Summary Report: Mapping Dust Fallout from the November 2022 Martinez Refining Company Incident Using Observations and Modeling

April 5, 2023
Bay Area Air Quality Management District

Background

On Friday, November 25, 2022, staff from the Bay Area Air Quality Management District (Air District) received complaints from citizens living near Martinez Refining Company (MRC) about a white, ash-like substance that was deposited on cars and other surfaces. After investigations by Air District staff, it was determined that the source of the dust fallout was a process unit upset at MRC's fluid catalytic cracking unit (FCCU). This upset resulted in the release of catalyst material from the FCCU and the subsequent deposition of catalyst dust on the ground and other surfaces in downwind areas.

In the FCCU, chemical reactions involving a catalyst material crack bonds within heavy oil feedstocks to supply other products that can be further treated within the refinery. Once the reaction is complete, the spent catalyst is regenerated by burning off deposited carbon, or coke, which produces flue gas that can still contain small quantities of the catalyst. The flue gas is sent to carbon monoxide boilers (COBs), thermal oxidizers that convert carbon monoxide (CO) in the exhaust stream to CO_2 and use the gas as fuel to produce steam for the refinery.

The COBs are equipped with abatement devices called electrostatic precipitators (ESP) that use electricity to remove most of the catalyst material and other particulate matter that remain entrained in the flue gas. The COBs are also equipped with opacity sensors to monitor levels of particles emitted with the flue gas under normal operating conditions. Under normal operations, the ESPs are online to prevent opacity excesses. However, MRC electively shuts down the ESPs during startup and shutdown of the FCCU for safety reasons. Because the FCCU experienced a unit upset on the night of Sunday, November 20, 2022, the ESPs were offline from the early morning of Monday, November 21, 2022, to Friday, November 25, 2022.

During the procedure of restarting the FCCU, MRC plant operators were unable to control pressure imbalances that built up in the catalyst flow. Separators that would normally collect and recycle the catalyst material were overfilled, allowing excess catalyst to exit the COBs. The opacity sensors in the COBs maxed out, meaning that catalyst emissions were so great that the opacity sensor readings were no longer proportional to the amount of particulate matter exiting. During this period, there was no abatement control to prevent opacity excesses at the COBs, and Air District staff found that MRC recorded 12 opacity excesses between November 24-25, 2022. MRC estimated that 20-24 tons of catalyst was emitted during those two days.

Project Purpose

In December 2022, Air District staff were approached by representatives of Contra Costa Health Services (CC Health) with a request to perform a modeling-based assessment of the catalyst release at MRC. CC Health has received multiple inquiries from the public about the degree to which the soils in and around the City of Martinez have been contaminated with toxic materials from the catalyst, which may have implication for safely growing food in residential areas.

In conversations with CC Health, it was determined that the primary purpose of a modeling-based assessment of the MRC incident was to map areas where maximum deposition of the catalyst from the incident was likely to have occurred. Such maps might then inform the sampling design of soil sampling to be led by a toxicologist consultant to be hired by CC Health. In these conversations, the Air District has stressed that, while the maps may serve as a useful starting point to guide the soil sampling efforts, they cannot delineate definitive areas with soil contamination or potential health impacts. Importantly, any application of the modeling-based maps should be constrained by the following considerations:

1. Several important modeling inputs are unknown or highly uncertain.
2. In view of the large amount of rain since the event, the catalyst material has likely moved since the initial fallout.
3. There may be catalyst material in the soil from decades of routine operations or events that took place before the modeled incident.
4. Soil sampling aims to determine how much catalyst material is currently in the soil. The County's Oversight Committee has selected a toxicologist to develop a sampling plan and determine the extent of community impact from the release.

The remainder of this document provides an overview of the methods used to evaluate catalyst deposition resulting from the MRC incident and presents maps showing observations of visible dust fallout combined with results of a modeling-based assessment of dust fallout.

