.ca.gov/qaweb/site.php?s_arb_code=40853), then the gravimetric method is 38% lower than BAM. The lower gravimetric mass concentrations are consistent with the expectation that the BAM method includes more water than the gravimetric reference method. The PM2.5 sampling reference method (https://www3.epa.gov/ttn/amtic/files/ambient/pm25/qa/m212.pdf) requires that samples be stored at 35% relative humidity for 24 hr in order to partially dry the particles. In contrast, BAM and EBAM measurements are made very close to ambient relative humidity (although there may be some heating in the instrument). At CDF relative humidity frequently exceeded 35%, meaning that the BAM and EBAM measurements were wetter (that is, contained more water than the gravimetric measurements). It is likely that the 38% difference in mass on high PM10 days is due to water evaporating, although other semivolatile components (ammonium nitrate and organic mass) could also be included in the BAM method and not in the gravimetric method. It is unlikely that any dust was lost by the gravimetric method. The water contribution could be assessed by repeating the gravimetric method at higher relative humidities.

b. The time series of dust from elemental composition by XRF frequently tracked gravimetric mass (Figure 3). The scatter plot showed that dust accounted for $\sim 17\%$ of PM2.5 gravimetric mass on average and salt accounted for $\sim 11\%$ for all 26 afternoon and overnight samples (Figure 4). If only the 10 afternoons with 24-hr PM10 exceeding 140 $\mu g \, m^{-3}$ are averaged, then the dust accounted for 33% and the salt for 7%. Dust and PM2.5 were strongly correlated with $R^2 \sim 0.8$, whereas salt and PM2.5 were only weakly correlated with $R^2 \sim 0.3$. The correlation of dust and PM2.5 could be explained by the lofted dust including a proportionate amount of water that contributes to the PM2.5. Other semi-volatile components that may associate with the higher surface area provided by the dust would also proportionately increase the PM2.5 concentration. The weak correlation between salt and PM2.5 is consistent with salt being a small fraction of PM2.5 that is affected by factors other than local wind speed (including offshore winds and whitecap coverage).

2. **Quantify the gravimetric mass and elemental component mass of PM10 aerosol particles at the Beach site.**
The time series of gravimetric mass and EBAM PM10 concentration measurements tracked reasonably well (Figure 5) and showed a moderate correlation ($R^2 \sim 0.5$), with the offline gravimetric method being on average ~28% lower than the online EBAM instrument for the 7 afternoons sampled (Figure 6). The poor correlation is limited by the small number of samples (7). The lower gravimetric mass concentrations are consistent with the expectation that the EBAM method includes more water than the gravimetric reference method, which requires 35% relative humidity even though ambient relative humidity at the Beach site frequently exceeded this value. This means that the gravimetric mass concentration includes less water than the EBAM measurement, although other semi-volatile components (ammonium nitrate and organic mass) could also be included in the EBAM method. This suggests that at least 28% of the EBAM mass concentration was water. It is unlikely that any dust was lost by the gravimetric method. The water contribution could be assessed by repeating the gravimetric method at higher and lower relative humidities.

The elemental composition showed that dust accounted for ~16% of PM10 gravimetric mass on average and salt accounted for ~7%. Both dust and salt were strongly correlated with PM10 and $R^2 \sim 0.9$. The correlations of dust, salt, and PM10 is likely caused by wind speed serving as the primary driver of all three. The lofted dust and salt may also bring with them water proportionate to their hygroscopicity, a property determined by the chemical composition of the suspended salt mixture. Other semi-volatile components that may associate with the higher surface area provided by the dust may also increase the PM10 concentration.

The breakdown by weight and by component of the BAM concentrations measured at the CDF and Beach sites are summarized in Figure 9, where we have interpreted the difference between BAM and gravimetric mass as the evaporated fraction that is likely water and illustrated the measured mass component contributions from Dust, Salt, and Other. The gravimetric fraction of BAM PM2.5 is lower at 62% on high PM10 afternoons compared to 74% for all samples measured. Dust accounts for 33% of gravimetric PM2.5 at CDF on high PM10 afternoons compared to only 17% for all samples measured. Combining the gravimetric and dust measurements, the end result is that on days with high 24-hr PM10 at CDF, the combination of the gravimetric mass as 62% of the BAM PM2.5 mass and the dust accounting for ~33% of gravimetric PM2.5 mass means that dust accounts for on average 20% of the BAM PM2.5 at CDF on high PM10 days. This means that on average one fifth of the BAM-based PM2.5 at CDF can be attributed to dust during the ten high PM10 days sampled in April-May 2020.
Conclusions

PM2.5 mass concentrations at CDF show large 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 with health effects at this location.

The association of high PM10 and PM2.5 with high wind conditions, even when recreational vehicles were not allowed at Oceano Dunes, indicates that dune-derived mineral dust is more likely to be caused by natural forces (i.e. wind) rather than human activities. 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. For this reason, the high dust 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.

The correlation between the online BAM and EBAM measurements with filter-based gravimetric measurements indicated good correspondence of the metrics given the limited sampling and differences in relative humidity. The moderate correlation of the gravimetric PM2.5 with the BAM PM2.5 ($R^2=0.7$) at CDF provides general support for the BAM PM2.5 calibration and operation with the moderate correlation being consistent with expected differences in relative humidity between the methods. The fact that the mass concentrations of the gravimetric PM2.5 (CDF) and PM10 (Beach) were consistently lower (by 26-38% and 28%, respectively) than the corresponding CDF BAM measurements supports the idea that a third or more of the BAM mass is likely water at coastal locations like the APCD CDF BAM site. The most probable reason for this is that the gravimetric measurements are partially dried by equilibrating at 35% relative humidity whereas the BAM measurements vary with ambient conditions. The more consistent fractions of PM10 (i.e. $R^2>0.95$) would be consistent with the remaining mass being controlled by the components present, which would be the case for water.

