Appendix B

Technical Report
Examination of the Potential for Adverse Off-Site Impacts of Petroleum Coke Particulate
at the Marathon Petroleum Detroit Refinery

Clean Air Engineering, Inc.

EXAMINATION OF POTENTIAL OFFSITE IMPACTS OF PETROLEUM COKE PARTICULATE AT MARATHON DETROIT REFINERY

Ambient Air Monitoring Data Analysis

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1.0 Executive Summary

To determine whether any off-site particulate impact results from the coke-cutting operation at Marathon Petroleum's Detroit Refinery, Marathon conducted ambient air monitoring over approximately 10 days from May 14 through May 23, 2019. This monitoring was in addition to the existing US EPA reference monitors that are permanently monitoring particulate and other compounds near the refinery fence line.

A combination of real-time total PM_{10} concentration data and analysis of PM_{10} filters collected over several 24-hour periods was used to determine whether petcoke particulate originating at the coke pit contributed to downwind PM_{10} concentrations. Individual PM_{10} particles collected on the filters were analyzed and categorized based on their composition.

Based on this analysis, we can reach the following conclusions:

1) Over the entire sampling period, PM_{10} emissions were 20% lower downwind of the coke pit than upwind.

2) Overall, there is no significant difference in average net PM_{10} concentrations between periods when coke cutting is occurring and periods when coke cutting is not occurring.

3) Based on the filter analysis, there is no significant net mass increase from petcoke particulate in downwind locations.

4) During peaks in PM_{10} concentration, the primary source of particulate is from geological/clay sources such as earthmoving, hauling on unpaved roads, or any activity that may cause loose clay particles to become airborne.

5) There is no consistent pattern for net particle size distribution for petcoke. At times 2.5-micron or 10-micron fractions are higher downwind. At other times, they are lower downwind.

6) Samples collected southeast of the MPC facility showed a higher average mass percent of petroleum coke upwind indicating that those particles may be generated and dispersed from an emission source located to the southeast of the MPC facility.

In summary, this study produced no evidence of a significant impact of petcoke particulate downwind of the coke pit during coke cutting activities or at any other time.

2.0 Overview

Marathon Petroleum produces gasoline, diesel fuel, and related petroleum-based products at its refinery in Detroit, Michigan. During this process, a solid material called petroleum coke, or petcoke, is produced. It is collected in a vessel called a coke drum. Periodically (typically every 16-24 hours), the coke is removed from the drum through a process called coke cutting. During this process the coke is first steamed to minimize volatile material and particulate matter. Then the coke is cut from the drum using a high-pressure water stream. The wet coke falls into a walled area called the coke pit to await removal.

To determine whether any off-site particulate impact results from this coke-cutting operation, Marathon conducted ambient air monitoring over a period covering several coke cutting events. This monitoring occurred over approximately 10 days from May 14 through May 23, 2019. This monitoring is in addition to the existing U.S. Environmental Protection Agency (US EPA) reference monitors that are permanently monitoring particulate and other compounds near the refinery fence line.

The refinery is located in an industrial area, surrounded by potential sources of ambient particulate matter (PM) emissions. This includes a steel plant, asphalt plants, salt piles, a gypsum plant, other coking facilities, a steelmaking and finishing plant (Zug Island), a highway, and numerous other sources. Figure 1 shows the MPC facility boundary, as well as other emission sources present in the area.

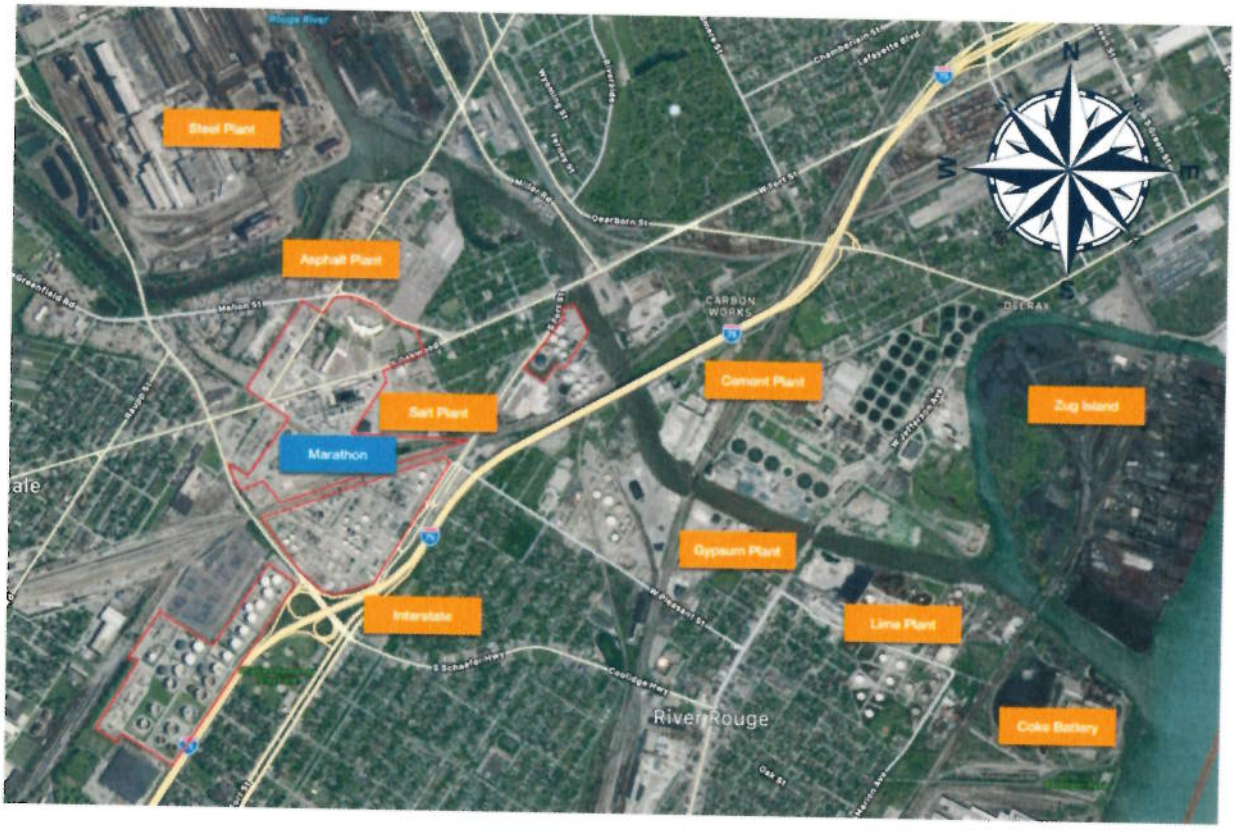

Figure 1: Detroit Refinery and Some Surrounding Emission Sources

The variety of particulate emission sources in the area makes it challenging to determine the origins of any particulate collected at a specific location at a specific time. One obviously important factor in determining particulate origin is wind direction. In order for any potential particulate from the coke pit to arrive at a particular off-site location, the wind would have to be blowing from the pit to that location.

In addition to wind direction, each particulate source generates particles with different characteristics, including particle size and elemental composition. For example, particulate from a gypsum plant would have very different composition than particulate from a steel mill or a coke pit. Using these characteristics, a "fingerprint" is developed for coke pit particulate to distinguish it from particulate generated by other sources.

A combination of wind direction and particle characteristics can be used to help determine whether there is any off-site impact from the coke pit at the Marathon refinery.

US EPA has widely used a method known as the upwind-downwind (UW/DW) technique to determine emission source impact at the downwind locations[1]. This technique has been used extensively to quantify emissions from different types of industrial emission sources. Using this technique, samples are collected at the upwind and downwind directions from the emission source.

A sampling instrument is located upwind of the source to collect a sample that represents the background PM generated from activities other than the source-of-interest (i.e., the coke pit). Other sampling instruments are also placed downwind. Upwind concentration (background concentration resulting from other sources) is subtracted from the corresponding downwind concentration ($\Delta C = C_{DW}-C_{UW}$), to determine the quantity of emissions potentially attributable to the source.

The major focus in this study is on particles with a diameter smaller than 10 microns, known as PM_{10}. In addition, further lab analysis is performed to investigate characteristics of the particles smaller than 2.5 microns ($PM_{2.5}$).

Figure 2 shows a summary of the general workflow for this project. The various phases of the project are explained in detail in subsequent sections of the report.

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[1] Kolnsberg, H. "Technical Manual for Measurement of Fugitive Emissions: Upwind/Downwind Sampling Method for Industrial Emissions", U. S. Environmental Protection Agency, EPA – 600/2-76-089a, April 1976

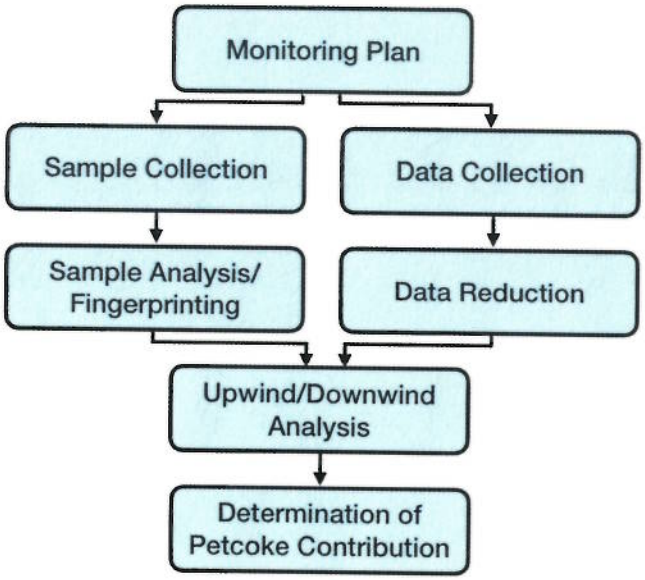


Figure 2: PM_{10} Study Methodology

During the planning phase of the project the number and location of samplers was determined based on both an assessment of likely wind directions and the availability within the refinery of adequate support infrastructure (i.e., accessibility, power, etc.). Once the samplers were deployed, sample/data collection began.