Dust Observations and Sampling

Starting on November 25, 2022, staff from both CC Health and the Air District visited the areas around Martinez where visible dust had been reported, including the Martinez Amtrak Station, Martinez Junior High School, Contra Costa Martinez Health Center, John Muir Elementary School, Morello Park Elementary School, and Las Juantas Elementary School. Staff from CC Health collected dust samples at two locations and had them analyzed to identify constituents in the catalyst material. Photographs were also taken of dust on vehicles and other surfaces, as shown in Figure 1. The streets visited, landmarks used for observations, and locations of samples are shown in Figure 2. Note that visible catalyst was observed along the surface streets shown in yellow in Figure 2, while visible catalyst was not observed along the surface streets shown in green. Staff from the Air District received and investigated seven complaints, observed visible fallout at five of these seven locations, and collected dust samples at the five locations where dust was observed. A sixth sample was taken from the FCCU at MRC.

Lab tests conducted on the collected samples showed that the catalyst primarily contained elements such as oxygen (O), silicon (Si), aluminum (Al), carbon (C), magnesium (Mg), and sulfur (S). It also contained trace elements of heavy metals such as nickel (Ni), vanadium (V), chromium (Cr), and zinc (Zn).

MRC provided particle size ranges for catalyst material in various stages of the catalyst processing chain under normal operating conditions. Under those conditions, particle diameters are typically about 85 micrometers (µm) in the regenerator, about 24 µm in the fourth stage separator, and about 3 µm when they exit the separator and enter the COBs.

Figure 1: White, ash-like material deposited on a car near the corner of Berrellesa and Main Streets in Martinez.

