New Hampshire
Department of Environmental Services
Air Resources Division

Fugitive Dust/Particulate Air Monitoring Report

To Assess Fugitive Emissions from Grimmel Industries, L.L.C and Pease Development Authority Division of Ports and Harbors Market Street Marine Terminal 555 Market Street Portsmouth, New Hampshire

September 2014

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and
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Division of Ports and Harbors
Market Street Marine Terminal
555 Market Street
Portsmouth, New Hampshire

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1.0 Introduction

At the request by the City of Portsmouth, the New Hampshire Department of Environmental Services (DES) conducted limited air monitoring in the area of the Pease Development Authority (PDA) Division of Ports and Harbors Market Street Marine Terminal[1] in Portsmouth, NH ("the Terminal"). This monitoring was intended to determine if fugitive dust and/or particulate emissions associated with site operations leave the site and potentially impact nearby residential areas and/or commercial establishments. The study was limited in scope and was only intended to be a screening tool for determining whether existing controls at the Terminal during the period of the study were effective in controlling fugitive dust. Since the monitoring was for a short duration and limited in scope, it was not intended to be representative of ambient air quality for determining attainment status of the area relative to National Ambient Air Quality Standards (NAAQS) established by EPA.

2.0 Background

The Market Street Terminal is located in the City of Portsmouth along the Piscataqua River and abuts Market Street to the north and east. The Terminal site juts out into the river and is bisected by Market Street, roughly running north to south. The Sarah Mildred Long Bridge to Kittery, ME crosses over the north end of the site. The surrounding area is a mix of residential, commercial, and industrial sites. A residential/commercial condominium complex abuts the site immediately across Market Street, to the west of the site. Industrial areas north and west of the site include Simplex Technologies and the Irving Oil Terminal. To the east across the river are primarily residential areas of Elliot and Kittery, ME, including Badgers Island. South and east of the site are primarily commercial establishments in downtown Portsmouth.

Figure 1: Market Street Marine Terminal Scrap Pile Operations

[1] See Division of Ports and Harbors Terminal website at www.portofnh.org/Terminal.html .

Grimmel Industries, L.L.C. operates a scrap metal recycling facility at the Terminal on property it leases from the PDA. The scrap metal is stockpiled at the Terminal and periodically bulk-loaded on to ships that originate overseas. In addition, road salt is also off-loaded from ships that originate from overseas and the material is stockpiled at the Terminal. The salt pile is generally kept covered by black tarps that are pulled back when trucks are loaded to take the material off-site.

Since 2004, DES has received 49 complaints regarding fugitive dust from the scrap metal operations and the salt piles. In response to these complaints, DES staff have visited the Terminal on numerous occasions, written reports and documented the findings of these visits, and spent numerous hours on the phone with the complainants and PDA staff. All of this information is documented in the DES complaint database and paper files. It has been extremely difficult to determine, by visual observation only, if the fugitive dust from operations at the Terminal is being carried by air currents beyond the boundary of the Terminal property. In response to the complaints, the PDA and Grimmel have instituted and continuously made efforts to improve their best management practices for controlling fugitive dust. Primarily, these practices have included an upgraded watering system to control the dust from the piles, especially during loading operations, as well as more frequent sweeping of the yard to minimize dust generated by vehicular traffic. Other changes in the site layout included moving the salt pile closer to the pier from its former location close to Market Street and moving the frag (shredded metal) pile to the approximate location where the salt pile was formerly located.

On May 14, 2013, DES received a letter from Eric Spear, Mayor, City of Portsmouth specifically requesting that DES locate equipment "*at or in close proximity of the Port, so data can be collected to characterize the airborne dust in this area and compare it to State and federal standards for airborne dust.*" On June 13, 2013, DES responded to the letter, stating that it would consider the request. In August 2013, DES prepared a "Fugitive Dust/Particulate Air Monitoring Plan to Assess Fugitive Emissions" from the Terminal. On September 19, 2013, DES initiated site specific monitoring which ran through late May 2014.

3.0 Applicable Regulatory Requirements

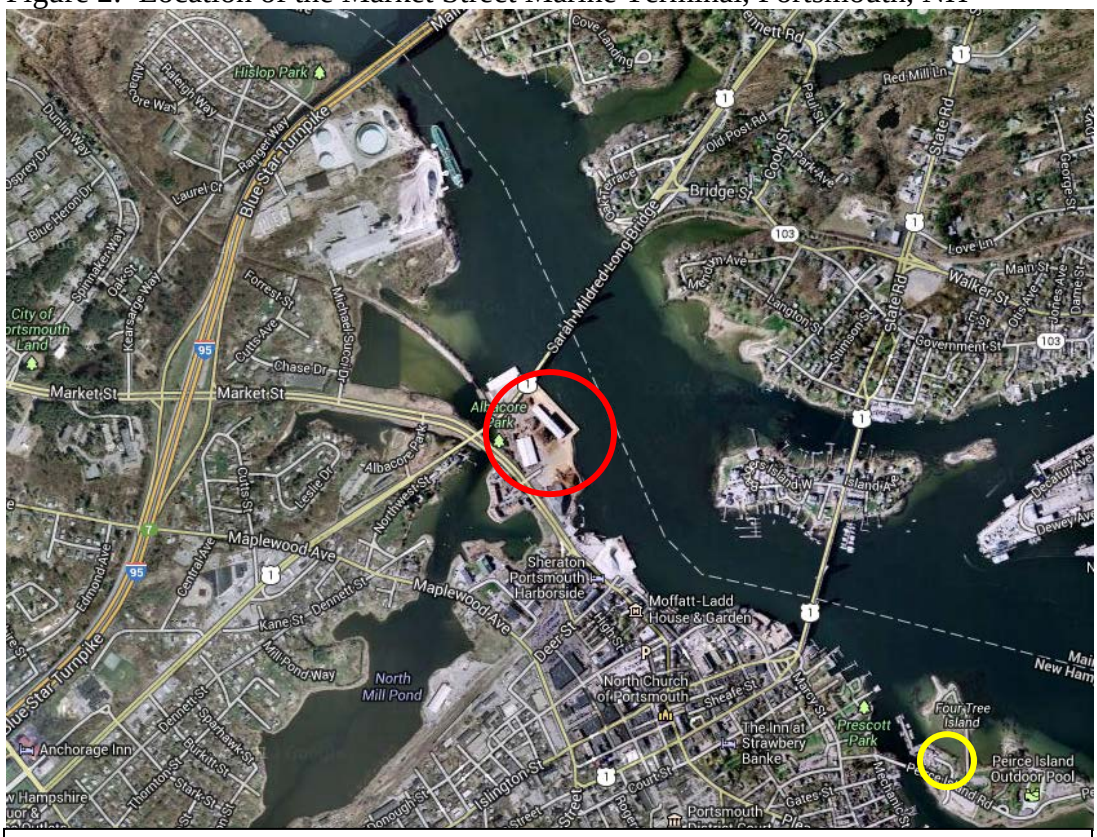
The purpose of the DES Environmental Rules Governing the Control of Air Pollution specific to fugitive dust (Env-A 1002[2]), is to limit pollution from open air sources by regulating the direct emissions of particulate matter from those activities that are most likely to generate airborne particulate matter, also known as fugitive dust. Specifically, Env-A 1002.02(a)(3) applies to fugitive dust emissions that are carried by air currents beyond the boundary of the lot, when created by a commercial or business activity, including pavement maintenance, sweeping or vacuuming. Env-A 1002.02(a)(5) applies to fugitive dust emissions that are carried by air currents beyond the boundary of the lot when created by a commercial or business activity that includes outdoor storage and material stockpiles, including the unloading, redistribution, and maintenance of those materials. Env-A 1002.03 requires any person engaged in these activities to take precautions to prevent, abate, and control the emissions of fugitive dust.

Health-based ambient air standards, referred to as National Ambient Air Quality Standards (NAAQS), are established by EPA. For particulate matter, there are currently two NAAQS; for particles smaller than 2.5 microns in diameter ($PM_{2.5}$) and particles smaller than 10 microns in

[2] Env-A 1002: http://des.nh.gov/organization/commissioner/legal/rules/documents/env-a1000.pdf

diameter (PM_{10}). Monitoring for compliance with the NAAQS in the Portsmouth region is conducted at the DES monitoring station, located on Peirce Island about one mile to the southeast of the Terminal (see Figure 2). The data measured at this monitoring station indicate that the general Portsmouth area is well below the NAAQS for both $PM_{2.5}$ and PM_{10}. Since the Peirce Island monitor is intended to be representative of general ambient air quality in the Seacoast area and was thus sited in a location where it would not be directly impacted by any nearby sources of particulate matter, data from this monitoring station serves as an ideal source of comparative data to data collected during this study.

Figure 2: Location of the Market Street Marine Terminal, Portsmouth, NH



The Market Street Marine Terminal is indicated by the red circle and the DES Portsmouth (Peirce Island) monitoring station is indicated by the yellow circle.

4.0 Study Design

DES used two types of specialized equipment approved by EPA for monitoring PM_{10} in the ambient air. One type of device collects PM_{10} on filter-based material over the course of 24-hours and provides a single concentration value for the collection period. It is referred to as a federal reference method (FRM) and provides the ability to precisely determine ambient air PM_{10} concentrations. The particles collected on filters used by the FRM can be further analyzed for metals or other content if desired. The other type of device collects PM_{10} on an hourly basis, allowing insight as to how PM_{10} changes over the short-term and in relation to changes in wind direction and speed. This device is referred to as a beta attenuation monitor (BAM) and is approved as a federal equivalent method (FEM). DES also operated sulfur dioxide (SO_2) and meteorological measurement devices at both monitoring stations. All DES monitoring was

conducted in accordance with EPA approved procedures and quality assurance (see Appendix A for more detail).

The filter-based FRM samples were collected over time periods in accordance with meteorological conditions selected by DES air quality forecasting staff. DES forecasters targeted conditions with the greatest potential for offsite migration of particulates. Such targeted sampling periods were representative of both active and non-active operations, including periods when the pile was being actively managed and/or cargo ship loading was occurring. Selected FRM filter sets were analyzed for metal content in order to gain more information regarding potential PM_{10} sources (see Appendix B).

4.1 Sampling Locations

Two monitoring locations were established to capture upwind and downwind measurements relative to the Terminal and, particularly, the scrap pile. Since wind direction is variable and constantly changing, these monitoring locations are simply designated as "Site A" and "Site B" (see Figure 3). Site A was located to the southeast of the Terminal in a PDA parking area. This site consisted of a single PM_{10} FRM filter-based monitoring device. Site B was located to the southwest of the Terminal, directly adjacent to a building whose occupants have reported fugitive dust impacts. This site included a filter-based PM_{10} FRM device, a BAM PM_{10} FEM monitor, an SO_2 monitor, and a meteorological station for wind direction and wind speed.

Figure 3: Location of sampling sites relative to scrap pile

Site A **Site B**

These sites were selected so that a clear upwind/downwind orientation in relation to the scrap pile could be maintained with regard to prevailing wind directions. When winds came from an easterly or southeasterly direction, they passed over Site A and then the Terminal before reaching Site B (i.e., in this instance Site A would be considered “upwind” and Site B

"downwind"). When winds came from the west, the pattern was reversed and Site A became the downwind monitor.

In addition, data collected at the DES Peirce Island monitoring station, located about three-quarters of a mile to the southeast of the Market Street monitors, provides comparative hourly PM_{10} concentrations, SO_2, and meteorology parameters with no influence from activities at the Port Authority site.

4.2 Special Considerations

Ship loading, idling ships, power plant emissions, vehicle traffic, road salt handling and road dust and/or entrained liquid ("spray") were considered as other PM_{10} sources in the Market Street area that could potentially impact sample results.