Sampling consisted of ambient air filter samples and bulk petcoke samples. Data included real-time PM_{10} concentrations and wind speed/direction. After collection, filters were sent to a laboratory for analysis of the collected particulate. Real-time data was analyzed for upwind/downwind pairing and PM_{10} concentration trends. Once the lab results were returned, analysis was performed on the contribution of petcoke particulate downwind of the coke pit.

Below are descriptions of each of the subsequent sections of the report.

Section 3 Data Collection – A description of the various samples and data collected during the project including the continuous real-time data (Total PM_{10}), the meteorological data, and the filter samples which were analyzed for petcoke.

Section 4 Lab Analysis of Collected Particulate – How the filter samples were analyzed and how the petcoke fingerprint was developed.

Section 5 Results and Discussion – Presentation of the results of the upwind/downwind analysis for both the real-time data (Total PM_{10}) and the petcoke-specific filter data.

Section 6 Impact from Other Facilities on Background PM_{10} Concentrations – An analysis of the background contribution from other facilities located to the southeast of the refinery.

Section 7 Conclusions

3.0 Data Collection

Site measurements were performed from May 14 through May 23, 2019. Five sets of data were collected in this study:

1) A bulk sample of petroleum coke from the pit. This sample was used to obtain the "purest" sample of the particle of interest and was used to develop the petroleum coke fingerprint later used to identify petroleum coke particulate on the collected filters.

2) Manual sampling filters. A total of six samples were collected manually very near the wall of the coke pit during various operations. The purpose for collecting these samples was to compare the airborne PM as close to the source as possible with the bulk sample collected from the pit. This essentially validates the fingerprint created.

3) Real-time ambient PM_{10} concentrations. Six e-Samplers were used to collect real-time particulate data. This allowed a "high temporal resolution" assessment of PM_{10} concentrations over time. It also provided information on which coke cutting events had the greatest potential for off-site contribution. The real-time data is total PM_{10} and does not speciate petcoke PM or any other specific category of PM.

4) E-Sampler filters. In addition to the real-time data, each e-sampler had the ability to collect the airborne particulate on a filter. These filters were changed out approximately every 24 hours. A total of 52 samples were collected. Selected samples were analyzed in the lab to determine particle characteristics, including composition and particle size distribution.

5) Meteorological data. Wind speed and wind direction data were collected and analyzed to determine which samplers were upwind and which were downwind during a particular coke cutting event.

The MET One e-Sampler measures and records real-time airborne PM_{10}, particulate concentration levels using the principle of forward laser light scatter. In addition, each e-Sampler has a built-in 47 mm filter to collect the particulate for subsequent gravimetric mass or laboratory evaluation.

Six MET One e-Sampler particulate monitoring stations were placed at various locations surrounding the coke pit to collect real-time ambient PM_{10} concentrations. Figure 3 shows the location of the sampling stations.

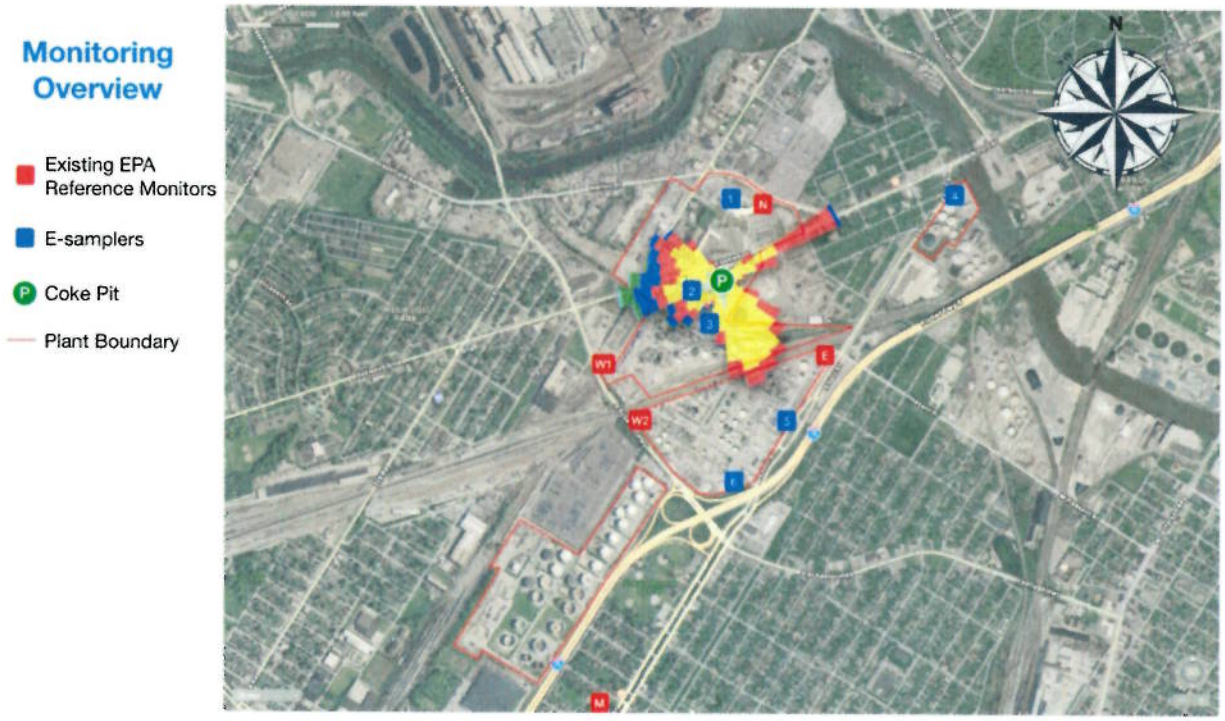


Figure 3: Location of Sampling Stations and Wind Rose for Entire Sampling Period

Out of the six sampling locations, wind speed and direction were captured at four of the locations with meteorological stations (MET stations) co-located with the samplers. In addition, meteorological data from the US EPA reference samplers located at the plant were also used to validate the data.

Meteorological data collected from the e-Samplers showed reasonably good correlation to the data collected by a sampler located at the plant. Perfect agreement is not expected due to the influence of structures located around the samplers. Meteorological data collected by the US EPA reference sampler (designated 2B-1) was used throughout this study for consistency. Figure 4 shows Sampling Station 5 that includes a meteorological station along with an e-Sampler.

Figure 4: e-Sampler and MET Station (Sampling Station 5)

Figure 5 shows an overview of all of the one-minute PM_{10} concentration data collected by the e-Samplers. This is approximately 132,000 data points collected over a period of two weeks. Coke cutting periods are shown with red dots. Periods of missing and invalid data are also shown. Estimated periods of rain are shown also. While precipitation was not tracked during the data collection period, periods of rain were estimated based on conditions recorded at Detroit Metropolitan Wayne County Airport located approximately 12 miles from the plant.

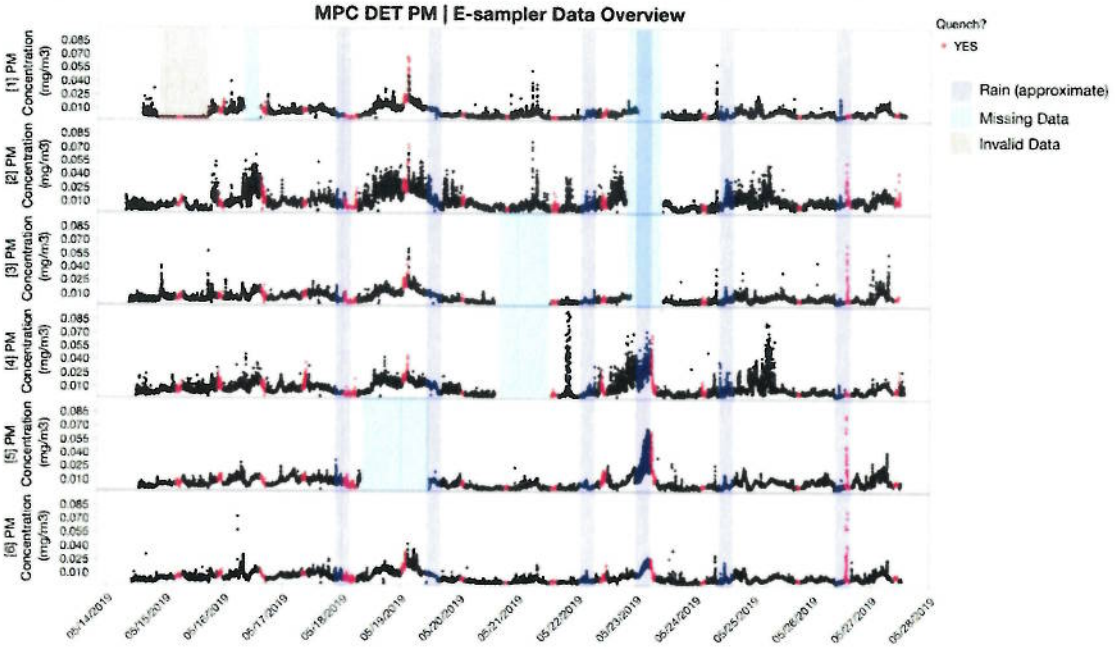


Figure 5: Overview of Real-Time PM_{10} Concentrations from e-Samplers (One-minute Data)

This data will be classified in subsequent analyses to correspond to upwind stations and downwind stations.

Note that PM_{10} concentration shows considerable variation during both coke cutting and non-coke cutting periods.

4.0 Lab Analysis of Collected Particulate

Particulate samples (bulk petcoke and ambient air samples) were characterized to assess their contribution to the ambient particulate concentrations in the vicinity of the facility. Particle characterization was performed by RJ Lee Group.

Ambient particulate samples were collected on a 47-millimeter (mm) polycarbonate filter. Polycarbonate provides a particulate-free and optically flat surface that facilitates the evaluation of the particles by computer-controlled scanning electron microscopy and energy dispersive x-ray spectrometry (CCSEM EDS).