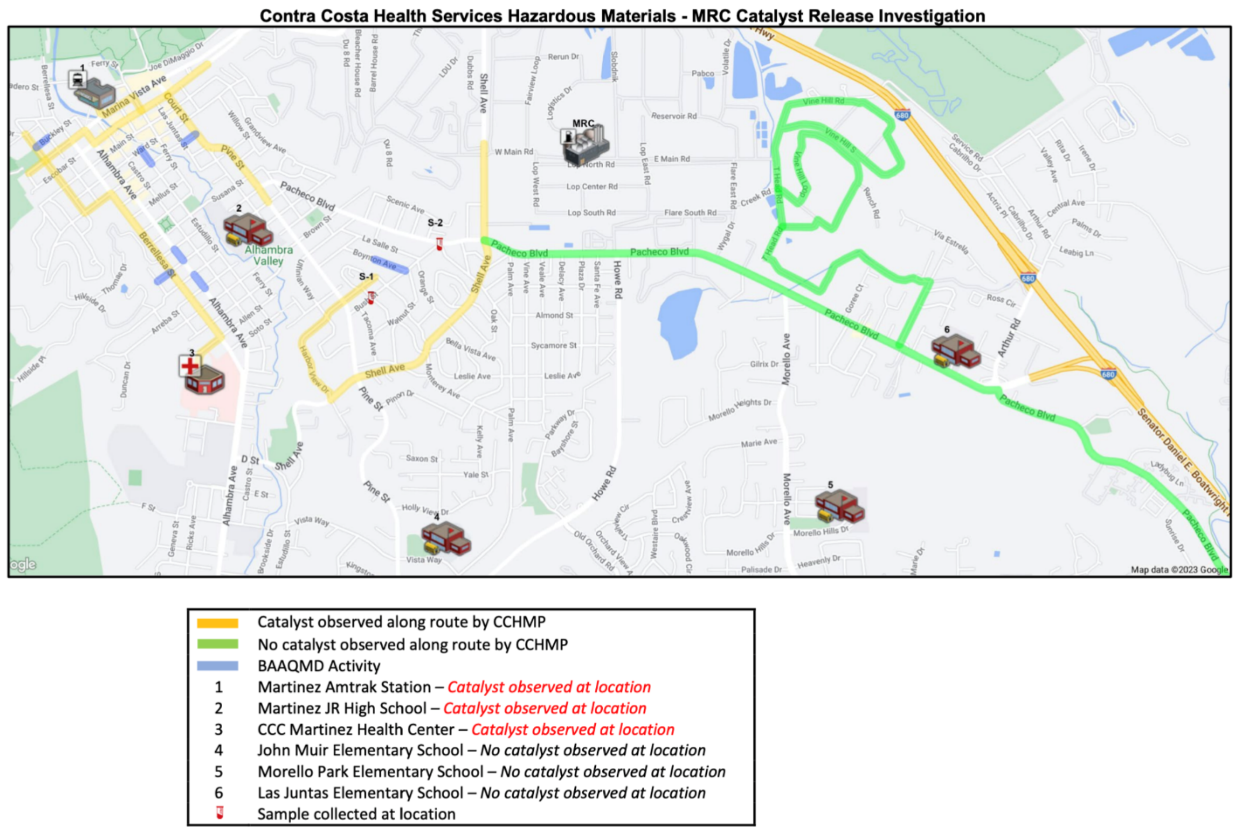

Figure 2: Locations where visible dust was observed and dust samples were collected. (Figure provided courtesy of Contra Costa Health.)

Technical Approach

Meteorological Analysis

The first step in analyzing the MRC incident was evaluating meteorological conditions during the incident period that affected the dispersion of emitted pollutants. For this assessment, Air District staff relied on two sources of meteorological data: (1) routine meteorological measurements collected within the MRC refinery; and (2) simulated meteorological data from the Weather Research and Forecasting (WRF) model (Skamarock et al., 2008). WRF is a state-of-the-science computer model which the Air District routinely applies to simulate winds and other weather conditions in preparing inputs for air quality modeling. Air District staff ran WRF at 1-kilometer (km) grid resolution for the November 2022 incident period using the same setup as prior WRF applications for the Bay Area (Tanrikulu et al., 2019).

MRC operates two meteorological stations, MRC East and MRC West, that are sited about 2.5 km apart from each other. At the MRC East station, which is closest to the COB stack locations, two sets of predominant wind regimes were evident during November 24–25, 2022: one with winds from the northeast at 1–3 meters per second (m/s), and the other with winds from the southeast at 1–2 m/s. Outputs from the WRF model corresponding to the MRC East station location showed a similar pattern, with winds predominantly from the northeast and east at 1–

4 m/s. These wind patterns are consistent with visible dust being observed in areas to the west and southwest of MRC.

Air Quality Modeling

After evaluating wind speeds and directions during the incident period, Air District staff conducted air quality modeling to help define areas likely impacted by deposited catalyst material. Such modeling is commonly used to estimate air concentrations and deposition rates resulting from the release of air pollutants by an emissions source. For this evaluation, Air District staff relied on the California Puff Model (CALPUFF), which models a continuous plume emitted by a source as a series of discrete packets, or puffs (Exponent, 2011). The evolution of these puffs in the atmosphere is governed by meteorological conditions that vary with time and location in the modeling domain. CALPUFF was run use three-dimensional, time-varying meteorological inputs from the WRF model, as described above, over the entire modeling domain, to simulate trajectories of puffs traveling to downwind areas where near-source measurements are no longer representative.[1]

In addition to information about winds and other meteorological conditions, to simulate the transport and deposition of particles, air quality models require information about the amount of material emitted by hour and the sizes of the particles emitted. MRC has estimated that, between November 24 and 25, 2022, approximately 20 to 24 tons of catalyst were lost from two active COB stacks (CO Boilers #1 and #2). For the air quality modeling, Air District staff used the higher estimate provided by MRC, taking the total amount of particulate matter released to be 24 tons from COB1 and COB2 combined during the 48-hour period.