5.0 Study Results and Discussion

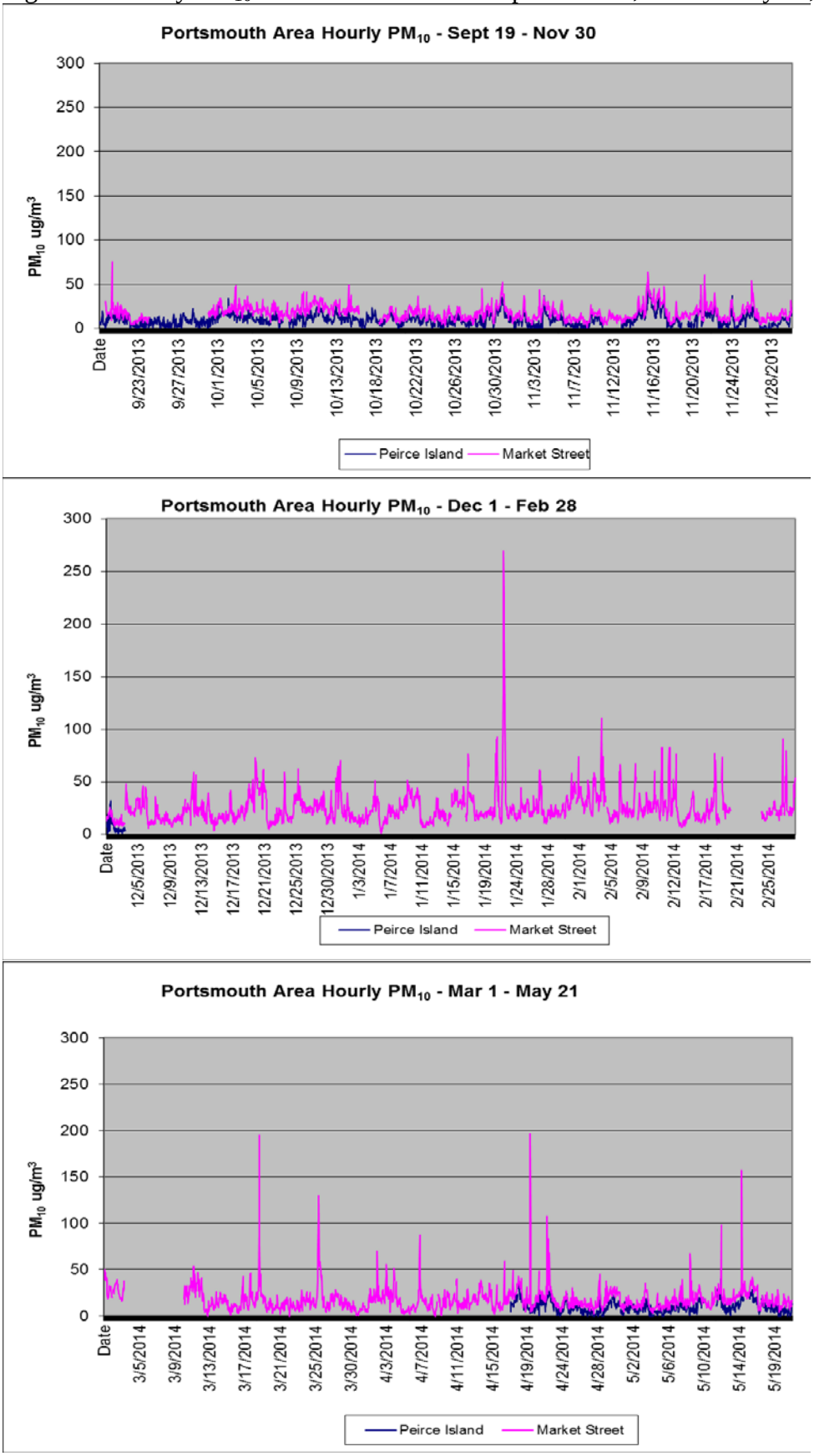
5.1 Hourly PM_{10} BAM Data

Figure 4 displays hourly PM_{10} (BAM) concentrations collected at Market Street (Site B) and Peirce Island. Concentrations are reported as the mass of particles per volume of air, or micrograms per cubic meter ($\mu g/m^3$). In general, both monitoring locations demonstrate low PM_{10} concentrations less than 50 $\mu g/m^3$. The average hourly PM_{10} concentrations measured over the duration of this study were 10 $\mu g/m^3$ at Peirce Island and 21$\mu g/m^3$ at Market Street. Both sites have similar patterns in PM_{10} concentrations, although the PM_{10} concentrations at Market Street were usually greater than the corresponding concentrations measured at Peirce Island. It is typical of more active industrial sites like the Market Street area to have higher PM_{10} concentrations than more isolated locations like Peirce Island.

The average hourlyPM_{10} concentrations for each hour of the day at Peirce Island and Market Street and are presented in Figure 5. This figure demonstrates more clearly the differences in the PM_{10} concentrations between the locations. Average hourly concentrations at Market Street are 7 to 15 $\mu g/m^3$ greater than at Peirce Island. The largest differences between the sites generally occur during the time period from 7 AM to noon and again at 5 PM. The early morning and 5 PM timeframes coincide with periods of increased traffic, suggesting that traffic should be considered as a potential source of PM_{10} in the Market Street area.

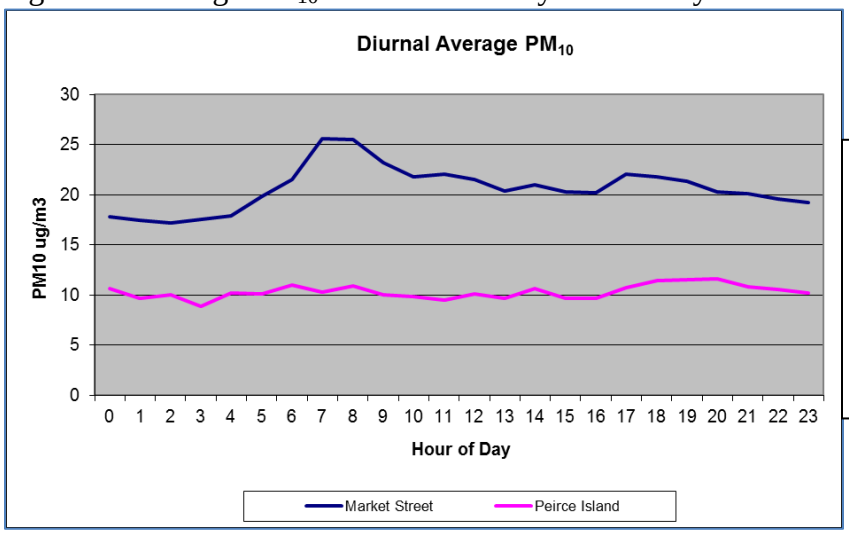
On several occasions there are large spikes in the hourly PM_{10} concentrations measured at the Market Street location, as shown in Figure 4. The first spike exceeding 100 $\mu g/m^3$ occurred on January 22, 2014. This event lasted a few hours before returning to more typical levels. Other large PM_{10} concentration spikes occurred at Market Street (Site B) on March 19, March 26, April 20 and May 15, 2014. Unfortunately, the hourly PM_{10} BAM unit at Peirce Island was out of operation from early December 2013 through early April 2014 so comparative PM_{10} concentrations are only available for the April and May spikes. Each elevated concentration in PM_{10} above 100 $\mu g/m^3$ that occurred at Market Street is examined in more detail in section 5.3 of this report.

Figure 4: Hourly PM_{10} Concentrations from September 19, 2013 – May 21, 2014



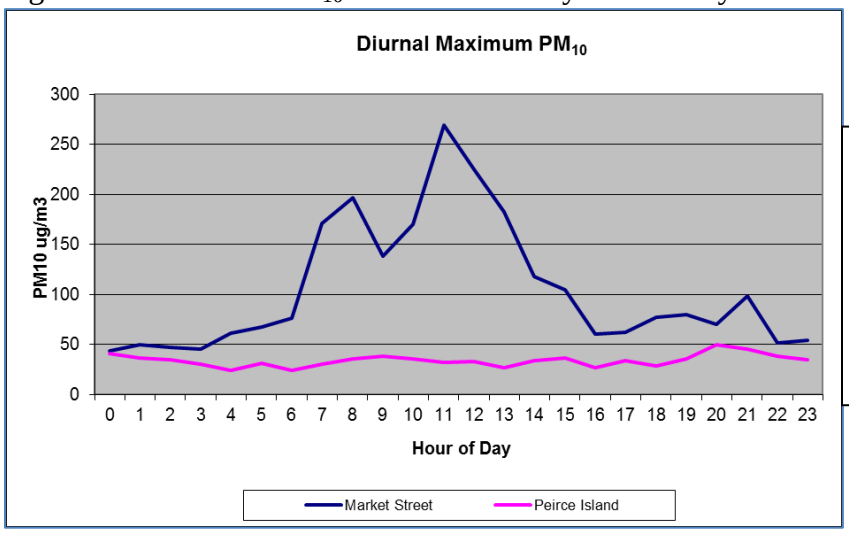
Analysis of maximum PM_{10} by hour of day (Figures 5 and 6) shows a stark contrast between the two locations. PM_{10} concentrations vary only mildly at Peirce Island regardless of the hour of day and do not exceed 50 µg/m^3. The maximum hourly PM_{10} concentration at the Market Street site is greater than 250 µg/m^3 and all the maximum concentrations greater than 100 µg/m^3 occur between the hours of 7 AM and 3 PM.

Figure 5: Average PM_{10} concentrations by hour of day



Both locations typically measure low PM_{10} concentration, but Market Street concentrations are about double those of Peirce Island.

Figure 6: Maximum PM_{10} concentrations by hour of day



Maximum PM_{10} concentrations at Market Street are significantly higher during daylight hours than those measured at Peirce Island.

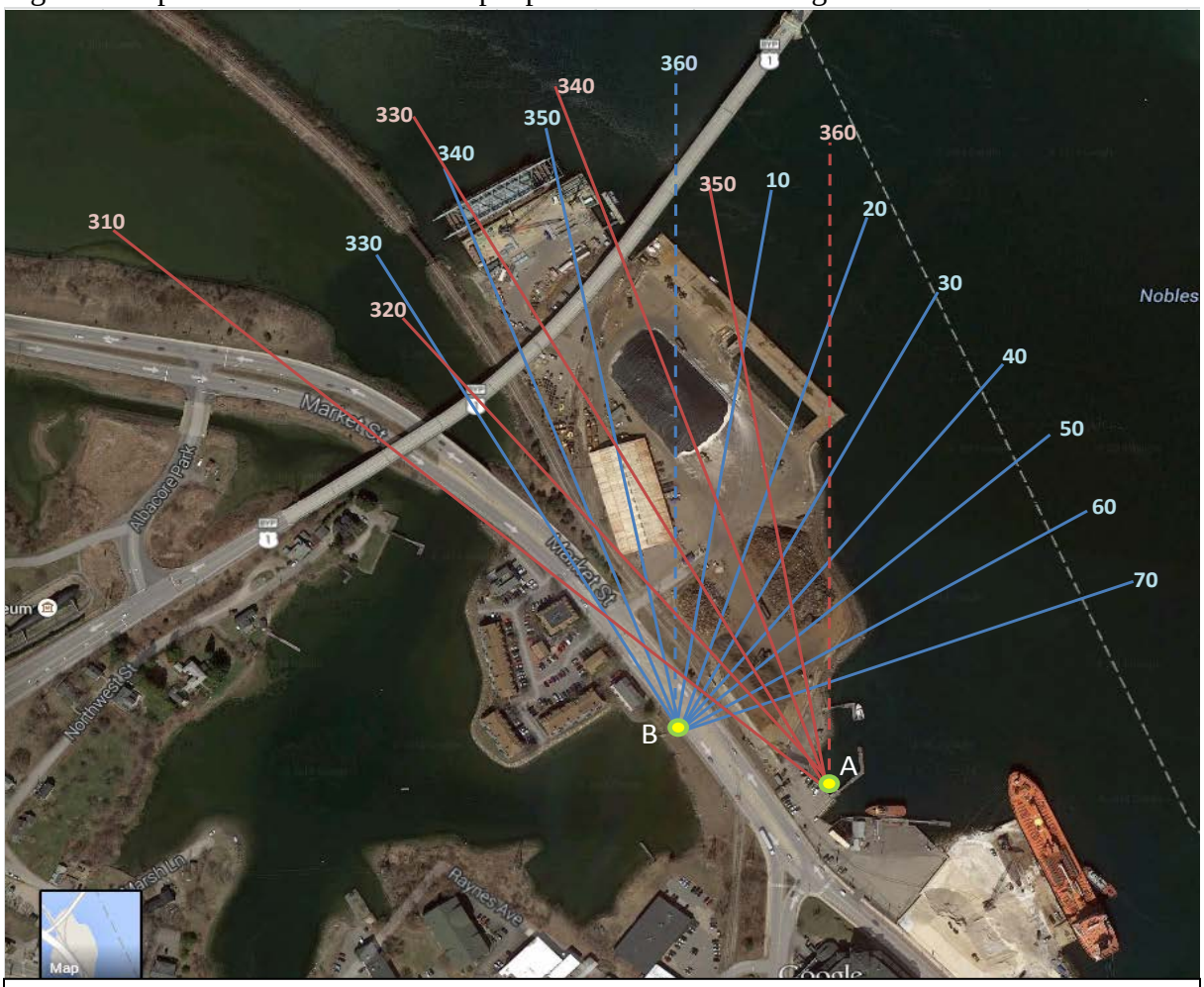
5.2 Hourly PM_{10} BAM and SO_2 Data Compared to Wind Direction and Speed

Wind direction and corresponding PM_{10} and SO_2 concentrations provide meaningful insight into potential sources of PM_{10}. Wind direction indicates the direction from which the source is located relative to the sampling location. For example, if elevated PM_{10} concentrations consistently occur when winds are from the north that would indicate a source located to the north. Atmospheric chemical data can also be useful for identifying sources. Elevated sulfur dioxide (SO_2) concentrations may be associated with coal burning power plants. If elevated PM_{10} concentrations consistently occur with simultaneous elevated SO_2 concentrations that might indicate the source of SO_2 is also potentially contributing to PM_{10} concentrations.