Analysis of particles smaller than the beam size causes interrogation of some polycarbonate by the electron beam, resulting in carbon and oxygen concentrations for that particle that are biased high. An elemental correction was applied to all particles with a minimum diameter of 5 microns to compensate for this bias. All filters were desiccated for one day prior to measuring the mass of the particles. Gross and net weights were obtained for the PM_{10} samples.

To determine the petroleum coke fingerprint, CCSEM EDS was used. In this technique, 1000-3000 discrete particles on each filter were analyzed for size, elemental composition, and particle morphology. Particulate categorization is done using specific rules written to identify types of particles based on their elemental composition. The composition of the petroleum coke was determined to identify elemental characteristics that were specific to petroleum coke.

4.1. Laboratory Analytical Results

This section describes the analyses performed on the results of the lab study on the characterization of particulate collected on the filters. Samples were collected at different locations (coke pit boundary and inside the boundaries of MPC refinery), as well as the bulk sample from the coke pit. Particulate mass was measured for all samples. Selected samples were analyzed for composition, particle size distribution, and average elemental composition. Consistent wind direction during the sampling period is the main criterion for the selection of samples to be further analyzed.

4.1.1 Analysis of the PM_{10} Characteristics

The bulk sample collected from the coke pit was analyzed to determine the composition of the petcoke. This analysis identified elemental characteristics that were specific to petroleum coke. Other facilities exist in close proximity to the MPC facility, where petroleum coke is transported, dumped, stored, and processed. Therefore, the coke pit located at the MPC facility is not the only source of petroleum coke particles in this area. A fingerprint was defined for petroleum coke, along with the fingerprints for other particulate types. A total of 25 distinct particulate types or "classes" were identified in the samples of which petcoke is one. Figure 7 lists the rules defined to determine particle classes.

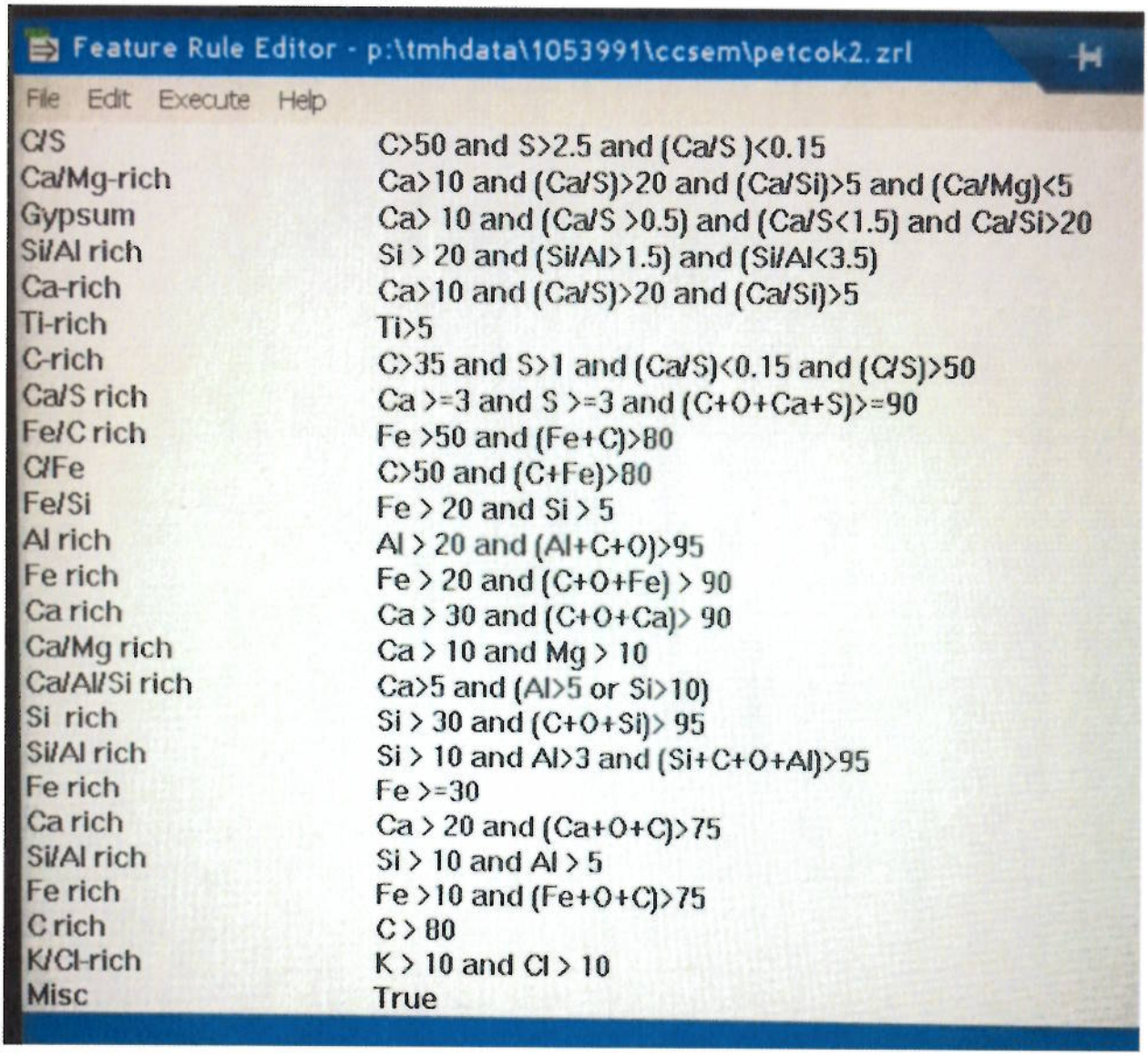


Figure 7: CCSEM EDS Rules for Particle Type Categories

Individual particles were analyzed on each filter and sorted into one of these 25 groups based on the rules shown. The first rule is for petcoke. A collected particle is classified as petcoke if its carbon content (wt%) is greater than 50, its sulfur content is greater than 2.5, and its calcium/sulfur ratio is less than 0.15.

4.1.2 Validation of the Petcoke Fingerprint

Six samples were collected at the coke pit boundary before, during, and after a coke cutting event. This provides a check on the reliability of the petcoke fingerprint. If the mass amount and the number of petroleum coke particles during a coke cutting process are significantly higher than a non-cutting period, it shows that the rules defined to petcoke work properly. This analysis is a quality check for the rules defined for the petroleum coke fingerprint.

At the time when coke cutting activity does not occur at the pit, wet material is handled by loading equipment. Due to the heavy watering of the petroleum coke, the material inside the pit has a high moisture content. Therefore, particulate emissions due to material handling activity are minimal. There is considerable activity around the coke pit at all times (during both coke cutting and non-coke cutting periods) which contribute some amount of non-coke pit related particulate to the filters. These filters also reflect the general background particulate concentration in the area.

As seen in Table 1, mass percent of petroleum coke particles for the non- cutting sample (7-1) compared to the coke cutting sample (7-2) increased from 2.36% to 72.71% (highlighted in green in Table 1). Since no other particulate class is expected to show a significant increase, the fingerprint for petcoke works well for accurately identifying petcoke particles.

Table 1: Particle Characterization for the Samples Collected Next to the Coke Pit

Particle Class	Possible Mineral Type	Before Coke Cutting				During Coke Cutting			
		Number of Particles	Number Percent	Mass Percent	Conc. (µg/cm²)	Number of Particles	Number Percent	Mass Percent	Conc. (µg/cm²)
C/S rich	Petroleum coke	46	1.67	2.36	0.075	2024	48.25	72.71	2.550
Ca/S rich	Gypsum	209	7.58	4.19	0.134	35	0.83	0.92	0.030
Si/Al rich	Geological/Clay	617	22.37	31.21	0.995	206	4.91	5.06	0.180
Ti-rich	Metal/Paint	133	4.82	4.19	0.134	19	0.45	0.12	0.000
Fe/C rich	Metal	165	5.98	0.75	0.024	32	0.76	0.47	0.020
C/Fe rich	Metal	489	17.73	4.59	0.146	1538	36.66	3.67	0.130
Fe/Si rich	Metal	50	1.81	1.36	0.043	13	0.31	0.29	0.010
Ca rich	Lime/Limestone	288	10.44	9.87	0.315	70	1.67	4.18	0.150
Ca/Mg rich	Dolomite	229	8.30	15.81	0.504	89	2.12	4.66	0.160
Ca/Al/Si rich	Geological/Clay	183	6.64	14.38	0.459	70	1.67	6.52	0.230
Si rich	Quartz	185	6.71	6.11	0.195	56	1.33	0.78	0.030
Al rich	Metal	8	0.29	0.19	0.006	3	0.07	0.00	0.000
Fe rich	Metal	80	2.90	1.69	0.054	17	0.41	0.04	0.000
Mixed	---	76	2.76	3.31	0.105	23	0.55	0.58	0.020
Total		2758	100	100	3.189	4195	100	100	3.500
Sampling Time		5/14/2019 15:15		5/15/2019 4:26		5/15/2019 4:27		5/15/2019 7:43	
Sampling Duration (hr:min)		13:11				3:16			
Sample		7-1				7-2			

Note: The concentration data shown here are concentration on the filter, not airborne concentration. Units are µg/cm² whereas airborne concentrations are typically expressed in mg/cm³ or mg/m³.

5.0. Results and Discussion

This section presents the results of the analyses and discusses the findings. In this section, two types of events, coke cutting and sampling, are important to differentiate. Coke cutting events are period of time during which coke cutting occurred. These events usually last about three to four hours and there are 15 of them referred to by a number from 2 to 16.

Sampling events are periods of time beginning with placing a filter in the sampler and ending when the filter is removed and replaced with a fresh filter. These events last for approximately 24 hours and there are nine of them referred to by a number from 1 to 9.