To estimate the timing, by hour, of the catalyst emissions released from the COB stacks, Air District staff relied on hourly opacity readings from the two COB stacks. Given that higher opacity is typically associated with higher emission levels, hourly particulate matter emissions for modeling were assumed to be proportional to hourly opacity readings. As shown in Figure 3, the total emissions of 24 tons were distributed similarly for the two CO boilers across 48 hours, with most of the emissions assumed to occur from 2:00 AM on November 24 to 6:00 AM on November 25. Air District staff recognizes that during times when the opacity sensors were maxed out, emissions are no longer proportional to opacity readings, but in the absence of more reliable information, the assumption of proportionality was made.

[1] As a test, Air District staff also modeled the MRC incident using the AERMOD dispersion model with meteorological measurements from the MRC East station. AERMOD is a steady-state model that assumes emissions and meteorology are constant over each hourly time step. Though AERMOD is somewhat simpler than CALPUFF, it produced similar deposition results for the incident period.

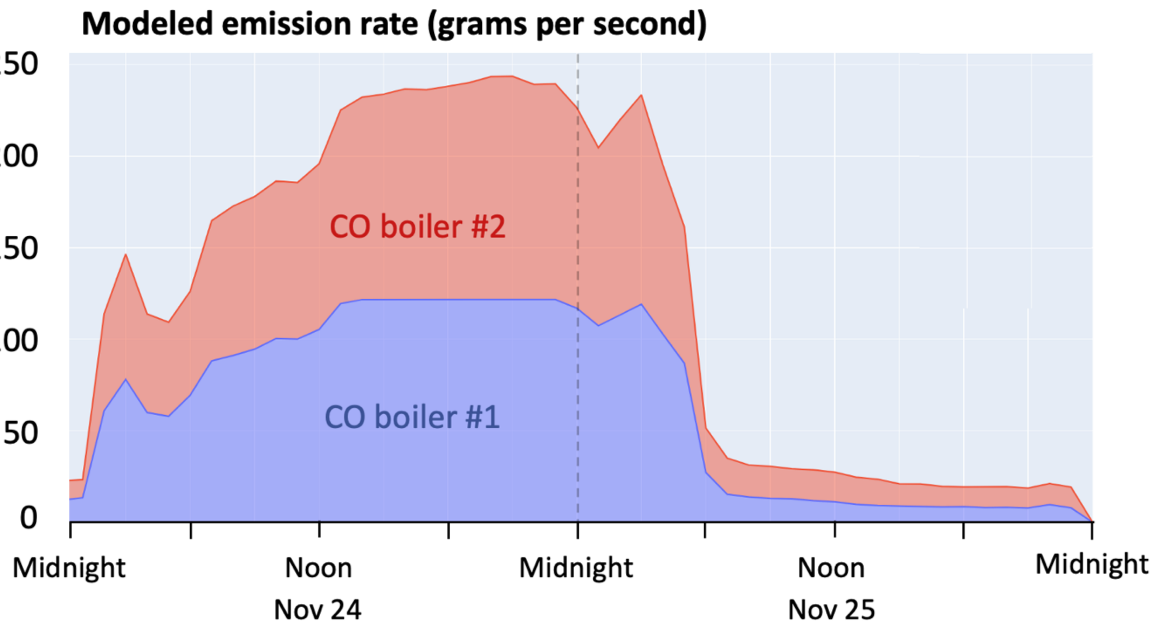

Figure 3. Hourly particulate matter emission rates (in grams per second) used for air quality modeling.

As previously noted, MRC provided particle sizes for normal operating conditions that ranged from 3 µm to 85 µm for different stages of the catalyst processing chain. Because the material deposited on cars and other surfaces around MRC consisted of coarse visible particles that were clearly larger than a few microns, Air District staff performed model runs with three different particle diameters: 24 µm, 50 µm, and 85 µm.

Lastly, the emission releases from COB1 and COB2 were configured for modeling using stack parameters provided by MRC. As shown in Table 1, these parameters included stack locations with UTM (Universal Transverse Mercator) coordinates, base elevation, stack height and diameter, and stack gas exit temperature and velocity.