Near the Terminal, there are a number of potential PM_{10} emission sources to consider. Besides the potential for fugitive PM_{10} emissions arising from scrap operations, emissions can come from vehicular traffic on Market Street, passing and docked ships along the river, operations at nearby docks, and nearby large industry/power plants. Potential sources and their compass directions relative to sampling Sites A and B are shown in Figures 7 and 8. Wind directions start at 0 degrees (due North) and increase clockwise through 360 degrees, returning to due north. Thus, east is 90 degrees, south is 180 degrees, and west is 270 degrees.

Potential PM_{10} emissions can reach the Market Street monitor (Site B) from the scrap pile operations associated with wind directions ranging from 320 to 360 compass degrees (west-northwest), and from 0 to 80 degrees (north-northeast). By design, Site A has a different range of upwind directions for Terminal operations ranging from 330 to 360 degrees (northwest). Ship operations from the river can range from 330 degrees eastward through about 150 degrees from Sites A and B. Market Street traffic can contribute to local concentrations with winds anywhere between 310 degrees, eastward to about 180 degrees. Roadway PM_{10} emissions can include vehicle emissions as well as tire-suspended dust and/or road treatment salt. A nearby dock with salt offloading operations is located to the southeast of the area. Schiller station is a nearby power plant that combusts coal and is located at about 316 degrees to the northwest from both sites A and B (Figure 8).

Figure 7: Upwind directions for Scrap Operations to Monitoring Sites A and B



The Terminal lies upwind of Site A in the compass directions of 330 to 36 degrees and of Site B in the directions of 320 to 360 degrees and 0 to 80 degrees.

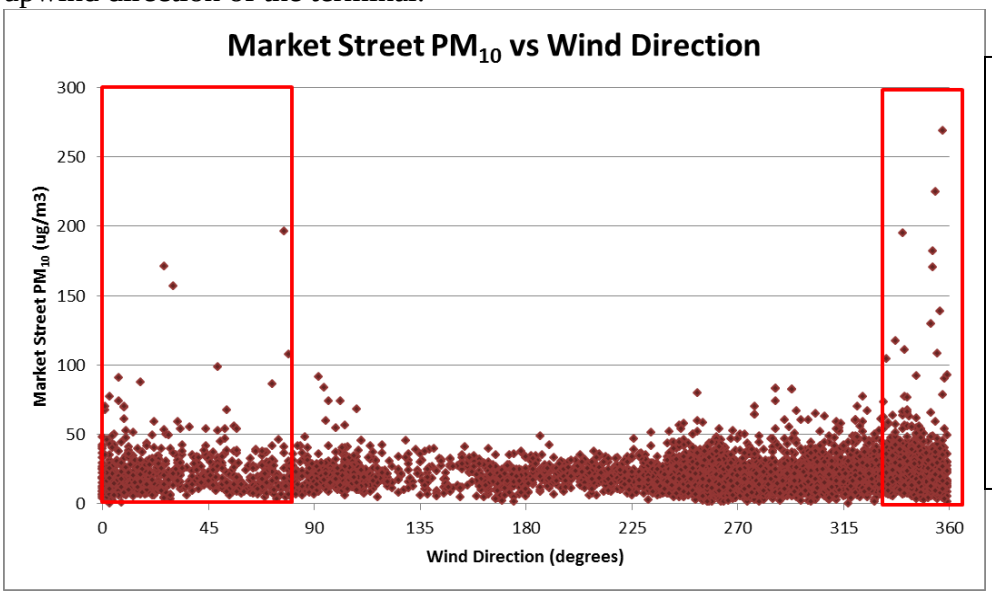
Figure 8: Upwind directions for nearby power plants to Market Street and Peirce Island

Schiller Station power plant lies upwind of the Market Street Site B monitor in the compass directions of 316 degrees and of the DES Peirce Island monitor in the direction of 310 degrees.

The relationship between PM_{10} and SO_2 hourly concentrations at Market Street Site B is plotted according to corresponding wind directions, shown in Figures 9 and 10. The Y-axis represents increasing concentrations and the X-axis represents wind directions associated with each concentration.

Figure 9 shows the Market Street hourly PM_{10} concentrations and corresponding wind directions. The red boxes encompass the wind direction associated with the Terminal as an upwind source. Patterns arising from the data show that PM_{10} concentrations less than 100 µg/m^3 can occur at Market Street when winds are from any direction; however the highest PM_{10} concentrations (exceeding 100 µg/m^3) only occur in wind directions associated with the red boxes. This strongly suggests a connection between the Terminal and PM_{10} concentrations exceeding 100 µg/m^3.

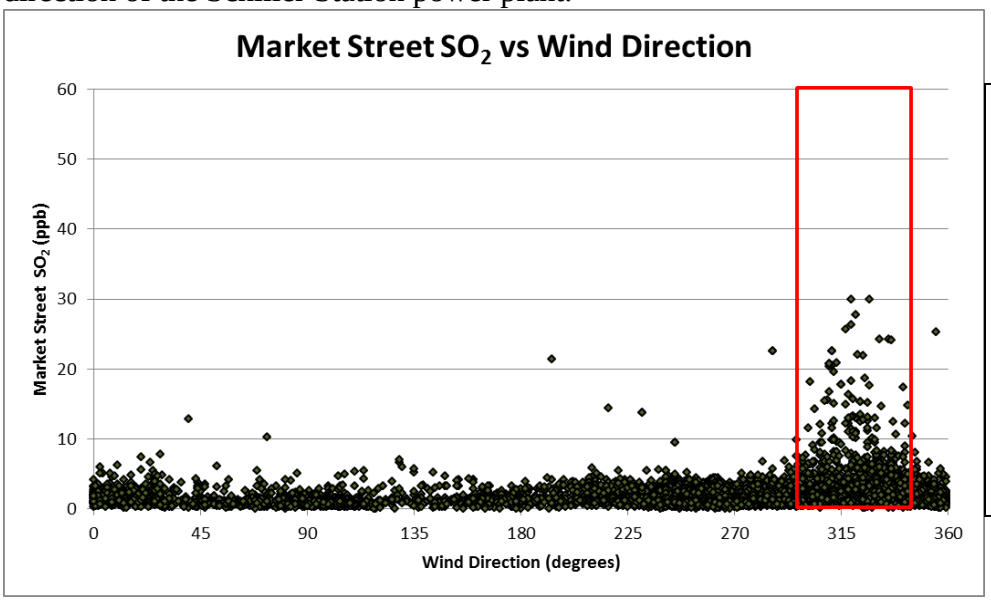
Figure 9: Hourly PM_{10} concentrations and wind direction at Market Street. Red boxes indicate upwind direction of the terminal.



All periods of PM_{10} concentrations exceeding 100 µg/m^3 fall within the red boxes and occur when winds came from the directions of 320 to 360 degrees and 0 to 80 degrees (direction of the scrap operations).

Figure 10 shows a different pattern for SO_2, with higher SO_2 concentrations (exceeding 10 parts per billion (ppb) related to winds in the range of 300 to 340 degrees. As discussed above, Schiller Station is located upwind at about 316 degrees and burns coal, which is relatively rich in sulfur, creating SO_2 emissions. In Figure 10 the red box encloses the general direction of Schiller Station power plant, a potential source of SO_2 emissions. Figures 9 and 10 indicate that there are two different source locations for PM_{10} and SO_2 at the Market Street location. These results also indicate that the upwind power plant is not associated with PM_{10} concentrations exceeding 100 µg/m^3 at Market Street.

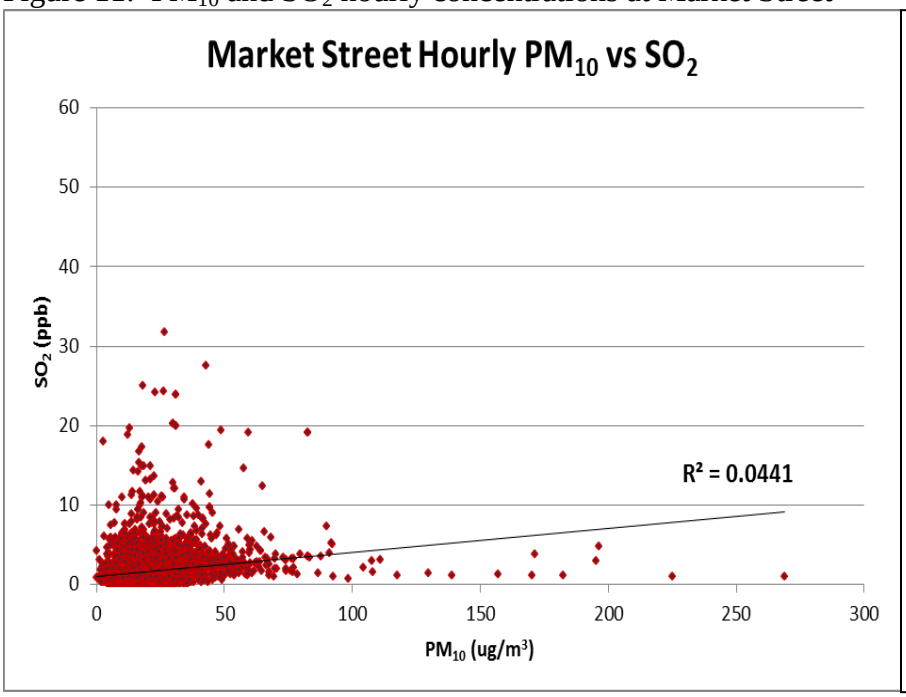
Figure 10: SO_2 concentrations and wind direction at Market Street. Red box indicates upwind direction of the Schiller Station power plant.



Most periods of SO_2 concentrations exceeding 15 ppb fall within the red box and occur when winds came from directions centered on 316 degrees (direction of Schiller Station power plant).

Figure 11 takes a closer look at the relationship between hourly PM_{10} and SO_2 concentrations regardless of wind direction. The highest PM_{10} concentrations occur when SO_2 concentrations are relatively low (<10 ppb). Conversely, when SO_2 concentrations are greater than 10 ppb, PM_{10} concentrations are usually below 50 µg/m^3. The weak relationship between PM_{10} and SO_2 provides further evidence that the upwind power plant is most likely not associated with the PM_{10} events in the Market Street area.

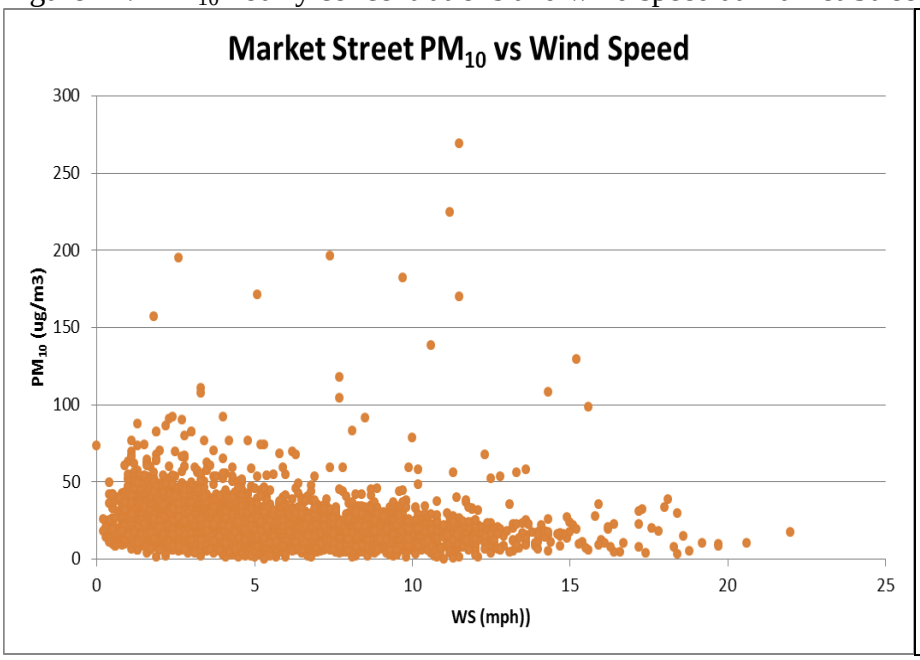
Figure 11: PM_{10} and SO_2 hourly concentrations at Market Street



If Schiller Station power plant were the dominant cause of the PM_{10} concentration spikes in the Market Street area, this chart would show a pattern where the highest PM_{10} concentrations also have the highest SO_2 concentrations. Since Figure 11 does not show such a pattern, Schiller Station is not a significant source causing the PM_{10} concentration spikes in the Market Street area.