To remove the contributions of the additional water in the BAM measurements, the chemical mass fractions are compared on the basis of the gravimetric mass. Relative to the partially dried gravimetric mass, the chemical mass measurements show that on average less than 33% of PM2.5 at CDF and less than 16% of PM10 at the Beach site can be attributed to dust. About 7-11% can be attributed to sea salt at both sites for the sizes measured. The remaining 60-72% of gravimetric PM2.5 at CDF and 77% of
gravimetric PM10 at the Beach is likely from additional water (beyond the 26-38% included in the BAM), organic components, ammonium, nitrate, and other semi-volatile chemical species.

On days with high 24-hr PM10 at CDF, the combination of the 38% water in the BAM method relative to the gravimetric method (leaving 62% of the BAM PM2.5 mass as non-water) and the dust accounting for ~33% of gravimetric PM2.5 means that dust accounts for on average 20% of the BAM PM2.5 at CDF (on high PM10 days). This means that on average one fifth of the BAM-based PM2.5 at CDF can be attributed to dust during the ten high PM10 days sampled in April-May 2020.

Since the sampling reported here was limited by resources because of other activities at Oceano Dunes, additional offline chemical and gravimetric analysis are planned in order to provide additional evidence of the variability of the fraction of PM2.5 that is dust on high PM2.5 days.

Methods

Aerosol particle sampling used sharp-cut cyclones operated with calibrated flows to collect particles for analysis at ambient diameters with a calibrated cut at 2.5 μm (SCC 2.229 operated at 7.5 lpm, BGI Inc., Waltham, MA) and a sampling head with nominal cut at 10 μm (16.7 lpm, provided by State Parks). 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]. Blank filters provided a measure of adsorption during sampling and contamination during handling (loading and unloading) and storage.

Simultaneous sampling by BAM, EBAM, and filters were used to check for sampling consistency by comparing gravimetric mass on filters to co-located BAM measurements. The hourly BAM and EBAM concentrations reported between the start and stop times for the filters were averaged (without interpolation) to provide approximate comparison points. Further refinement would be provided by a more exact integration and interpolation of beginning and ending hours.

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 of 35%+/−5% 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 and EBAM may also be drier than ambient humidity due to heating of the air when it is drawn into the instrument. Other differences may result from the hour-to-hour differences in the online measurements compared to the offline storage at constant conditions.

Each sample (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 heavier than Na [Maria et al., 2003]. Elemental concentrations were above detection for 30% to 100% of the ambient teflon filters collected.

Acknowledgments

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References


Figure 1. Time series of PM2.5 mass concentrations [$\mu$g m$^{-3}$] by Gravimetric, EBAM, and BAM methods at CDF for sampling from 27 April to 17 May 2020.
Figure 2. Scatter plot of PM2.5 mass concentrations [μg m⁻³] by Gravimetric and BAM methods at CDF for sampling from 27 April to 17 May 2020. The fitted trendline indicates that the Gravimetric concentrations correlate to BAM concentrations with $R^2=0.687$. 
Figure 3. Time series of PM2.5 mass concentrations [μg m⁻³] for Dust, Salt and Gravimetric (total) concentrations at CDF for sampling from 27 April to 17 May 2020.
Figure 4. Scatter plot of PM2.5 mass concentrations [μg m$^{-3}$] for Dust, Salt and Gravimetric (total) concentrations at CDF for sampling from 27 April to 17 May 2020. The fitted trendline indicates that for this limited data set the Dust concentrations correlate to Gravimetric concentrations with $R^2=0.817$ and the Salt concentrations correlate to Gravimetric concentrations with $R^2=0.308$. 
Figure 5. Time series of PM10 mass concentrations [μg m$^{-3}$] by Gravimetric and EBAM methods at Beach for sampling from 27 April to 17 May 2020.
Figure 6. Scatter plot of PM10 mass concentrations [μg m⁻³] by Gravimetric and EBAM methods at Beach for sampling from 27 April to 17 May 2020. The fitted trendline indicates that for this limited data set the Gravimetric concentrations correlate to EBAM with $R^2=0.535$. 
Figure 7. Time series of PM10 mass concentrations [μg m^{-3}] for Dust, Salt and Gravimetric (total) concentrations at Beach for sampling from 27 April to 17 May 2020.
Figure 8. Scatter plot of PM10 mass concentrations [μg m⁻³] for Dust, Salt and Gravimetric (total) concentrations at Beach for sampling from 27 April to 17 May 2020. The fitted trendline indicates that for this limited data set the Dust concentrations correlate to Gravimetric concentrations with $R^2=0.939$ and the Salt concentrations correlate to Gravimetric concentrations with $R^2=0.907$. 
Figure 9. Summary of apportionment of BAM mass concentrations by Weight (a,c,e) and by Component (b,d,f) for (a,b) all CDF BAM2.5 (26 afternoon and overnight samples), (c,d) high PM10 day CDF BAM2.5 (10 afternoon samples), and (e,f) Beach PM10 (7 afternoon samples). High PM10 day samples are those with 24-hr PM10 exceeding 140 μg m⁻³. The category labeled “Other” (green) may include additional water, ammonium, nitrate, sulfate and organic components, and trace metals.