Chemical Speciation and Source Attribution of PM₁₀ Samples Collected in 2021 at the CDF Monitoring Site

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Accurate attribution of PM_{10} is needed to inform Parks of the best management practices that will lead to compliance with the Stipulated Order of Abatement. Previous measurements and modeling suggest high PM_{10} concentrations observed within the ODSVRA contribute substantially to elevated PM_{10} measured downwind of the ODSVRA. The attribution of the PM_{10} measured at the CDF monitoring location to sources has, however, been a source of recent debate.

To aid in resolving the uncertainty of the source attribution of PM_{10} at the CDF monitoring site a PM_{10} measurement campaign was undertaken in 2021. Using Federal Reference Method (FRM) PM_{10} filter samplers and following US EPA Designation RFPS-1298-127 for PM_{10} sample collection, paired, preweighed Teflon-membrane and pre-treated quartz-fiber filters were used to collect 24-hour PM_{10} samples between April to October 2021. The exposed filters were weighed to calculate the 24-hour PM_{10} concentration and analyzed using x-ray fluorescence to quantify elemental composition, ion chromatography to quantify the water-soluble ions, and thermal/optical reflectance to quantify organic carbon (OC) and elemental carbon (EC) in the collected particulate matter. These are well-established methods for determining particulate matter composition. Using these speciated data, the source attribution of PM_{10} was estimated.

The identification of PM_{10} sources and estimation of source contributions used a weight-of evidence approach. First, measured PM_{10} species were grouped into seven major compositions, including fresh sea salt (FS), aged sea salt (AS), non-sea salt sulfate (nssSO₄²⁻), mineral dust (MD), elemental carbon (EC), organic matter (OM = OC × multiplier), and other measured species (Na to U). The sum of these seven composition groups is defined as the reconstructed mass, and the difference between the gravimetric and reconstructed mass is reported as the "Unidentified" mass.

For the days that exceeded the State 24 hour mean concentration limit (\geq 50 µg m⁻³) between April-October 2021 (8 days), the mean percent composition of the PM₁₀ was MD (43.1% ±15.3%) followed by sea salt (22.4% ±11.7% for FS and 2.6% ±2.8% for AS), and the Unidentified category (20.4% ±2.9%). We infer the Unidentified category represents the oxide components of PM₁₀ sized mineral particles, including carbonate, and hydrated water in clay minerals. If the unidentified category is included in the MD category, the mean exceedance day attribution increases to 63.5% (±18.2%). Sea salt can be sourced to ocean spray and the sand, as deposited salt could be emitted during saltation. The relative contribution for these two sources, however, remains unresolved. The wind and PM₁₀ data record at CDF (2019-2022) shows that exceedance of the State 24-hour PM₁₀ standard has the greatest likelihood of occurring when wind direction at CDF is between 236°-326° bringing PM₁₀ to the CDF station from the direction of the ODSVRA and that as wind speed increases from this directional range the probability of an exceedance increases. Only MD (and by its association with MD, the unidentified category) and SS emissions, of the seven categories of sources defined, increase with increasing wind speed.

For non-exceedance days the mean percent composition of the PM $_{10}$ is SS 40.5% (±24.0%) followed by MD 24.2% (±14.6%), OM 22.4% (±16.6%), sulfate 7.5% (±6.0%), Others 2.8% (±2.5%) and Unidentified, 6.6% (±6.0%). PM $_{10}$ on non-exceedance days reflects more the regional attribution of sources when MD is not actively being emitted in the ODSVRA under conditions of elevated wind speed.

For the period of time, April to October, PM_{10} sampling was undertaken in 2021, the speciation data strongly supports that the principal source affecting the CDF site is wind-generated mineral dust from the ODSVRA.