Elevated wind speeds can cause an increase in PM_{10} concentrations due to entrainment of dust and conversely, stagnant wind conditions can also cause an accumulation of atmospheric particulate matter within a region. Such relationships between wind speed and PM_{10} were also examined as possible factors for PM_{10} at Market Street with the results shown in Figure 12. PM_{10} concentrations above 100 µg/m^3 at Market Street occur across the range of wind speeds, thus wind speed does not appear to be a significant factor regarding PM_{10} concentrations.

Figure 12: PM_{10} hourly concentrations and wind speed at Market Street



If strong winds blowing sand and dirt was the dominant cause of the PM_{10} concentration spikes in the Market Street area, this chart would show a pattern where the highest PM_{10} concentrations also have the highest wind speeds. Since Figure 12 does not show such a pattern, wind-blown sand and dirt is not a significant source causing the PM_{10} concentration spikes in the Market Street area.

5.3 Elevated PM_{10} Events

The greatest hourly PM_{10} concentrations occurring throughout the period of the study are summarized in Table 1, along with the corresponding SO_2 concentrations, wind direction and wind speed. Table 1 lists the events in the order of decreasing hourly PM_{10} concentrations. All events where PM_{10} concentrations exceed 100 µg/m^3 occurred when the winds ranged from 333 degrees (north-northwest) to 92 degrees (east). As stated above and shown in Figure 7, the upwind direction of the Terminal ranges from 320 to 80 degrees. These results indicate that a majority of these high PM_{10} events occurred when winds crossed a portion of the Terminal. These events are represented by the red box in Table 1. These high PM_{10} events occurred during five distinct events and are reviewed in more depth below.

Table 1: Peak hourly PM_{10} hourly concentrations at Market Street (Site B). DOW is day of week, WDR is wind direction, WSP is wind speed. The red box denotes time periods when the Terminal is upwind.

	DOW	Date	PM10	SO2	WDR	WSP
1	Wed	1/22/2014 11:00	269.1	3	357	11.5
2	Wed	1/22/2014 12:00	225	2.9	354	11.2
3	Sun	4/20/2014 8:00	196.5	1.2	77	7.4
4	Wed	3/19/2014 8:00	195.2	3	340	2.6
5	Wed	1/22/2014 13:00	182.4	2.8	353	9.7
6	Sun	4/20/2014 7:00	171.4	3.9	26	5.1
7	Wed	1/22/2014 10:00	170.3	3	353	11.5
8	Thur	5/15/2014 7:00	156.9	1	30	1.8
9	Wed	1/22/2014 9:00	138.8	3	356	10.6
10	Wed	3/26/2014 8:00	129.8	0.9	352	15.2
11	Wed	1/22/2014 14:00	117.6	4.5	337	7.7
12	Tue	2/4/2014 9:00	110.8	5.6	341	3.3
13	Wed	3/26/2014 7:00	108.1	1	355	14.3
14	Tue	4/22/2014 8:00	107.6	2.5	79	3.3
15	Wed	1/22/2014 15:00	104.4	8.2	333	7.7
16	Mon	5/12/2014 21:00	98.3	0.7	49	15.6
17	Tue	1/21/2014 14:00	92.4	2.5	359	4
18	Wed	3/19/2014 7:00	92.2	3	346	2.4
19	Sun	4/20/2014 9:00	91.7	1.2	92	8.5
20	Thur	2/27/2014 8:00	90.9	2.8	7	2.3
21	Tue	1/21/2014 12:00	89.9	4.9	358	2.7
22	Mon	4/7/2014 7:00	87.7	3.2	16	1.3
23	Tue	2/4/2014 10:00	86.5	3.5	72	2.2
24	Tue	4/22/2014 11:00	83.3	1.9	94	8.1
25	Wed	2/12/2014 10:00	82.7	22.6	286	3
26	Wed	2/12/2014 8:00	82.6	5.5	293	1.9

The highest PM_{10} concentrations at Market Street occur when winds cross the Terminal.

Note Regarding Wind Directions:

Wind direction information provided in this report is based on averages of instantaneous values. By nature, winds vary in direction and speed from moment to moment and should be interpreted as a guide and not as proof or disproof that upwind sources are affecting downwind locations. However, consistent patterns can strongly suggest such relationships.

Table 1 identifies five distinct periods where PM_{10} concentration spikes occurred at the Market Street monitor (Site B). These PM_{10} concentration spikes occurred on January 22, March 19, March 26, April 20 & 22 and May 15, 2014. Each event is reviewed in greater detail below.

January 22, 2014

A peak hourly PM_{10} concentration of 269 µg/m^3 was recorded at 11 AM on January 22, 2014 at the Market Street monitoring Site B. This peak PM_{10} concentration was the highest recorded in this study and occurred under a moderate north wind that had low SO_2 concentrations. The monitor recorded 5 hours where PM_{10} concentrations exceeded 100 µg/m^3 during the event. See data points 1, 2, 5, 7, 9, 11, and 15 in Table 1.

Figure 13 presents a 3-day running summary of Market Street PM_{10} and SO_2 concentrations and Peirce Island $PM_{2.5}$ and SO_2 concentrations centered on the January 22, 2014 event. PM_{10} was not available at Peirce Island during this event and $PM_{2.5}$ was used as a surrogate to track the 2.5 micrometer subset of PM_{10}. There are not co-occurring peaks of PM_{10} with any of the other parameters, indicating that the increase in PM_{10} at Market Street is likely not associated with the upwind power plant.

Figure 13: Hourly concentrations of PM_{10} and SO_2 concentrations at Market Street and Peirce Island for the January 22, 2014 event

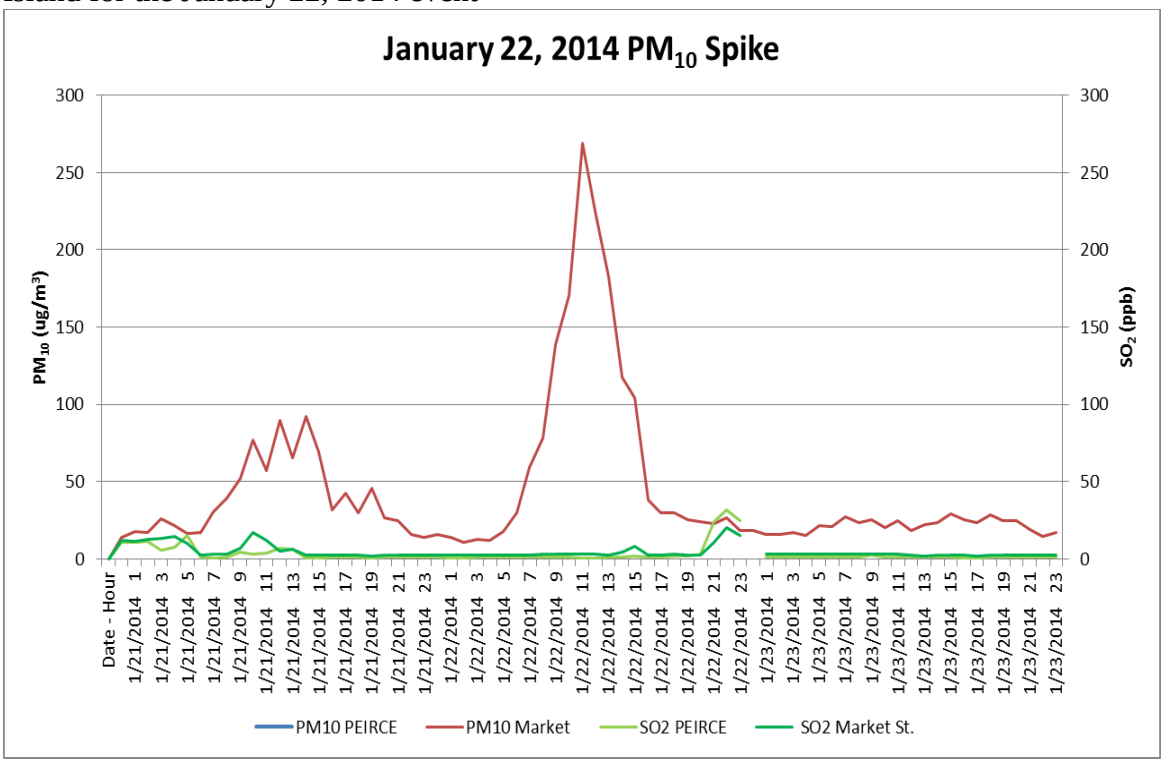
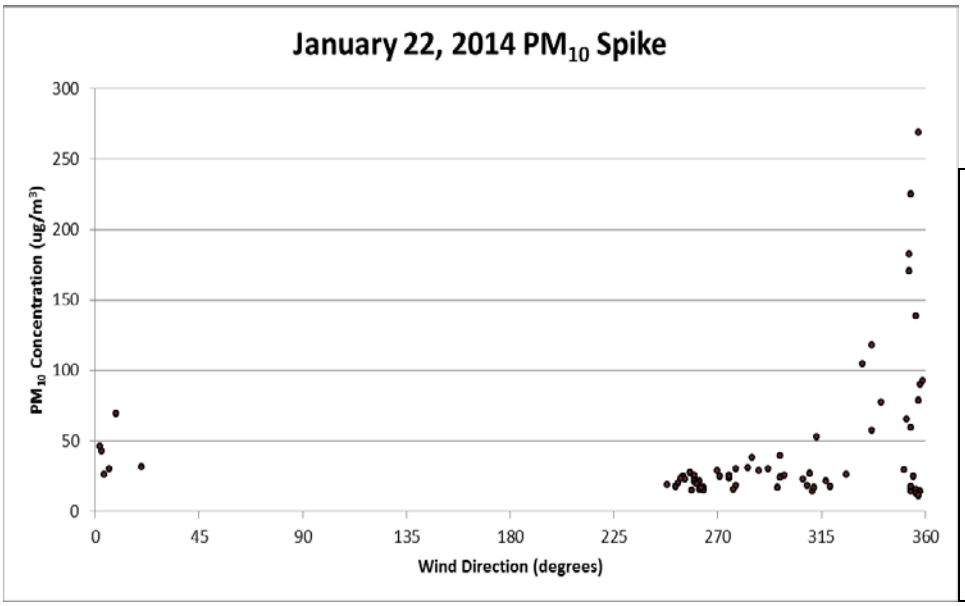


Figure 14 shows hourly PM_{10} concentrations compared to wind direction during the corresponding 3-day period. Peak PM_{10} concentrations are wind direction specific and range from 330 to 360 degrees, which corresponds to the location of the Terminal property.

Figure 14: Hourly PM_{10} concentrations and wind direction at Market Street for the January 22, 2014 event



All periods of PM_{10} concentrations exceeding 100 $\mu g/m^3$ occur when winds came from the directions of 320 to 360 degrees and 0 to 80 degrees (direction of the scrap operations).

March 19, 2014

A peak hourly PM_{10} concentration of 195 µg/m^3 was recorded at 8 AM on March 19, 2014 at the Market Street monitoring Site B. It occurred under a light north-northwest wind with SO_2 concentrations less than 10 ppb. The monitor recorded only 1 hour where PM_{10} concentrations exceeded 100 µg/m^3, however the concentration during the preceding hour was 92 µg/m^{3}and during the following hour was 74 µg/m^3. See data point 4 in Table 1.

Figure 15 presents a 3-day running summary of Market Street PM_{10} and SO_2 concentrations and Peirce Island $PM_{2.5}$ and SO_2 concentrations. PM_{10} was not available at Peirce Island during this event and $PM_{2.5}$ was used as a surrogate. There is a slight increase in $PM_{2.5}$ at Peirce Island with concentrations approaching 20 µg/m^3. Due to the lack of PM_{10} data at Peirce Island it is not known if there was also an increase in PM_{10}. Slightly elevated concentrations of SO_2 also occur within the same timeframe at both locations although they remain generally low (3ppb – 5ppb).