Table 1. Stack parameters for the MRC CO boiler sources

Stack ID	UTM Coordinates		Base Elevation	Stack Height	Exit Temperature	Exit Velocity	Stack Diameter
	X (meters)	Y (meters)	(m)	(m)	(K)	(m/s)	(m)
COB1	577737.70	4207908.53	16.45	49.3776	839.05	16.71	2.4
COB2	577768.54	4207909.07	16.41	49.3776	566.67	18.42	2.4

Synthesized Assessment of Dust Fallout

Summary

The Air District used CALPUFF modeling simulations and field observations to identify candidate areas for soil sampling. CALPUFF outputs modeled hourly deposition rates at pre-defined receptor locations, and for the MRC modeling, receptors were spaced 50 meters (m) apart over a 16 km by 19 km area centered on the COB stacks and spaced 1 km apart in areas farther downwind. Hourly deposition values at each receptor were summed over November 24-25, 2022, to obtain the total dust fallout during the 48-hour period. Then, since separate CALPUFF runs were performed for three particle sizes (24µm, 50µm, and 85µm), results for each of those three simulations were averaged at each receptor to obtain a final modeled product,[2] which is shown in Figure 4.

In this figure, the area with the highest simulated deposition is shown in the contour with the darkest blue color, which corresponds to values exceeding 0.1 grams per square meter (g/m^2). This cutoff was used because the modeled deposition at the Martinez Amtrak station was approximately 0.1 g/m^2, and this is the further point from the refinery where visible deposition was observed. For the remaining two contours with lighter blue colors, total deposition fell below 0.1 g/m^2 but exceeded 0.01 g/m^2. For remaining areas, total deposition was below 0.01 g/m^2, or more than 10 times lower than that at the edges of the areas with the highest modeled deposition.

Note that the main area with total deposition exceeding 0.1 g/m^2 extends about 8 km to the west-southwest of MRC. A second area with total deposition exceeding 0.1 g/m^2 extends about 4 km to the north-northwest of the facility toward Benicia.

Figure 4 also shows locations where staff from the Air District or from CC Health observed visible dust (shown as yellow lines and symbols); also shown are locations where visible dust was not observed (green lines and symbols). The model-simulated contours of 0.1 g/m^2 generally match the locations where visible dust was observed.

Uses and Limitations of the Maps

The modeling-based map shown in Figure 4 is intended to inform future soil sampling, but uses of the map should consider the following:

1. Several important modeling inputs are unknown or highly uncertain, limiting the accuracy of the map, including the exact timing of the catalyst release and the sizes of the catalyst particles released when they were released.
2. Recent rain events have likely moved the catalyst dust since the initial fallout.
3. There may be catalyst material in the soil from deposition before the modeled incident.
4. The map does not show areas of community impact. The County's Oversight Committee has selected a toxicologist to develop a soil sampling plan. This soil sampling will be used to determine the extent of community impact from the release.

[2] Note that this averaged deposition field is equivalent to assuming that one-third of all emitted particles fall into each of the three size bins.