Typically, one coke cutting event occurs during each sampling event so that each filter captures a complete cycle from one coke cutting event to the next. In one case, two coke cutting events were captured during a single sampling event. In another case, filters were being changed during coke cutting so a partial coke cutting event was captured during two sampling events.

5.1. Long-term Downwind Impact Based on Real-Time Sampling Data (Total PM_{10})

Results from all six air monitoring stations for the whole period of sampling (regardless of the type of activity performed), were used for this analysis. This includes both coke cutting and non-cutting periods. This data also includes 1-minute wind speed and wind direction for the sampling period.

Eight wind direction classes were defined as: N, NE, E, SE, S, SW, W, and NW. Each wind class represents 45 degrees. Based on the meteorological data, the predominant wind direction was determined for every minute and sampling stations were classified as upwind, downwind, or none for every minute of sampling. The net concentration ($\Delta C = C_{DW}-C_{UW}$) can be calculated for the given period. This value represents PM_{10} concentration originating from sources located between the downwind and upwind stations.

Depending on the predominant wind direction and the location of the stations, sometimes more than one station may be identified as upwind or downwind stations. In this case, concentration values from those stations are averaged to determine one representative concentration value. 156 hours of sampling data were included in this analysis. It includes coke cutting events, as well as leading and lagging time periods. Since coke cutting occurs for only a portion of the day, this set of analysis will be more representative of the overall longer-term impact of the coke pit on the downwind vicinities.

The average concentrations during the sampling period are shown in Table 2. The average values were measured based on 9,367 minutes of sampling. It excludes the data points with a lack of real-time measurements at both upwind and downwind stations.

Table 2: Real-Time PM_{10} Samples Analysis Results for the Whole Period of Sampling

PM10 Concentration (mg/m^3)			PM10 Pickup (%)
Upwind	Downwind	DW - UW	
0.0072	0.0058	-0.0015	-20.1

Note that over the entire period of real-time data collection, the sampler downwind of the coke pit averaged 20% lower PM_{10} concentrations than the upwind sampler. This result indicates no on-going long-term impact from coke cutting operations.

5.2. Short-Term Downwind Impact Based on Real-Time Sampling Data (Total PM_{10})

Real-time samplers were used for this project in order to capture short duration events. PM_{10} concentrations were recorded every minute during the sampling period. This is a measurement of all PM_{10}, not just potential coke pit emissions.

The top chart in Figure 7 shows the concentration difference between downwind and upwind samplers for the whole period of sampling, from about noon of May 14, 2019, until about noon of May 27, 2019. Negative values represent periods when the upwind concentration was higher than downwind. The blue points correspond to times when coke cutting was occurring. The red shaded area is explained below.

The difference between downwind and upwind PM_{10} concentration will be referred to in this report as either "net concentration" or more succinctly as ΔC.

Recall that filters were also collected at each sampler for laboratory analysis. The bottom chart in Figure 7 shows the period of time for each filter sampling event. The width of the block indicates the sampling duration, the period of time between when the filter was loaded into the sampler to the time it was removed – approximately 24 hours. The height of the block is arbitrary. The blue points indicate coke cutting events.

Note that the real-time data continues beyond the point where filter sampling ended. This is simply a reflection of the logistics involved with de-commissioning the samplers. For all analysis correlating the real-time data with the filter sampling, only the real-time data collected during the filter sampling events is used.

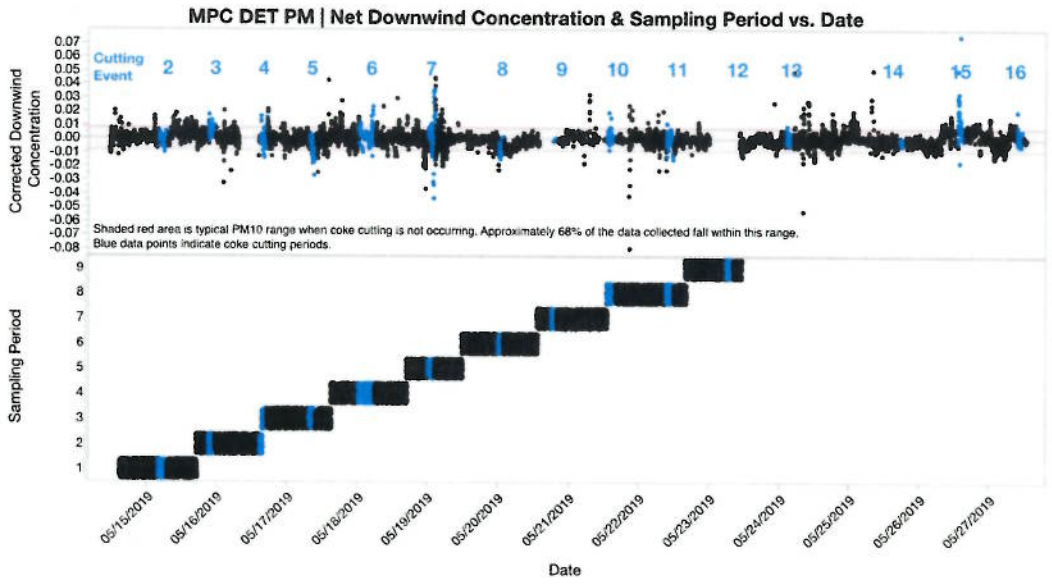


Figure 7: Net Concentrations of Total PM_{10} Over the Sampling Period (One-minute Data)

Figure 7 shows that net concentrations fluctuate around zero. Much of this fluctuation is simply a reflection of the uncertainty of the various particulate and wind flow measurements. It's the noise in the data. Some of this fluctuation, however, captures real change in particulate concentration. The question, then, is how to distinguish true change from noise.

To make a reasonable estimate of data uncertainty, we calculated the mean and standard deviation of all the net concentration data taken during non-coke cutting periods. The red region in Figure 7 shows two standard deviations from the mean. This provides an idea of a "typical" net PM_{10} concentration range when coke cutting is not occurring.

Any potential impact from cutting operations would have to fall outside this range or it would be too small to differentiate from typical PM_{10} variation. Data falling outside of this range may indicate concentrations (either high or low) that are not typical. We say "may indicate" since using this approach, we would still expect about 5% of typical data to fall outside the range. Note that a peak in PM_{10} concentration that occurs during a cutting event is not necessarily attributable to that event. Attribution to a specific source requires an analysis of wind and particle characteristics. This will be covered later in this report.

If there is an impact from cutting operations, the periods where the blue data points fall outside the red region are the most likely places to look. Therefore, Cutting Events 6, 7, and 15 are of particular interest. Cutting Event 15 occurred after sampling had concluded and no analysis was possible. To determine whether coke cutting contributed to Cutting Events 6 or 7, an analysis of wind direction and particle composition is needed. This is discussed in subsequent sections of this report.

One final observation on Figure 7, out of a total of 3,304 minutes of sampling with a positive ΔC, only 547 minutes of sampling (16.6%) capture particles during a coke cutting

activity. This means that 83.4% of the time when ΔC was positive, activities and sources other than coke cutting were responsible for the higher downwind PM_{10} concentrations. Even during the 16.6 % of the time associated with a coke cutting activity, coke cuttingcannot be attributed as the cause of the positive ΔC since other sources contribute to the total PM_{10} measured.

5.3 Identifying Sampling Events with Consistent Wind

The more consistent the wind direction is during a sampling event, the more reliably we can determine from where the particulate on the filter originated. Recall that sampling event duration is about 24 hours while coke cutting event duration is about four hours. Even if the wind was consistent during the cutting event, prior or subsequent winds coming from other directions could introduce particulate to the filter from other sources.

Each sampling event was evaluated for wind consistency by examining wind roses for each sampling event. These are shown in Figure 8. Depending on the variations in wind direction, sampling stations were classified into three classes; consistent wind direction, partially consistent wind direction, and inconsistent wind direction. As the next step, samples collected during the coke cutting events at each of the upwind or downwind stations were identified. In Figure 8, the blue circles represent Sampling Events and the CC numbers represent corresponding Coke Cutting Events.

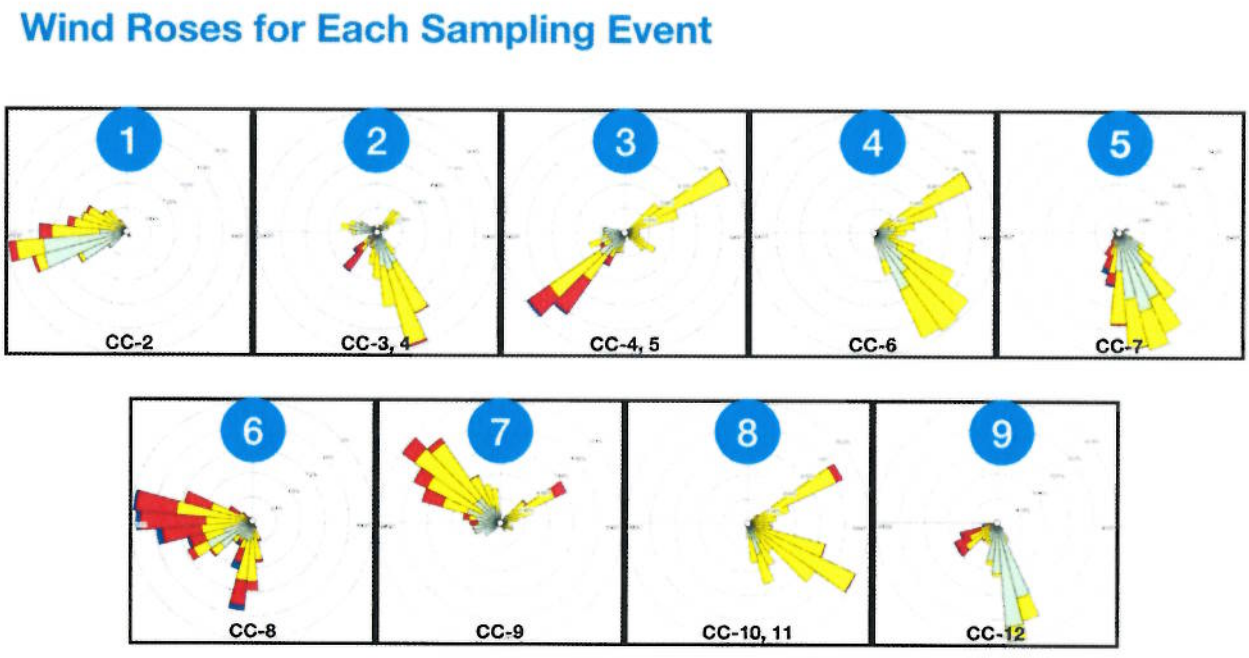


Figure 8: Sampling Event Wind Roses

Table 3 shows upwind and downwind stations and samples associated with each coke cutting event. As seen in this table, the wind direction was consistent during Cutting Events 2, 4, 8, and 12. A partially consistent wind direction was observed during Cutting Events 3, 5, 6, and 10.