Figure 15: Hourly concentrations of PM_{10} and SO_2 concentrations at Market Street and Peirce Island for March 19, 2014 event

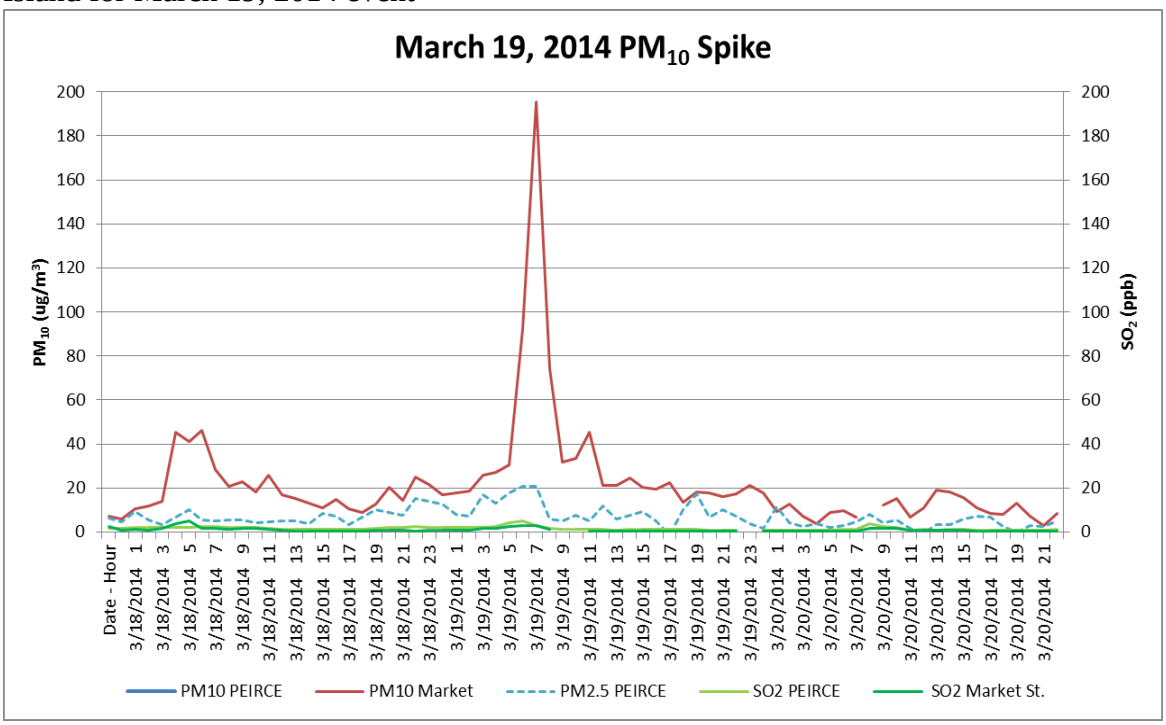
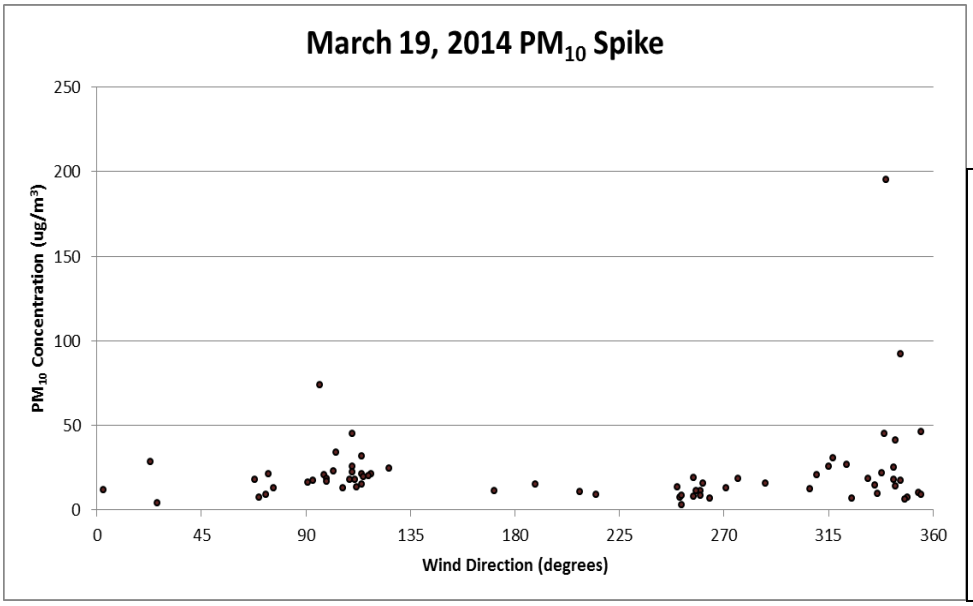


Figure 16 shows hourly PM_{10} concentrations compared to wind direction during the same 3-day period at Market Street. Peak PM_{10} concentrations occur at approximately 345 degrees (north-northwest) and 95 degrees (east-southeast).

Figure 16: Hourly PM_{10} concentrations and wind direction at Market Street for the March 19, 2014 event



All periods of PM_{10} concentrations exceeding 100 µg/m^3 occur when winds came from the directions of 320 to 360 degrees and 0 to 80 degrees (direction of the scrap operations).

March 26, 2014

A peak hourly PM_{10} concentration of 130µg/m^3 was recorded at 8 AM on March 26, 2014 at the Market Street monitoring Site B. The monitor recorded 2 hours where PM_{10} concentrations exceeded 100 µg/m^3 and concentrations remained somewhat elevated for several hours before returning to typical concentrations below 20 µg/m^3. See data points 10 and 13 in Table 1.

Figure 17 presents a 3-day running summary of Market Street PM_{10} and SO_2 concentrations and Peirce Island $PM_{2.5}$ and SO_2 concentrations. PM_{10} was not available at Peirce Island during this event and $PM_{2.5}$ is used as a surrogate. The Market Street PM_{10} concentrations above 100 µg/m^3 occur with no other peaks in other parameters at either site. However, the portion of the PM_{10} peak that remains above 40 µg/m^3 for several hours following the initial peak does occur with concurrent with somewhat elevated levels of SO_2 at both Market Street and Peirce Island. During this period, winds shifted between directions where Schiller Station or the scrap operations would be upwind. Without a steady wind direction from source to monitor, neither pollutant measured low to mid-moderate concentrations.

Figure 17: Hourly concentrations of PM_{10} and SO_2 concentrations at Market Street and Peirce Island for the March 26, 2014 event

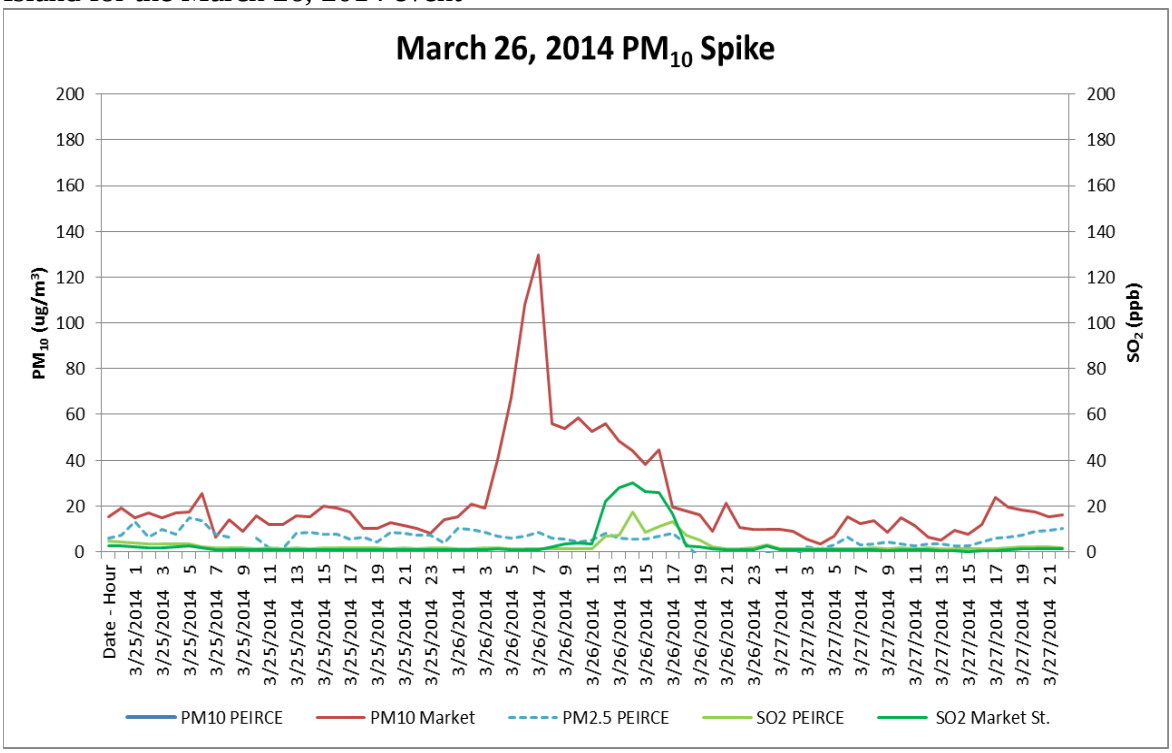
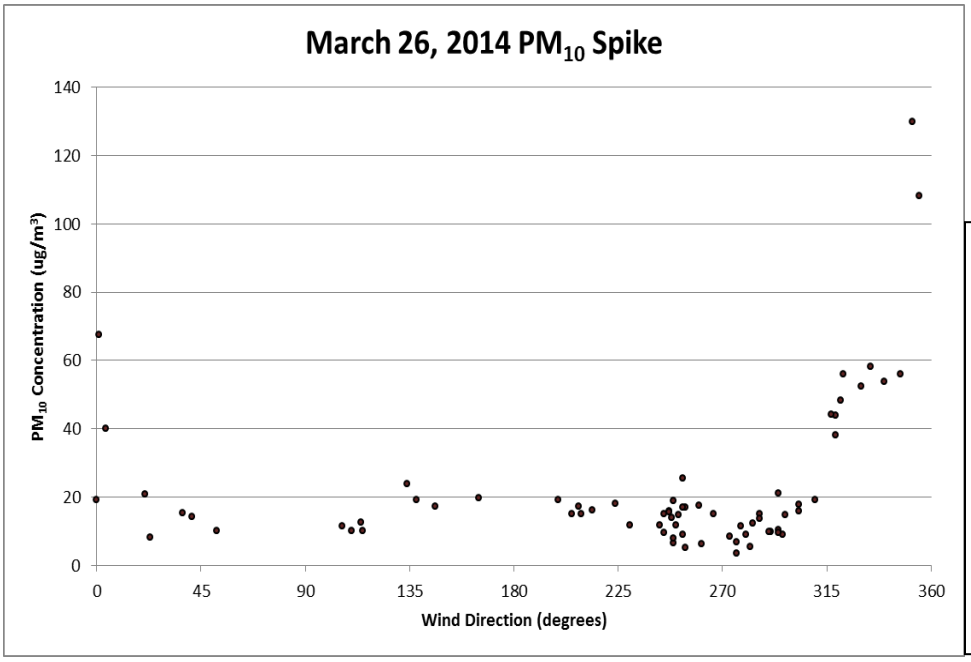


Figure 18 shows hourly PM_{10} concentrations compared to wind direction at Market Street during the same 3-day period. Peak PM_{10} concentrations occur at a wind direction of approximately 360 degrees (north).

Figure 18: Hourly PM_{10} concentrations and wind direction at Market Street for the March 26, 2014 event



All periods of PM_{10} concentrations exceeding 100 $\mu g/m^3$ occur when winds came from the directions of 320 to 360 degrees and 0 to 80 degrees (direction of the scrap operations).

April 20/22, 2014

A peak hourly PM_{10} concentration of 197µg/m^3 was recorded at 8 AM on April 20, 2014 at the Market Street monitoring Site B. The monitor recorded 2 hours where PM_{10} concentrations exceeded 100 µg/m^3. On April 22 at 8 AM, a second PM_{10} event occurred where concentrations spiked to 108 µg/m^3. There were two additional PM_{10} peaks above 60 µg/m^3 shortly thereafter. See data points 3, 6 and 22 in Table 1.

Figure 19 presents a 4-day running summary of Market Street PM_{10} and SO_2 concentrations and Peirce Island PM_{10}, $PM_{2.5}$ and SO_2 concentrations. The Market Street PM_{10} concentration peak on April 20 occurs by itself with no other peaks in particulate matter or SO_2 at either Market Street or Peirce Island. During the April 22 peaks in PM_{10} at Market Street there were also slight increases in PM_{10} at Peirce Island with concentrations above 20 µg/m^3. The less dramatic increase in PM_{10} concentrations at Peirce Island compared to Market Street suggests that the Market Street location is nearer to an emission source that may also impact the Peirce Island location to a lesser degree. SO_2 concentrations were not elevated at either location during these spikes.