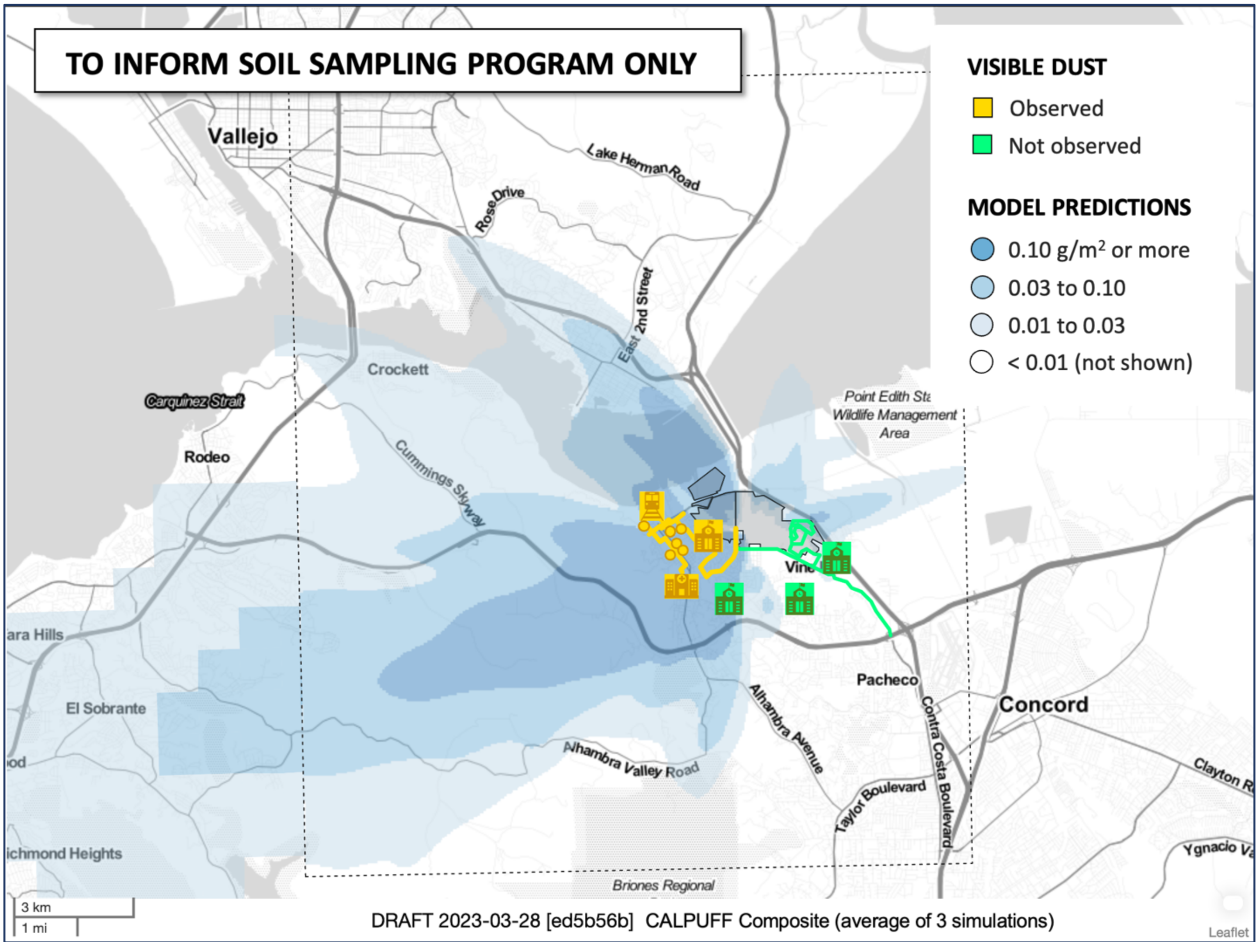

Figure 4. Map of modeled deposition values for purposes of informing the soil sampling program. This is **not** a map of where residents are impacted by catalyst material, as discussed in the Project Purpose section on page 1.

References

Exponent, 2011. CALPUFF Modeling System Version 6 User Instructions. Available at: http://www.src.com/calpuff/download/CALPUFF_Version6_UserInstructions.pdf

Skamarock, W. C., Klemp, J. B., Dudhia, J., Gill, D. O., Barker, D., M., Duda, M. G., Huang, X.Y., Wang, W., Powers, J. G., 2008. A description of the Advanced Research WRF Version 3. NCAR/TN-475+STR. Technical Report. Boulder, Colorado, USA: National Center for Atmospheric Research: Mesoscale and Micrometeorology Division, 113 pages.

Tanrikulu, S., Reid, S., Koo, B., Jia, Y., Cordova, J., Matsuoka, J., and Fang, Y., 2019. Fine Particulate Matter Data Analysis and Regional Modeling in the San Francisco Bay Area to Support AB 617. BAAQMD Air Quality Modeling and Data Analysis Section Publication No: 201901-017-PM.