Table 3: Upwind and Downwind Samples During Each Coke Cutting Event

Cutting Event	Predominant Wind Direction (First,Second)		Station #				Sample #			
			First Predominant WD		Second Predominant WD		First Predominant WD		Second Predominant WD	
			Upwind	Downwind	Upwind	Downwind	Upwind	Downwind	Upwind	Downwind
1	NW	W	-	-	2	4				
2	W	SW	3	1	2	4	3-1	1-1	2-1	4-1
3	NW	W	-	-	2	4			2-2	4-2
4	SW		3	1			3-3	1-3*		
5	NE		1	2			1-3*	2-3		
6	NE	SE	4	2	-	-	4-4	2-4		
7**	SE	NW	-	-	-	-				
8	SW	W	3	1	2	4	3-6	1-6	2-6	4-6
9	NW		-	-						
10	NE	SE	1	2	-	-	1-8	2-8		
11	SE		-	-						
12	SW		3	1			3-9	1-9		

Legend	
	Good quality data
	Use with caution
	Low quality data
	Unusable

* Since sample 1-3 was a DW sample for Event 4 and an UW sample for Event 5, it cannot be used in this analys
** No filter from Sampler #5 for Event 7

In general, there is a higher sensitivity in wind direction when it comes to the downwind samples. A sample can be classified as upwind, as long as (i) it can be determined that no particles from the source-under-study (in this case the coke pit) pass through the station, and (ii) the station is representative for the background concentration at the upwind side of the source-under-study.

Coke Cutting Events 2, 4, 8, and 12 are the most representative samples for this analysis because (i) the whole coke cutting events, as well as its leading and lagging periods, were sampled on the upwind and downwind samples, (ii) the wind direction during these coke cutting events were consistent, (iii) the wind directions during the whole sampling periods were consistent, and (iv) both upwind and downwind samples exist for those sampling periods.

In addition, the sampling event that corresponds to Coke Cutting Event 6 was also analyzed because it showed a significant positive net concentration (see Figure 7). It should be noted, however, that due to the changing wind direction during this sampling event, the results of analysis for Coke Cutting Event 6 will include particles originating from several sources. The result of this analysis can be compared with the other samples to better understand the impact of wind direction on PM_{10} concentrations.

5.4 Determining Petcoke Contribution to Downwind PM_{10} Concentrations

Based on the determination of consistent wind conditions described above, several coke cutting events are suitable for further analysis. These are Events 2, 4, 6, 8, and 12. These correspond to Filter Sampling Events 1, 3, 4, 6, and 9. Using a combination of the real-time PM_{10} concentration data and the filter analysis results, an estimate of petcoke contribution may be made. A summary of the results of this analysis are shown in Table 4.

Table 4: Upwind and Downwind Samples During Each Coke Cutting Event

		From Real-time Data (mg/m3)			From Filter Analysis
Filter Sampling Event	Cutting Event	(A) Upwind Concentration	(B) Downwind Concentration	(C) Net Concentration DW-UW	(D) Net Mass % Petcoke (% of total PM10 mass)
1	2	0.0048	0.0057	0.0009	0.07%
3	4	0.0072	0.0070	-0.0002	
4	6	0.0071	0.0103	0.0032	-0.76%
6	8	0.0059	0.0037	-0.0023	1.21%
9	12	0.0038	0.0034	-0.0004	0.39%

Note that net mass change cannot be determined for Cutting Event 4 since the filter was both upwind and downwind during the sampling period. Column C values less than ± 0.01 and Column D values less than ±5% are not significant.

The first step is to calculate the net PM_{10} concentration downwind of the coke pit over the 24-hour sampling period that includes these cutting events. Using the real-time data upwind background (Column A) is subtracted from the downwind concentration (Column B). The result (Column C) is the net PM_{10} concentration.

Due to uncertainty in the individual measurements and local winds, the net concentration may be either positive (net increase in PM_{10}) or negative (net decrease in PM_{10}). Recall that Figure 7 showed that any PM_{10} change less than about 0.01 mg/m^3 is too small to differentiate from normal net PM_{10} variation. In effect, the change is below the detection limit of the method. Note than none of the values in Column C show a change greater than 0.01 mg/m^3. This means that over the 24-hour sampling period, the average PM_{10} concentration downwind of the coke pit was the essentially same as the upwind background PM_{10}.

Also, recall that Figure 7 showed that Sampling Event 4, (corresponding to Coke Cutting Event 6) showed some blue data points above red uncertainty range. Figure 7 shows one-minute data points. This means that for a few minutes during the cutting event, net PM_{10} concentrations were higher than typical concentrations. Can this be attributed to petcoke from the cutting event? To answer that question requires results from the filter analysis.

Each filter was analyzed for petcoke along with other categories of particulate. The total mass of each category was determined. We can use the same downwind – upwind approach to determine whether there is any net change in the mass of petcoke. This is shown in Column D.

Just as with the real-time data, there are uncertainties associated with the filter analysis. After consultation with the laboratory, it was determined that any mass change less than about 5% is indistinguishable from the background variability of the method. This is a very conservative estimate with the true uncertainty likely being somewhat higher. However, we wanted to keep the error band for this analysis as narrow as possible to maximize the opportunity for significant petcoke increases to be observed.

Looking again at Sampling Event 4 as an example, Column D shows that petcoke mass is a smaller percentage of total PM_{10} mass downwind of the coke pit than upwind. This, despite the higher PM_{10} net concentration. However, all of the net mass changes are too small to be considered significant.

The following sections describe the analysis of each of the events in more detail.

5.4.1 Particle Characteristics Analysis for Coke Cutting Event 2

Figure 9 shows the net mass for each particle class (downwind mass % – upwind mass %). This number may be positive (net concentration increase) or negative (net concentration decrease). The shaded blue area shows the ±5% uncertainty of the measurement. Increases or decreases within this blue band cannot be reliably distinguished from measurement noise.

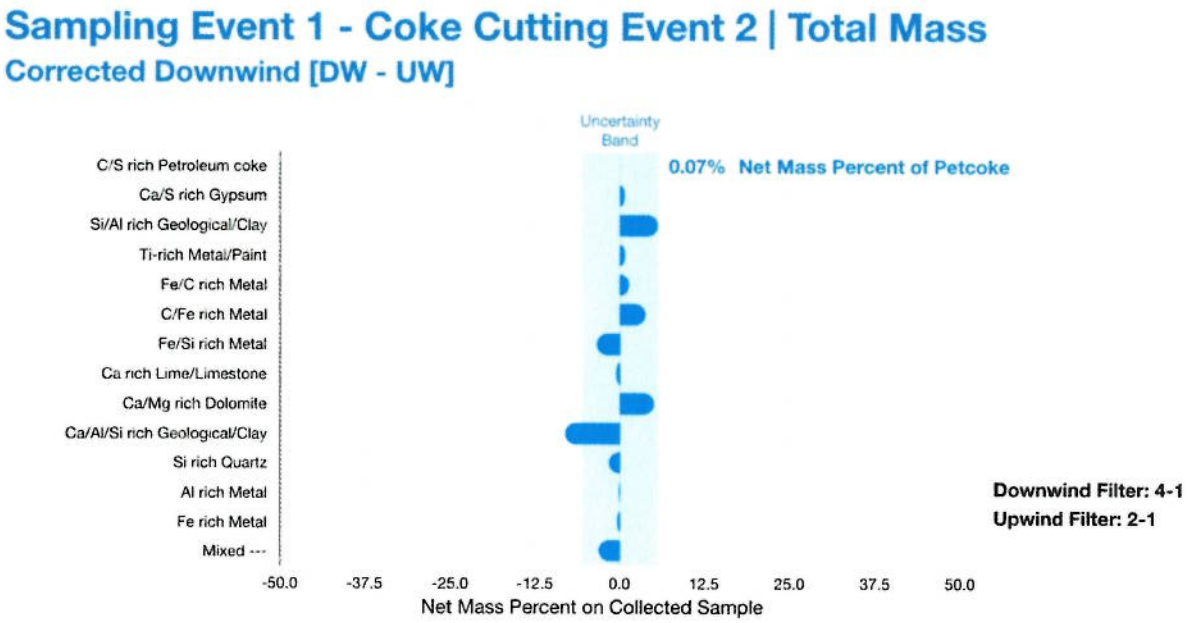


Figure 9: Net Mass Percent of Particle Classes from Cutting Event 2

This figure shows that the mass of petcoke particles as a fraction of total PM_{10} mass did not change significantly from upwind to downwind of the coke pit. There was no detectable contribution from coke cutting operations.

Results show that the majority of particles picked up at the locations between the upwind and downwind samples are of geological/clay and dolomite classes. Given that there are some other sources located between sampling points 2 and 4, particles classified as geological/clay and dolomite are most likely to be generated by sources other than the coke pit.

Table 5 shows the mass-based net particle size distribution for Cutting Event 2.