Figure 19: Hourly concentrations of PM_{10} and SO_2 concentrations at Market Street and Peirce Island for the April 20-22, 2014 event

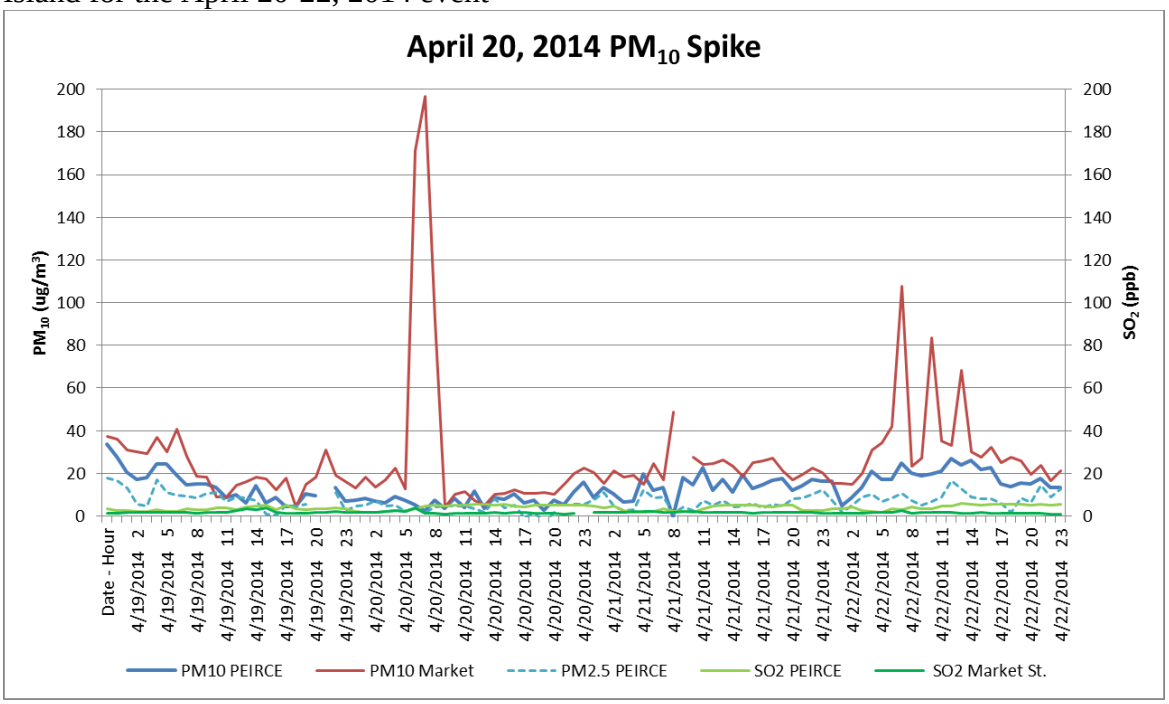
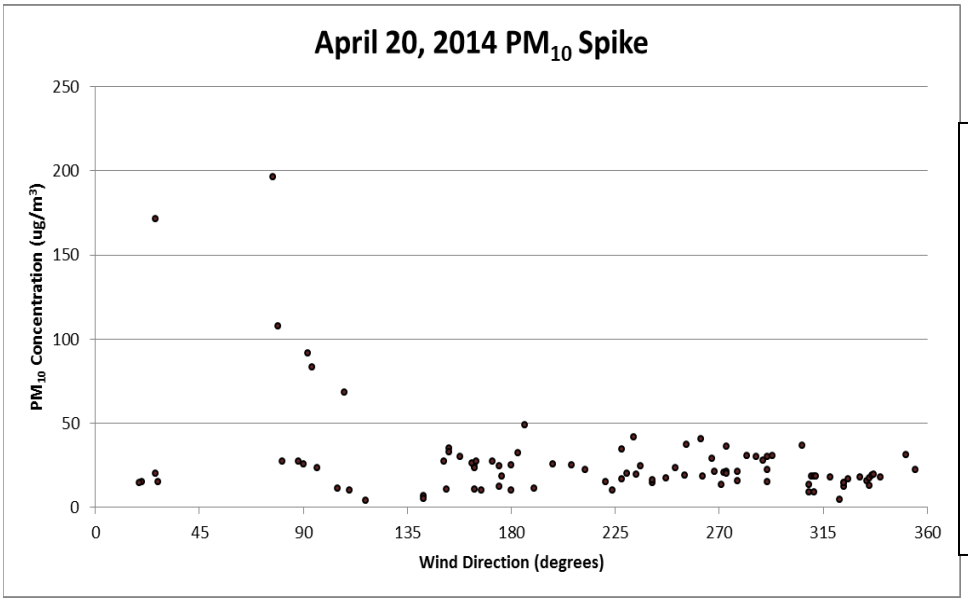


Figure 20 shows hourly PM_{10} concentrations compared to wind direction at Market Street during the same 4-day period. Peak PM_{10} concentrations occur from the wind direction of 26 to 80 degrees (north-northeast). The Terminal property is located within this direction for the Market Street sampling location. The period of the PM10 concentration spike corresponds with known ship scrap-loading operations.

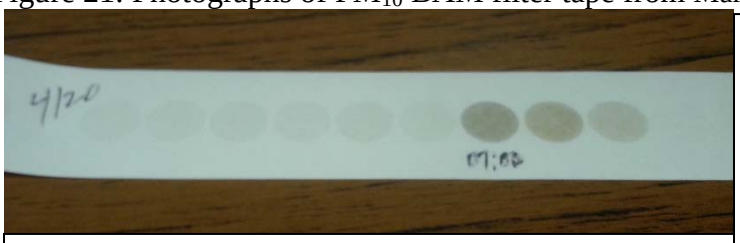
Figure 20: Hourly PM_{10} concentrations and wind direction at Market Street for the April 20-22, 2014 event



All periods of PM_{10} concentrations exceeding 75 µg/m^3 occur when winds came from the directions of 320 to 360 degrees and 0 to 80 degrees (direction of the scrap operations).

Photographs of the filter tape from the continuous PM_{10} BAM monitor for the April 20, 2014 event are shown in Figure 21. The recordings prior to 7AM show a typical off-white circle pattern when PM_{10} concentrations were approximately 20 µg/m^3. Beginning with the 7 AM circle, dark staining occurs for a period of 3 hours and represents the PM_{10} spike of 197 µg/m^3. The PM_{10} collected on the filter tape at 8 AM and 9AM also shows a distinctive rust color. The filter set collected by the FRM devices during this event was further evaluated by laboratory analysis (see section 5.5).

Figure 21: Photographs of PM_{10} BAM filter tape from Market Street on April 20, 2014



Note the reddish-brown (rust-colored) color stains on the filter tape during periods with the highest PM_{10} concentrations.

May 12/15, 2014

A peak hourly PM_{10} concentration of 98.3 µg/m^3 was recorded at 9 PM on May 12, 2014 at the Market Street monitoring Site B. This concentration spike occurred after normal daylight scrap pile operations, however there were unusually strong wind gusts from the northeast during this hour that were strong enough to suspend loose dust particles (including scrap dust from the Terminal property). This peak did not have correspondingly elevated SO_2 concentrations. On May 15 at 7 AM, a second PM_{10} event occurred where concentrations spiked to 157 µg/m^3, under a very light northeast wind and with low SO_2 concentrations. See data points 8 and 16 in Table 1.

Figure 22 presents a 4-day running summary of Market Street PM_{10} and SO_2 and Peirce Island PM_{10}, $PM_{2.5,}$ and SO_2 concentrations. During these two elevated PM_{10} events at Market Street, there were also slight increases in PM_{10} at Peirce Island (above 20 µg/m^3). This is similar to the pattern observed on April 22, 2014. During these May 2014 spikes in PM_{10} there were no corresponding increases in SO_2 concentrations.

Figure 22: Hourly concentrations of PM_{10} and SO_2 concentrations at Market Street and Peirce Island for May 12-15, 2014

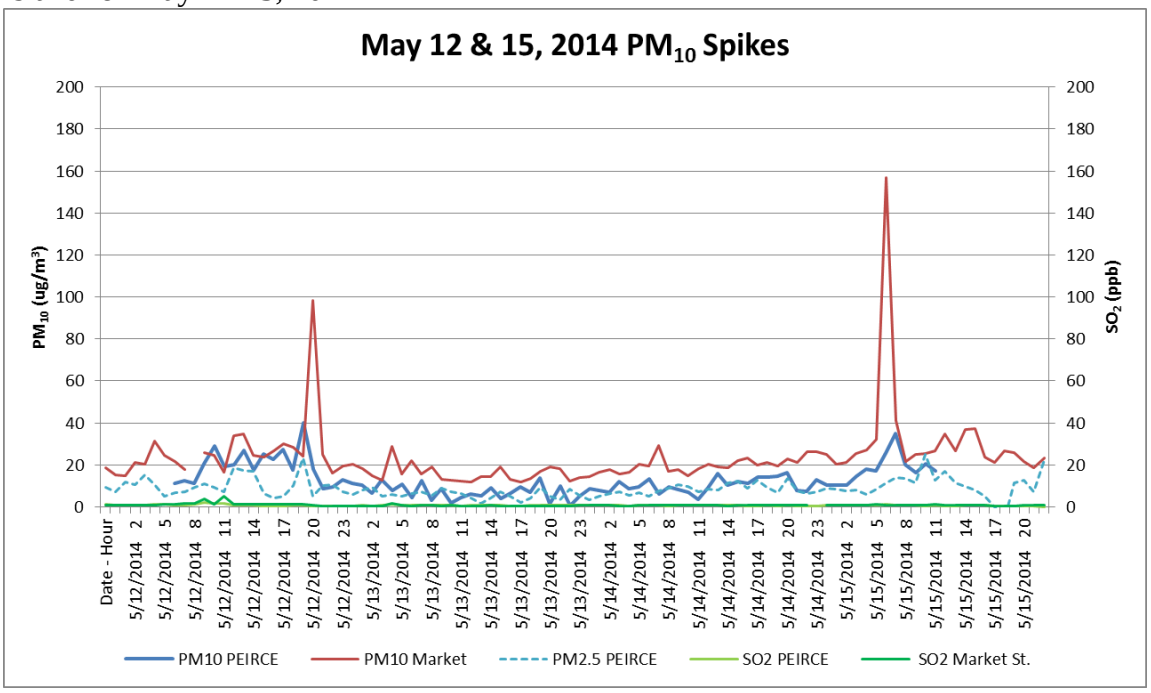
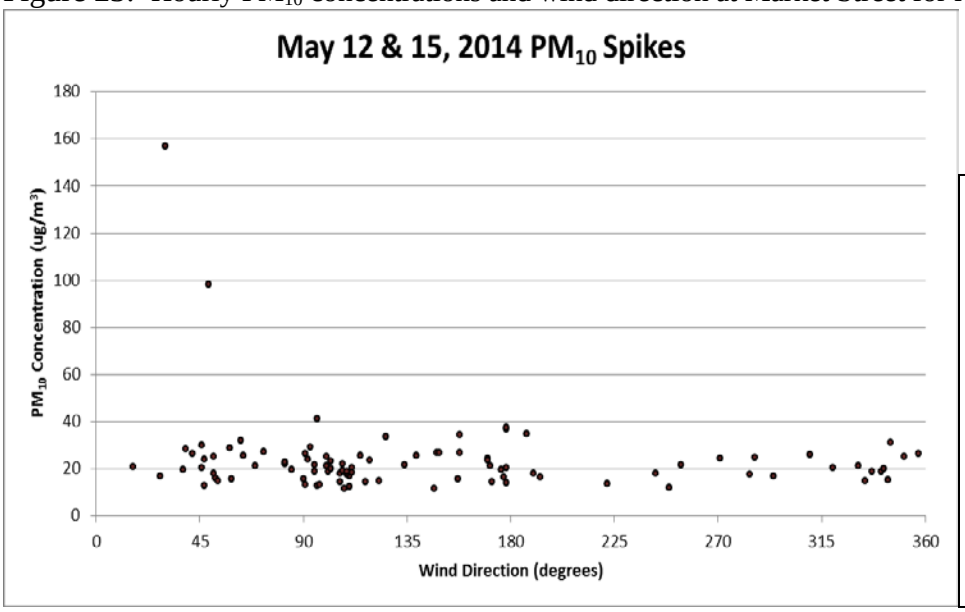


Figure 23 shows hourly PM_{10} concentrations compared to wind direction at the Market Street location during the same 4-day period. The peak PM_{10} concentrations occur when wind directions are from 30 to 49 degrees, the general direction of the Terminal (northeast).

Figure 23: Hourly PM_{10} concentrations and wind direction at Market Street for May 12-15, 2014



All periods of PM_{10} concentrations exceeding 75 µg/m^3 occur when winds came from the directions of 320 to 360 degrees and 0 to 80 degrees (direction of the scrap operations).

5.4 Filter-Based FRM PM_{10} Samples

On eleven dates during the sampling period, 24 hour PM_{10} filter sets were collected with Federal Reference Method (FRM) devices at locations upwind and downwind of the Terminal (Sites A and B). DES forecast periods where wind and other weather patterns were favorable for the two Market Street sampling sites to be upwind and downwind PM_{10} receptors of Terminal operations. Site A is located east of Site B (Figure 2) and ideal wind conditions for sample collections at Site A or B would consist of sustained winds from either the east or west. Each PM_{10} FRM device was operated simultaneously for a period of approximately 24-hours. Once collected, filter sets were sealed and sent to the DES laboratory to determine PM_{10} concentrations (see Appendix B). Table 2 summarizes the filter set collection events. In almost every sample set, PM_{10} concentration increases between the upwind and downwind location. In some samples, the wind direction changed unexpectedly leading to a mix of hours where Sites A and B were each downwind causing inconclusive concentration changes in the samples.

Table 2: 24 Hour PM_{10} Filter Set Events

Date	Day of Week	Site B (µg/m^3)	Site A (µg/m^3)	Prevailing Wind	Concentration Change Upwind to Downwind (µg/m^3)
9/23/2013	Mon	5.5	7.7	NW	2.2
9/26/2013	Thur	13.7	8.5	SE	5.2
10/12/2013	Sat	15.8	16.2	Mixed	-0.4
11/8/2013	Fri	2.5	--*	W	--*
11/19/2013	Sat	6.6	7.6	NW	1.0
11/23/2013	Sat	5.5	7.5	W	2.0
11/28/2013	Thur	4.1	4.2	W	0.1
12/11/2013	Wed	22.2	30.8	W	8.6
2/11/2014	Tue	17.6	31.8	WNW	14.2
2/16/2014	Sun	5.2	13.2	W	8.0
4/20/2014	Sun	24.3	10.0	ENE	14.3

** – Filter weight error*

5.5 Analyses for Metals

Three filter sets were chosen for further chemical analysis and were analyzed for a suite of metals including aluminum (Al), chromium (Cr), copper (Cu), iron (Fe), lead (Pb), and zinc (Zn). The chemical composition of the particulate matter can provide additional insights into the potential sources. Metals were selected based on the likelihood of being present within the scrap operations as well as for their ability to act as a tracer compound for other potential sources of PM_{10} in the area. Scrap operations can contain a variety of metals, including all of the metals targeted for analysis in this study. However, iron is expected to be the dominant metal from the scrap metal operations.

Sample filter sets were selected as follows:

1. October 12, 2013 – A mixed wind event was used as a control sample. The maximum one-hour PM_{10} concentration was 35.8 µg/m^3.
2. December 11, 2013 – West to East wind direction. Maximum one-hour PM_{10} concentration was 59.1 µg/m^3.
3. April 20, 2014 –East to West wind direction. This filter set was collected at a time when the Terminal was actively loading a docked ship and there was a one-hour PM_{10} concentration spike of 196.5 µg/m^3.

Many of the analytical results for the October 12, 2013 sampling event were below the analytical detection limit. This sample is used as a control because there was not a clear upwind or downwind monitor. Because of the consistent wind directions from upwind to downwind monitor, the sampling events on December 11, 2013 (Filter Set 2) and April 20, 2014 (Filter Set 3) had greater PM_{10} concentrations and most metals were measured at above the detection limit. These two events were chose for metals analysis because the winds crossed the scrap yard in different directions. Consistent findings between samples collected with opposite wind directions (Filter Sets 2 and 3) strongly suggest a dominant source lies between the two monitoring sites (A and B). The metal concentrations for each of the analyzed three filter sets are shown in Table 3. The metal concentrations indicate that the downwind filter was greater than found in the upwind filter. In some cases, the amount of increase could not be precisely quantified because the amount collected at the upwind site was below the detection limit.

Table 3: PM_{10} Concentration Changes in Metal Content for Tested Filter Sets ($\mu g/m^3$)

	Filter Set 1			**Filter Set 2**			**Filter Set 3**		
($\mu g/m^3$)	October 12, 2013			December 11, 2013			April 20, 2014		
	Upwind	Downwind	**Change**	Upwind	Downwind	**Change**	Upwind	Downwind	**Change**
Aluminum (Al)	ND	ND	**ND**	0.092	0.133	**0.042**	0.024	0.171	**0.147**
Chromium (Cr)	0.006	0.008	**0.002**	0.003	0.005	**0.002**	0.004	0.012	**0.008**
Copper (Cu)	ND	0.006	**0.004**[2]	0.003	0.009	**0.006**	0.002	0.011	**0.009**
Iron (Fe)	ND	0.233	**0.129**[2]	0.179	0.682	**0.503**	0.374	3.162	**2.187**
Lead (Pb)	ND	ND	**ND**	0.002	0.007	**0.004**	0.002	0.021	**0.019**
Zinc (Zn)	ND	ND	**ND**	ND	0.096	**0.054**[2]	0.083	0.541	**0.458**

ND indicates sample was below detection limits for the analytical method. This should not be interpreted as no or invalid data. Instead, it means the actual value is between 0 and the lower limit for reliable detection as established for the analytical method for that compound.

[2]- Change in concentration is based on use of the analytical detection limit in place of non-detection (ND) for upwind filters. This allows an estimate of the minimum possible change in concentration because non-detection can mean values ranging from zero up to the detection limit

Filter Set 1 (October 12, 2013): Cr, Cu and Fe concentrations increased slightly, whereas the Al, Pb and Zn concentrations could not be assessed because upwind and downwind concentrations were below the analytical detection limitations. It should be noted that due to shifting winds, upwind and downwind monitoring sites could not be distinctly designated.

Filter Set 2 (December 11, 2013): All metal concentrations increased by at least 45% between upwind and downwind sample locations. Cu and Pb increased by about 160% and the Fe concentration downwind was approximately three times greater than the upwind concentration.

Filter Set 3 (April 20, 2014): All metals for both upwind and downwind samples were above analytical detection limits. Concentrations of all metals more than doubled between the upwind and downwind samples. Iron increased by 788% and accounted for a sizable portion of the PM_{10} concentration increase in the downwind filter. Iron accounted for nearly 20% of the sample weight gain between upwind and downwind filters. If all the iron was bound in rust particles it would then account for nearly 28 to 37% of the weight gain.

Large increases in metals concentrations, particularly for iron, occurred with winds blowing from west to east (Filter Set 2) and when winds blew from east to west (Filter Set 3). Iron dominates the PM_{10} mass that was collected in both sample sets. Simple triangulation determines there is a large source of iron-containing PM_{10} located between monitoring Sites A and B.

5.6 Analysis of Potential Sources

Converting the metal concentrations to parts per million by weight (ppmw) allows convenient comparison to some potential PM_{10} sources in the area (wind-blown soils and road salt)(see Table 4). For this assessment, only Filter Sets 2 and 3 are chosen because of their clear upwind to downwind wind conditions. Iron concentrations in both filter sets were much higher than values found in published research for either soil or road salt. Similar results were found with Cr, Cu, Pb, and Zn. Aluminum in the sample sets was lower than documented for average soil content and higher than that in road salt. Another interpretation of results looks at relative ratios of metals found in each filter sample. These calculations and comparisons are included in Appendix B and reference material is located in Appendix C. The ratio analysis results confirm the high iron concentration findings discussed in section 5.5.

Table 4: PM_{10} Metal Concentration Changes Compared to Soil and Salt (ppmw)

(ppm)	**Filter Set 2**	**Filter Set 3**	**Average Soil***	**Road Salt***
Aluminum (Al)	4,800	10,300	33,000	150
Chromium (Cr)	220	560	33	ND
Copper (Cu)	650	620	13	ND
Iron (Fe)	58,00	195,000	14,000	160
Lead (Pb)	490	1,300	14	ND
Zinc (Zn)	6,250	32,000	40	ND

**- Source content citations are listed in Appendix C*

Discussion

Construction, land management, and winds are capable of suspending soils and sands into airborne PM_{10}. Soil and sand composition vary significantly, but the majority is composed of silicon oxides. Aluminum and iron oxides, calcium, magnesium, potassium, and organic carbon make up notable percentages. Copper, chromium, lead and zinc are considered trace species. The iron and copper concentrations are much higher relative to other metal species in the sample sets and thus soils are not likely to be a primary cause of PM_{10} concentration increases in the Market Street area.

There is a roadway that passes by the Terminal in close proximity to both monitoring sites A and B. Because sampling took place during colder months when salt was actively shipped, managed, and applied to nearby roadways, it should be considered as a potential PM_{10} source. Road salts are dominantly sodium chloride, however calcium, potassium, and magnesium based salts are also sometimes used. Ferrocyanide ($K_4Fe(CN)_6$), which contains iron, is sometimes used as an anti-caking compound in large salt supplies, however studies conducted by the Pennsylvania Department of Environmental found only trace amounts of iron in road salt. Based on the data presented in Table 4 and corroborated by ratio analysis, road salt is not likely to be associated with the PM_{10} concentration increases measured in this study.

Ships that pass or dock at the Terminal usually burn oil or diesel fuels which are composed of hydrocarbons with traces of other materials including sulfur, chromium, copper, nickel, vanadium, and zinc. Oil combustion emissions are very low in iron and based on chemical ratio assessment, there is too much iron and aluminum relative to other metal species. Therefore it is unlikely that oil combustion is causing the PM_{10} concentration spikes measured in this study.

Roadways and the nearby drayage vehicle activity in the area also can produce PM_{10} emissions. Gasoline and diesel burning vehicles, similar to other oil-burning sources, have only trace amounts of iron and aluminum. Aluminum and iron concentrations (measured in Sample Sets 2

and 3) are too high in proportion to the other metals for cars and trucks to be a significant source of the PM_{10} concentration spikes measured in the Market Street area.

Scrap operations can contain a variety of metals, including all of the metals targeted for analysis in this study, however iron is expected to be the dominant metal from. Elemental ratios show PM_{10} samples are rich in iron compared to other metals, consistent with scrap metal at the Terminal. While other sources in the region and in the local area are likely to contribute to the measured PM_{10} background concentrations in the area, it is highly likely that fugitive dust emissions from scrap operations are the dominant source of PM_{10} concentration spikes in the Market Street area.

6.0 Conclusions

This study was intended as a screening tool for determining whether the existing control program used at the Market Street Port Authority Terminal scrap operation is effective in controlling and preventing fugitive dust from leaving the site. The sampling period occurred during normal operations in late 2013 and winter/spring 2014. PM_{10} monitoring and weather equipment were strategically located to identify potential PM_{10} emission sources in the area of the Market Street Terminal. Several PM_{10} concentration spikes were measured over the duration of this study.

Data indicate PM_{10} concentration spikes generally occur:

- during daylight working hours; and
- when wind directions cross the Market Street Port Authority scrap pile operations.

PM_{10} concentration spikes also:

- produce filter stains of a rust-color;
- have high iron content;
- do not correlate well with SO2 emissions known to be associated with a nearby power plant;
- are too high in iron and aluminum content to be caused by road salt, cars, trucks, boats and ships; and
- are not commonly associated with high wind speeds needed to suspend sand and soils from the ground.

The results suggest that the scrap metal operations at the Terminal are the predominant source of elevated PM_{10} concentrations in the Market Street area and that fugitive dust emissions are leaving the site.

Appendix A – FRM and Sampling Device Information

The following methods for measuring ambient concentrations of specified air pollutants have been designated as "reference methods" or "equivalent methods" in accordance with Title 40, Part 53 of the Code of Federal Regulations (40 CFR Part 53). Each method is acceptable for use in state or local air quality surveillance systems under 40 CFR Part 58.