Table 5: Net Mass-based Particle Size Distribution for Cutting Event 2

Particle Class	Possible Mineral Type	DW-UW Difference		
		< 2.5 μm	< 10.0 μm	> 10.0 μm
C/S rich	Petroleum coke	-76.59	0.00	0.00
Ca/S rich	Gypsum	-35.03	-0.01	0.00
Si/Al rich	Geological/Clay	-2.59	-3.74	3.75
Ti-rich	Metal/Paint	-10.28	-0.01	0.00
Fe/C rich	Metal	16.03	0.00	0.00
C/Fe rich	Metal	-17.05	-45.05	45.04
Fe/Si rich	Metal	12.42	39.77	-39.77
Ca rich	Lime/Limestone	2.13	27.84	-27.84
Ca/Mg rich	Dolomite	0.89	0.28	-0.28
Ca/Al/Si rich	Geological/Clay	2.81	41.02	-41.03
Si rich	Quartz	5.76	21.61	-21.62
Al rich	Metal	86.40	0.00	0.00
Fe rich	Metal	-8.60	0.00	0.00
Mixed	---	-13.83	23.37	-23.35
Total		-0.23	13.33	-13.33

* In each ***COLUMN***, differences in DW-UW mass-based particle size distributions are colored from smallest to largest, from green to red.

As seen in Table 5, the mass of petroleum coke particles for $PM_{2.5}$ size fraction was at the downwind sample and 76.6% lower than upwind. Al rich particles are the major particle class with increased $PM_{2.5}$ mass from UW to DW with 86.4% increase in the mass percent. Geological/clay, as well as Fe/Si rich particle classes, showed increases in PM_{10} size fraction. The major increases in the mass of particles larger than 10 microns belong to the C/Fe rich particle class.

5.4.2. Particle Characteristics Analysis for Coke Cutting Event 6

Figure 10 shows the net mass for each particle class (downwind mass % – upwind mass %). This number may be positive (net concentration increase) or negative (net concentration decrease). The shaded blue area shows the ±5% uncertainty of the measurement. Increases or decreases within this blue band cannot be reliably distinguished from measurement noise.

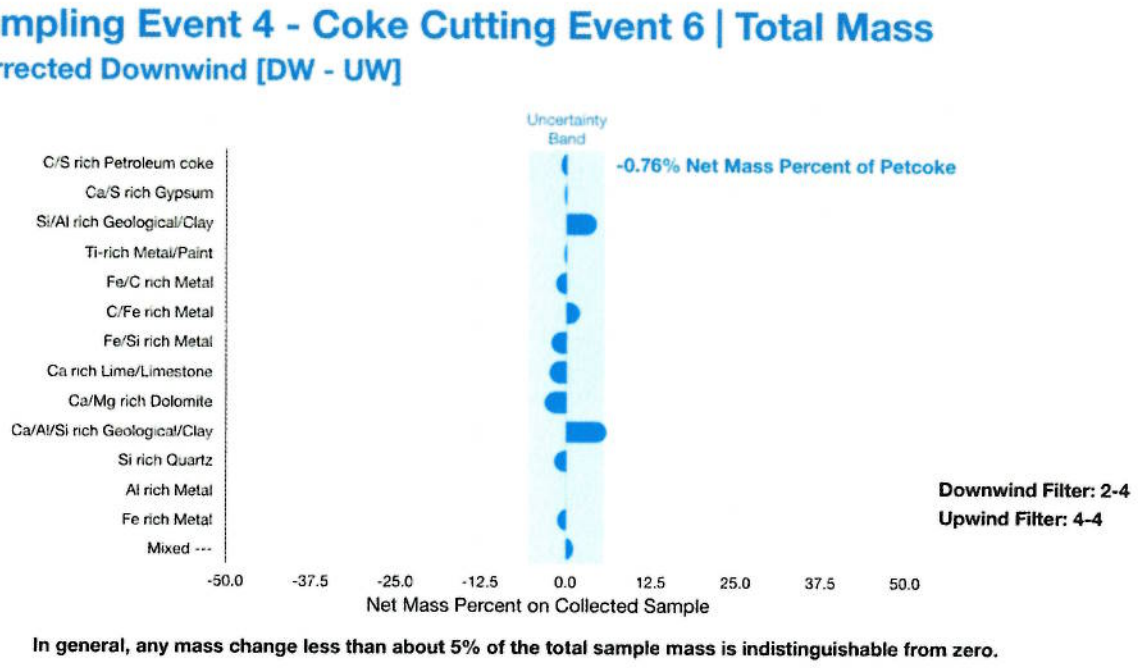


Figure 10: Net Mass Percent of Particle Classes from Coke Cutting Event 6

This figure shows that the mass of petcoke particles as a fraction of total PM_{10} mass did not change significantly from upwind to downwind of the coke pit. There was no detectable contribution from coke cutting operations.

Recall that the wind conditions during Cutting Event 6 were not ideal and that this event was included for further analysis due to the net increase in PM_{10} during the coke cutting event.

Results show once again that the majority of particles picked up at the locations between the upwind and downwind samples are of geologic/clay classes. Given that there are some other sources located between sampling points 2 and 4, the particles are most likely to be generated by sources other than the coke pit.

Table 6 shows the difference in the mass-based particle size distribution of the DW and UW samples. The mass of petroleum coke particles for $PM_{2.5}$ size fraction was higher in the downwind. However, it did not contribute to an overall increase in the mass of petroleum coke in DW sample, compared to UW. It is due to a decrease in the mass of PM_{10} size fraction. Ti-rich particles are the other particle class with increased $PM_{2.5}$ mass from UW to

DW. The mixed particles, as well as lime/limestone particle classes, showed increases in PM_{10} size fraction. The major increases in the mass of particles larger than 10 microns belong to C/Fe-rich and geological/clay particle classes.

Table 6: Net Mass-based Particle Size Distribution for Cutting Event 6

Particle Class	Possible Mineral Type	DW-UW Difference		
		< 2.5 µm	< 10.0 µm	> 10.0 µm
C/S rich	Petroleum coke	43.17	0.01	0.00
Ca/S rich	Gypsum	-2.57	-0.02	0.00
Si/Al rich	Geological/Clay	-2.51	-0.01	0.00
Ti-rich	Metal/Paint	25.94	0.00	0.00
Fe/C rich	Metal	13.06	0.00	0.00
C/Fe rich	Metal	-13.90	-10.34	10.35
Fe/Si rich	Metal	2.81	-0.01	0.00
Ca rich	Lime/Limestone	1.29	27.30	-27.29
Ca/Mg rich	Dolomite	1.91	0.00	0.00
Ca/Al/Si rich	Geological/Clay	-4.29	-6.78	6.78
Si rich	Quartz	10.64	0.00	0.00
Al rich	Metal	0.00	0.00	0.00
Fe rich	Metal	8.45	-0.01	0.00
Mixed	---	-0.77	40.69	-40.68
Total		-0.64	1.98	-1.97

* In each ***COLUMN***, differences in DW-UW mass-based particle size distributions are colored from smallest to largest, from green to red.

5.4.3 Particle Characteristics Analysis for Coke Cutting Event 8

Figure 11 shows the net mass for each particle class (downwind mass % – upwind mass %). This number may be positive (net concentration increase) or negative (net concentration decrease). The shaded blue area shows the ±5% uncertainty of the measurement. Increases or decreases within this blue band cannot be reliably distinguished from measurement noise.

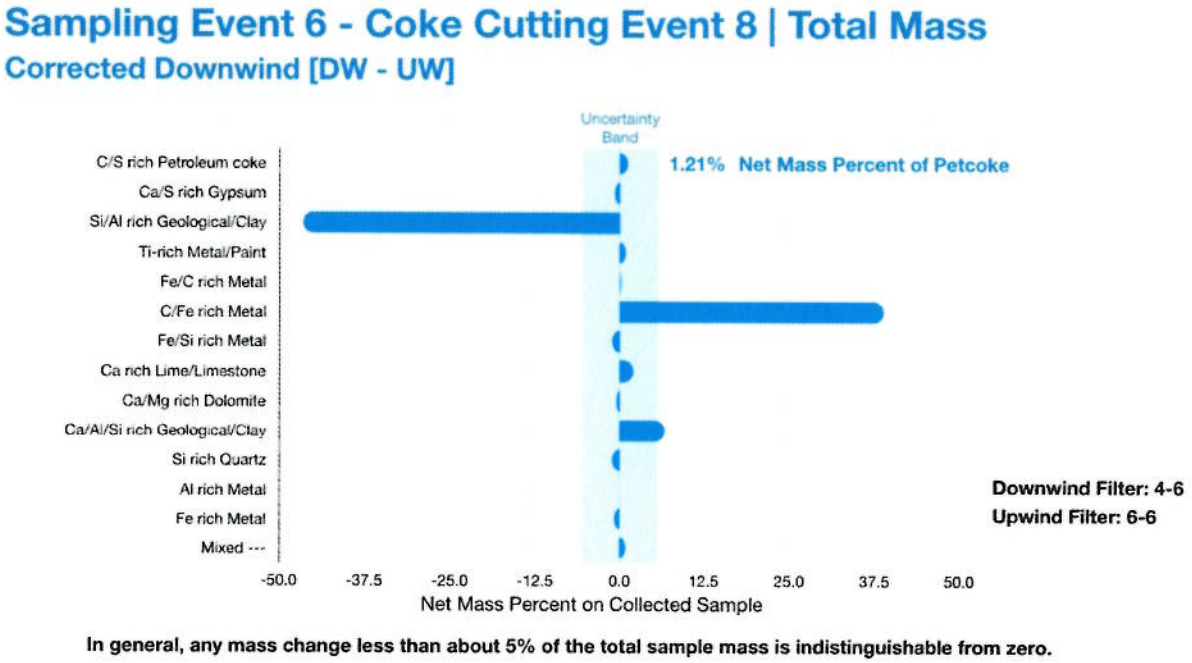


Figure 11: Net Mass Percent of Particle Classes from Coke Cutting Event 8

This figure shows that the mass of petcoke particles as a fraction of total PM_{10} mass did not change significantly from upwind to downwind of the coke pit. There was no detectable contribution from coke cutting operations.

Table 7 shows the difference in the mass-based particle size distribution of the DW and UW samples. The mass of petroleum coke particles for $PM_{2.5}$ size fraction was lower in the downwind. A single petroleum coke particle with a size of 5 to 10 microns was captured on the downwind filter causing an increase of 72.8% increase in the downwind petroleum coke mass. This increase, while appearing large as a relative increase, is a very small absolute increase since petcoke is a very small percentage of the total PM_{10} collected and is well within the margin of error.

Table 7: Net Mass-based Particle Size Distribution for Cutting Event 8

Particle Class	Possible Mineral Type	DW-UW Difference		
		< 2.5 μm	< 10.0 μm	> 10.0 μm
C/S rich	Petroleum coke	-3.53	72.78	-72.79
Ca/S rich	Gypsum	82.91	0.00	0.00
Si/Al rich	Geological/Clay	20.23	82.61	-82.62
Ti-rich	Metal/Paint	-18.46	0.01	0.00
Fe/C rich	Metal	-6.28	0.00	0.00
C/Fe rich	Metal	-5.14	-29.03	29.03
Fe/Si rich	Metal	17.14	0.00	0.00
Ca rich	Lime/Limestone	-1.00	0.00	0.00
Ca/Mg rich	Dolomite	6.05	-25.53	25.53
Ca/Al/Si rich	Geological/Clay	0.49	-33.13	33.14
Si rich	Quartz	26.04	22.40	-22.39
Al rich	Metal	0.00	0.00	0.00
Fe rich	Metal	87.51	0.00	0.00
Mixed	---	3.06	-1.54	1.54
Total		5.86	18.37	-18.40

* In each ***COLUMN***, differences in DW-UW mass-based particle size distributions are colored from smallest to largest, from green to red.

Fe-rich and gypsum particles are the biggest contributor to the increase in the mass percent of $PM_{2.5}$ particles from UW to DW. The geological/clay particle class showed an increase in PM_{10} size fraction. The major increases in the mass of particles larger than 10 microns belong to geological/clay, metal, and dolomite particle classes.

5.4.4 Particle Characteristics Analysis for Coke Cutting Event 12

Figure 12 shows the net mass for each particle class (downwind mass % – upwind mass %). This number may be positive (net concentration increase) or negative (net concentration decrease). The shaded blue area shows the ±5% uncertainty of the measurement. Increases or decreases within this blue band cannot be reliably distinguished from measurement noise.

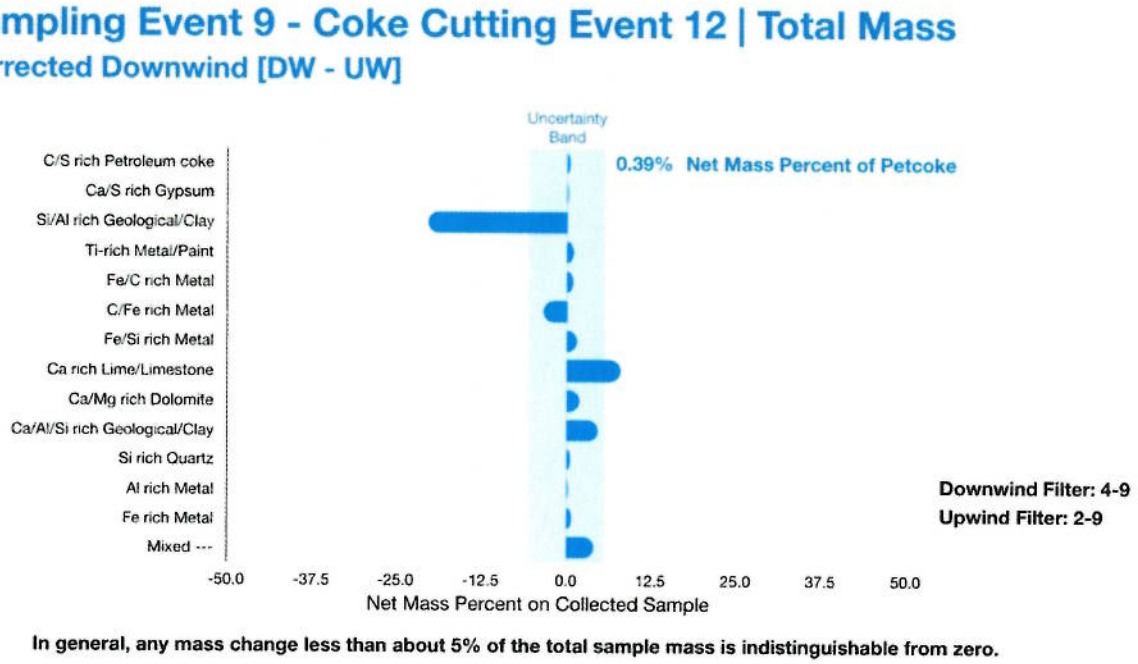


Figure 12: Net Mass Percent of Particle Classes from Coke Cutting Event 12

This figure shows that the mass of petcoke particles as a fraction of total PM_{10} mass did not change significantly from upwind to downwind of the coke pit. There was no detectable contribution from coke cutting operations.

Results show that the majority of particles picked up at the locations between the upwind and downwind samples are of lime/limestone, geologic/clay, and mixed particle classes. Given that there are some other sources located between sampling points 2 and 4, the particles are most likely to be generated by sources other than the coke pit.

Table 8 shows the mass-based particle size distributions for different particle classes in UW and DW samples.

Table 8: Net Mass-based Particle Size Distribution for Coke Cutting Event 12

Particle Class	Possible Mineral Type	DW-UW Difference		
		< 2.5 µm	< 10.0 µm	> 10.0 µm
C/S rich	Petroleum coke	-71.33	0.00	0.00
Ca/S rich	Gypsum	-22.07	0.02	0.00
Si/Al rich	Geological/Clay	-7.99	-13.46	13.46
Ti-rich	Metal/Paint	-18.76	-0.02	0.00
Fe/C rich	Metal	-9.87	0.00	0.00
C/Fe rich	Metal	-4.05	-26.36	26.36
Fe/Si rich	Metal	-3.41	0.00	0.00
Ca rich	Lime/Limestone	-2.75	-33.70	33.71
Ca/Mg rich	Dolomite	-13.82	0.00	0.00
Ca/Al/Si rich	Geological/Clay	-7.66	-19.35	19.36
Si rich	Quartz	-26.22	0.00	0.00
Al rich	Metal	-99.19	0.00	0.00
Fe rich	Metal	31.44	0.00	0.00
Mixed	---	-22.60	0.00	0.00
Total		-8.95	-13.91	13.91

* In each ***COLUMN***, differences in DW-UW mass-based particle size distributions are colored from smallest to largest, from green to red.

The mass of petroleum coke particles for $PM_{2.5}$ size fraction significantly decreased from upwind to downwind. All particle classes but Fe rich particles exhibit a reduction in the mass percent of $PM_{2.5}$ fraction. Gypsum is the only particle class that shows an increase in PM_{10} size fraction. However, for particles larger than 10 microns several particle classes, including C/Fe rich, lime/limestone, and geological/clay particle classes show increases in the mass percent of particles. It can be concluded that there is a higher chance that unpaved areas close to the Station 4 location contributed to the downwind particle sample.

5.5 Another Way to Look at the Data

Figure 13 presents another way to summarize the real-time PM_{10} concentrations. For this analysis, the real time net concentration data (downwind – upwind) are separated into periods where coke cutting is not occurring (NO) and period where it is (YES). The range of data in each group is shown along with the average from each group (green line).

Note that the average net concentration for each group is approximately zero with non-coke cutting periods showing greater variability than coke cutting periods. This means that over the entire sampling period, there is no significant net PM_{10} concentration difference between coke cutting periods and non-coke cutting periods.

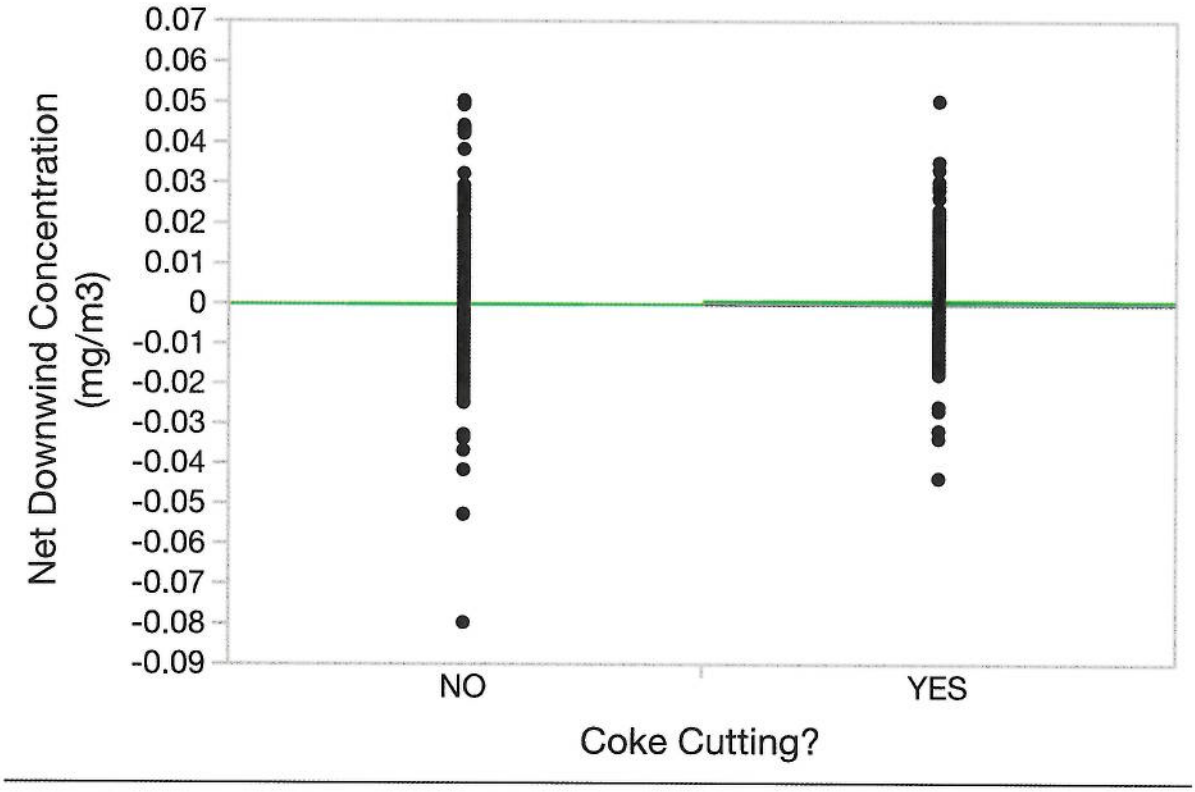


Figure 13: Analysis of Coke Cutting vs. Non-Coke Cutting Periods

6.0 Impact From Other Facilities on Background PM_{10} Concentrations

We identified trends in the particulate levels indicating that several sources located at the southeast of the MPC facility may significantly contribute to the PM_{10} concentrations in the vicinity of the plant. We performed two sets of analyses; (1) a background emission level study based on the real-time PM_{10} concentration measurements to define a benchmark for the background particulate concentration levels originating from sources located to the southeast of the MPC facility, and (2) a particle characterization study of the same samples to determine the characteristics of the particles generates outside the MPC facility.

The primary criteria in selection of these samples were (1) to have consistent wind direction from east, southeast, or south, and (2) sampling station to be in a location where no interference of potential particles from the coke pit exists. This ensures the particles are all generated by the outside sources. Samples 2-5, 2-9, 4-4, 4-5, 4-8, 6-5, and 6-6 were selected and particle characterization of samples were analyzed in this section. Figure 14 shows the layout of sampling stations as well as predominant wind directions and sources located to the east and southeast of the MPC facility.

Figure14: Station Layout for Evaluation of PM_{10} Concentration from Sources East and Southeast of the MPC Facility

The average PM_{10} concentration for the seven samples ranges from 0.003 to 0.023 mg/m^3, with a maximum PM_{10} concentration of 0.114 mg/m^3. Three of the samples collected during the Sampling Event 5. These samples exhibit significantly higher PM_{10} concentration values. A comparison of the results from Sampling Event 5 to the average downwind concentrations shows that emissions resulted from the sources located at the southeast of the facility are significantly higher than the average downwind concentration. Table 9 shows the median, mean, and maximum concentration value for this study.

Table 9: Background PM_{10} Concentration Southeast of the MPC Facility

	PM10 Concentration (mg/m3)		
	Average	Median	Maximum
Average of seven samples with particles transferred from southeast of the MPC facility	0.012	0.013	0.052

A more in-depth analysis was performed on the particles collected on filters during these sampling events. Particle characteristics of the samples were studied by classifying the collected particles into the particle classes. If particle classes correspond to the sources located at the southeast of the MPC facility, then it can be concluded that it is most likely that those particles are generated from the nearby sources at the southeast of the MPC facility.

Given that the density of different particle classes varies depending on their composition, it is helpful to consider both mass percent and the number of particles. Table 10 shows the average of each parameter for different particle classes. As seen in this table, based on the number of particles, PM_{10} particles that are generated at the southeast of the MPC facility are rich in geological/clay and C/Fe rich metal. Mass percent result shows that 42.6% of particles belong to geological/clay class.

Table 10: Average Particle Characteristics for the Upwind Samples Located Southeast of the MPC Facility and Samples Downwind of the Coke Pit

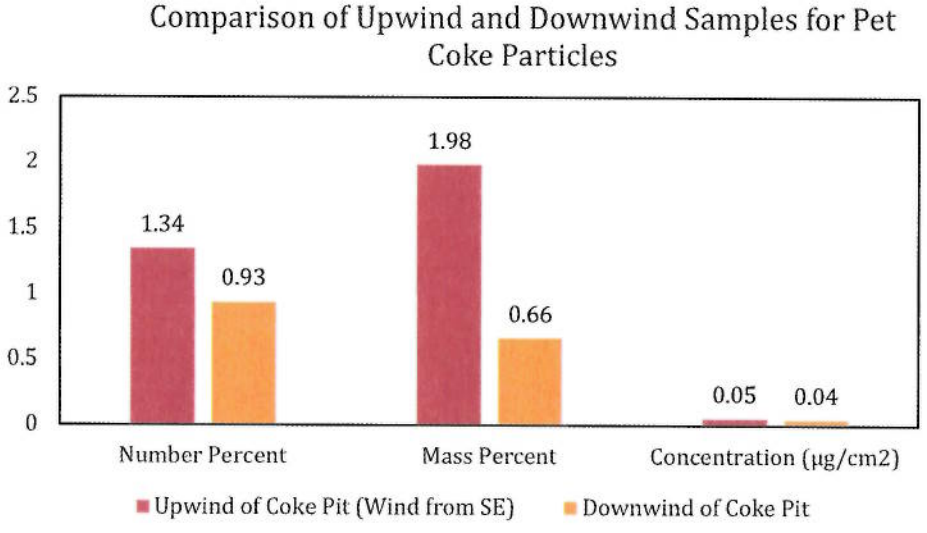
Particle Class	Possible Mineral Type	Average Composition							
		Average of 7 Samples Upwind of the Coke Pit (Collected when Wind Blows from the SE)				Average of 4 Samples Collected Downwind of the Coke Pit			
		Number of Particles	Number Percent	Mass Percent	Concentration ($\mu g/cm^2$)	Number of Particles	Number Percent	Mass Percent	Concentration ($\mu g/cm^2$)
C/S rich	Petcoke	34	1.34	1.98	0.05	23.25	0.93	0.66	0.04
Ca/S rich	Gypsum	143	5.70	1.58	0.06	98.50	3.94	1.14	0.06
Si/Al rich	Geological/Clay	542	21.69	28.96	1.08	532.00	21.28	22.51	1.48
Ti-rich	Metal/Paint	153	6.13	7.09	0.27	34.00	1.36	1.26	0.07
Fe/C rich	Metal	105	4.19	2.78	0.07	99.00	3.96	2.16	0.12
C/Fe rich	Metal	605	24.21	14.43	0.41	771.00	30.84	20.48	1.19
Fe/Si rich	Metal	22	0.89	2.26	0.06	29.50	1.18	2.31	0.11
Ca rich	Lime/Limestone	114	4.58	5.59	0.19	165.50	6.62	9.83	0.61
Ca/Mg rich	Dolomite	88	3.51	7.50	0.25	132.75	5.31	10.70	0.79
Ca/Al/Si rich	Geological/Clay	284	11.35	13.67	0.46	285.50	11.42	19.29	1.20
Si rich	Quartz	118	4.72	2.98	0.09	136.25	5.45	2.87	0.16
Al rich	Metal	4	0.15	0.19	0.01	4.25	0.17	0.12	0.00
Fe rich	Metal	36	1.43	3.01	0.09	41.00	1.64	2.25	0.12
Mixed	---	253	10.11	8.00	0.30	147.50	5.90	4.45	0.27
Total		2500	100.00	100.00	2.88	2500.00	100.00	100.00	6.19
* In each ***COLUMN***, values are colored from smallest to largest, from white to red.									

It should be noted that on average 1.98% of the upwind PM_{10} belongs to petroleum coke particle class. It means that sources located at the southeast of the MPC facility generate petroleum coke particles. It corresponds to an average of 1.34% of the overall number of particles of each filter.

Let's assume that a benchmark of 1.98% of petroleum coke particles is generated and dispersed by the sourced located at the southeast of the MPC facility. The mass percent of downwind samples that were studied above were 0.07 %, 0.24%, and 0.43%. It shows that the mass percent of petroleum coke at the downwind location of the coke pit has been lower than the average mass percent of petroleum coke for the upwind samples located at the southeast of the MPC facility. Therefore, it is most likely that the petroleum coke particles are originated from another source located at the southeast of the plant.

Table 11 shows a summary of the petcoke particles discussed above. Note that by any measure – number, mass, or concentration – petcoke particles downwind from the coke pit are lower than the background when winds are blowing from the southeast.

Table 11: Summary of Average Upwind/Downwind Petcoke Particles From Southeast



7.0 Conclusions

A combination of real-time PM_{10} concentration data and analysis of PM_{10} filters collected over several 24-hour periods was used to determine whether petcoke particulate originating at the coke pit contributed to downwind PM_{10} concentrations. Individual PM_{10} particles collected on the filters were analyzed and categorized based on their composition. This allowed a determination of petcoke contribution to total PM_{10} particulate.

Based on this analysis, we can reach the following conclusions:

1) Over the entire sampling period, PM_{10} emissions were 20% lower downwind of the coke pit than upwind.

2) Overall, there is no significant difference in average net PM_{10} concentrations between periods when coke cutting is occurring and periods when coke cutting is not occurring.

3) Based on the filter analysis, there is no significant net mass increase from petcoke particulate in downwind locations.

4) During peaks in PM_{10} concentration, the primary source of particulate is from geological/clay sources such as earthmoving, hauling on unpaved roads, or any activity that may cause loose clay particles to become airborne.

5) There is no consistent pattern for net particle size distribution for petcoke. At times 2.5-micron or 10-micron fractions are higher downwind. At other times, they are lower downwind.

6) Samples collected southeast of the MPC facility showed a higher average mass percent of petroleum coke upwind indicating that those particles may be generated and dispersed from an emission source located to the southeast of the MPC facility.

In summary, this study produced no evidence of a significant impact of petcoke particulate downwind of the coke pit during coke cutting activities or at any other time.

Appendix C

Technical Report
Atmospheric Dispersion Modeling Analyses
Petroleum Coke Processing and Handling Operations

Barr Engineering Company