PM10 FRM
Thermo Scientific or Rupprecht & Patashnick Partisol® Model 2000 Air Sampler
(see http://www.thermoscientific.com/ecomm/servlet/productsdetail_11152___11960560_-1)
Manual Reference Method: RFPS-0694-098
"Thermo Scientific Partisol® 2000 Air Sampler" or "Rupprecht & Patashnick Partisol® Model 2000 Air Sampler," consisting of a Hub Unit and 0, 1, 2, or 3 Satellite Units, with each sampling station used for PM10 measurements equipped with a Rupprecht & Patashnick PM10 inlet and operated for continuous 24-hour periods using the Basic, Manual, Time, Analog Input, or Serial Input programming modes, and with or without any of the following options: PM2.5-style filter cassette holder; louvered inlet specified in 40 CFR 50 Appendix L, Figs. L-2 thru L-19 in lieu of standard inlet; 57-002320 Stand for Hub or Satellite; 59-002542 Advanced EPROM; 10-001403 Large Pump (1/4 hp); 120 VAC. Hardware for Indoor Installation consists of: 51-002638-xxxx Temperature Sensor (Extended Length); 55-001289 Roof Flange (1 1/4"); 57- 000604 Support Tripod for Inlet; 57-002526-0001 Sample Tube Extension (1 m); 57-002526-0002 Sample Tube Extension (2 m). Hardware for Outdoor Installation in Extreme Cold Environments consists of: 10-002645 Insulating Jacket for Hub Unit.
Federal Register: Vol. 59, page 35338, 07/11/1994

PM10 FEM
Met One Model BAM 1020
(*see http://www.metone.com/documents/BAM-1020_6-08.pdf*)
Automated Equivalent Method: EQPM-0798-122
"Met One Instruments or Sibata Scientific Technology Models BAM 1020, GBAM 1020, BAM 1020-1, GBAM 1020-1, Horiba APDA-371 PM_{10} Beta Attenuation Monitor, or Ecotech Spirant BAM1000" including the BX-802 EPA PM_{10} inlet (or alternative louvered PM_{10} inlet meeting 40 CFR 50 Appendix L specifications), operated for 24-hour average measurements, with a filter change frequency of one hour, with glass fiber filter tape, and with or without any of the following options: BX-823, tube extension; BX-825, heater kit; BX-826, 230 VAC heater kit; BX-827 "Smart Heater" set for maintaining moisture between 35% and 45% and no _T control; BX-828, roof tripod; BX-902, exterior enclosure; BX-903, exterior enclosure with temperature control; BX-961, mass flow controller; BX-967, internal calibration device, BX-970 touch-screen display with USB interface. For software (firmware) versions V3.0 or higher, a user-selectable measurement time (COUNT TIME) of 4, 6, 8 or 10 minutes selected, along with appropriate sample time (BAM SAMPLE) setting of 50, 46, 42 or 38 minutes, respectively, to maintain a 60-minute measurement cycle. For software (firmware) versions V3.5 or higher, user-selectable option to sample under actual conditions (Flow Type: ACTUAL) and report under standard conditions (Reporting: STD), which requires the use of P/N BX-592 external temperature sensor or P/N BX-596 external temperature/barometric pressure sensor. The user may also sample under standard conditions (Flow Type: STD) and report under standard conditions (Reporting: STD) with any software/firmware 2.0 or higher. Instrument must be operated in accordance with the appropriate instrument manual.
Federal Register: Vol. 63, page 41253, 08/03/1998

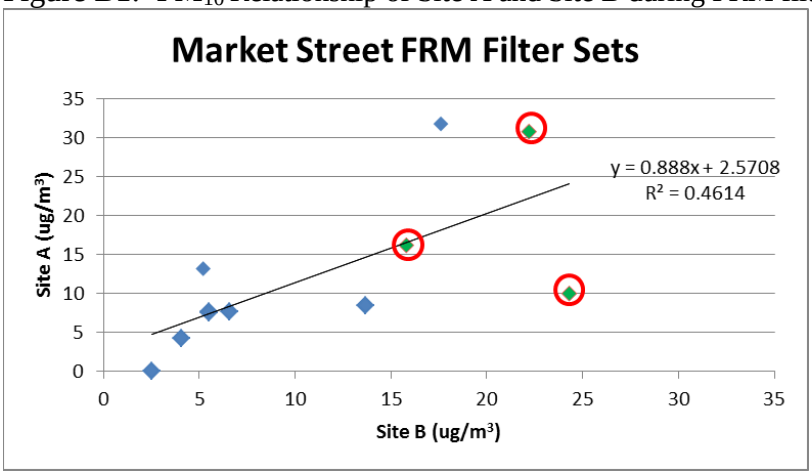
Appendix B – Analyses for Metals

Measuring PM_{10} concentrations upwind and downwind of a potential emission source is sometimes not enough to confirm if that source is indeed contributing to locally high PM_{10} levels. In this case, DES identified three sample filter sets to analyze for metals that would be expected from Terminal operations. A methodology was applied to select filter sets that showed the greatest differential between upwind and downwind PM_{10} concentrations, actively seeking the best candidates for finding off-property migration of particles from the Terminal site.

To identify the filter sample sets to analyze, DES plotted upwind and downwind PM_{10} concentrations (Figure B1). The linear best-fit line is used to approximate a "normal" relationship between the two sites. Sample sets that vary the most from the best-fit line identify the greatest differential between upwind and downwind collected PM_{10} concentrations. Inherent differences in the nature of Sites A and B (variables in sampling equipment, location, and processes) are therefore accounted-for with this process.

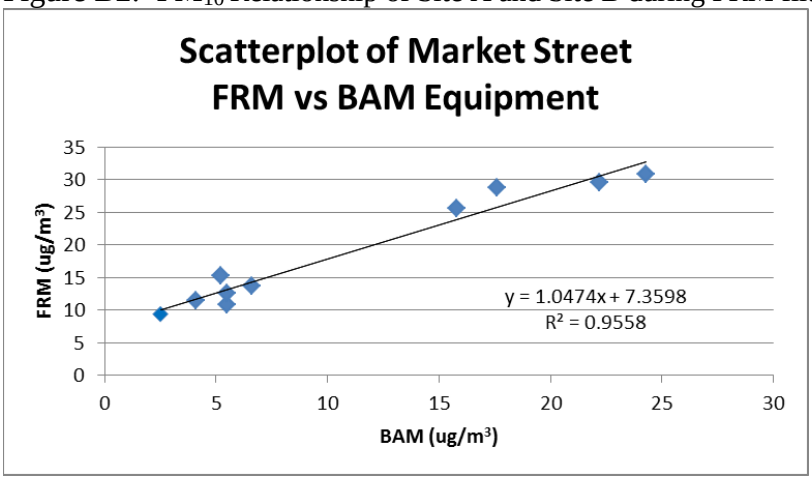
Three filter sets (circled in red in Figure B1) were selected for chemical analysis (one on either side of the best-fit line and one approximately on it). These are filters collected on October 12, 2013, December 11, 2013, and April 20, 2014.

Figure B1: PM_{10} Relationship of Site A and Site B during FRM filter sampling dates



For quality assurance, FRM filter sets from the 11 samples were compared to concurrent data collected by the BAM. Both devices were co-located at Site B on Market Street. The results in Figure B2 show a strong linear relationship, indicating that the devices operated as expected.

Figure B2: PM_{10} Relationship of Site A and Site B during FRM filter sampling dates



The three filter sets that were chosen for further chemical analysis were analyzed for a suite of metals including aluminum (Al), chromium (Cr), copper (Cu), iron (Fe), lead (Pb), and zinc (Zn). The chemical composition of the particulate matter can provide additional insights into the potential sources. Metals selected were based on the likelihood of being present within the scrap operations as well as potential tracer compounds for other potential sources of PM_{10} in the area. Scrap operations can contain a variety of metals, including all of the metals targeted for analysis in this study. However, iron is expected to be the dominant metal from the scrap operations. Much of this iron will likely be in the form of iron oxide, or rust dust.

Sample filter sets were selected as follows:

1. October 12, 2013 – A mixed wind event used as a control sample.
2. December 11, 2013 – West to East wind direction. Maximum one-hour PM_{10} concentration was 59.1 $\mu g/m^3$.
3. April 20, 2014 –East to West wind direction. This filter set was collected at a time when the Terminal was actively loading a docked ship and there was a one-hour PM_{10} concentration spike of 196.5 $\mu g/m^3$.

Many of the analytical results for the October 12, 2013 sampling event were below the detection limit, complicating this analysis. Detection limits are determined by the analytical device's ability to accurately measure analyte concentrations with reproducibility. When samples are determined to be below detection limit, the true concentration lies somewhere between the unit's detection limit and zero and often designated as a non-detect (ND).

Sample blanks were also processed to account for any metals that may be present on the filters prior to sample collection. All sample blanks were reported to have below detection limit concentrations, except for one (April 20, 2014) where a measurable amount of chromium was detected. This value for chromium was deducted from the corresponding chromium sample masses.

The sampling events on December 11, 2013 and April 20, 2014 had greater PM_{10} concentrations and most metals occurred above the detection limit. The laboratory analyses results are presented in Table B1 and calculated metal concentrations in sampled PM_{10} for this sampling event are shown in Table B2. The metals concentration results indicate that for all the metals measured their concentration in the downwind filter was greater than in the upwind filter. In some cases, the amount of increase could not be quantified because the upwind site was below the detection limit.

Table B1: Laboratory Filter Metal Content in Tested Filter Sets (µg)

	Filter Set 1		**Filter Set 2**		**Filter Set 3**				
	October 12, 2013		December 11, 2013		April 20, 2014				
	Site B	Site A	Site B	Site A	Site B	Site A			
	T3589477	T3589478	T3589681	T3589682	T4579703	T4579704	**Analytic Detection Limts**		
Lab	Market St	Star Isl	Market St	Star Isl	Market St	Star Isl		Value used	Process
Mass (ug)	380	389	535	743	586	242	RDL	For ND	Blank
Al	ND	ND	2.20	3.20	4.11	0.5706	1.5	0	ND
Fe	5.60	ND	4.30	16.40	76	9	2.5	0	ND
Zn	ND	ND	ND	2.30	13	2	1.0	0.0	ND
Cr	0.4720	0.4200	0.3330	0.3790	0.4078	0.2144	0.0100	0.0000	0.27
Cu	0.1550	ND	0.0820	0.2170	0.2633	ND	0.0500	0.0000	ND
Pb	ND	ND	0.0590	0.1610	0.5028	0.0428	0.0500	0.0000	ND
					4/20/2014 sample chromium blank =				0.1250

ND indicates sample was below detection limits for the analytical device.

Table B2: PM_{10} Concentration Changes in Metal Content in Tested Filter Sets (µg/m^3)

	Filter Set 1			**Filter Set 2**			**Filter Set 3**		
(µg/m^3)	October 12, 2013			December 11, 2013			April 20, 2014		
	Upwind	Downwind	**Change**	Upwind	Downwind	**Change**	Upwind	Downwind	**Change**
Aluminum (Al)	ND	ND	**ND**	0.092	0.133	**0.042**	0.024	0.171	**0.147**
Chromium (Cr)	0.006	0.008	**0.002**	0.003	0.005	**0.002**	0.004	0.012	**0.008**
Copper (Cu)	ND	0.006	**0.004***	0.003	0.009	**0.006**	0.002	0.011	**0.009**
Iron (Fe)	ND	0.233	**0.129***	0.179	0.682	**0.503**	0.374	3.162	**2.187**
Lead (Pb)	ND	ND	**ND**	0.002	0.007	**0.004**	0.002	0.021	**0.019**
Zinc (Zn)	ND	ND	**ND**	ND	0.096	**0.054***	0.083	0.541	**0.458**

* Change in concentration is based on use of the analytical detection limit in place of non-detection (ND) for upwind filters. This allows an estimate of the minimum possible change in concentration because non-detection can mean values ranging from zero up to the detection limit.

Calculations for upwind to downwind mass and concentration changes are summarized in Table B3 for filter sets 2 and 3. Filter set 1 was not included because it had light and variable wind directions making both monitor sites A and B, upwind and downwind.

Table B3: PM_{10} Metal Content Mass and Concentration Changes (Upwind to Downwind)

	Filter Set 2			**Filter Set 3**		
	12/11/2013			**4/20/2014**		
	Change in Mass (µg)	**Change in Conc (µg/m^3)**	**% of Mass**	**Change in Mass (µg)**	**Change in Conc (µg/m^3)**	**% of Mass**
Total	*208.0*	*8.6*	*100%*	*344.0*	*14.3*	*100%*
Al	1.00	0.042	0.5%	3.54	0.147	1%
Cr	0.05	0.002	0%	0.19	0.008	0.1%
Cu	0.14	0.006	0.1%	0.26	0.011	0.1%
Fe	12.10	0.503	6%	67.00	2.787	20%
Pb	0.10	0.004	0%	0.46	0.019	0.1%
Zn	2.30*	0.095*	1%	11.00	0.458	3.2%

Filter Set 1: Cr, Cu and Fe masses and concentrations all increased very slightly, whereas the Al, Pb and Zn concentrations could not be assessed because of analytical detection limitations.

Filter Set 2: All metal masses and concentrations increased by at least 45% between upwind and downwind sample locations. Zinc was below detection limits for the upwind location and for this assessment was reset to the detection limit value. Since the real Zinc values could be anywhere between zero and the detection limit value, actual increases in zinc for this sample set may be greater than presented in Table B3. Cu and Pb increased by about 160% and the Fe concentration downwind was approximately three times greater than the upwind concentration.

Filter Set 3: All metals for both upwind and downwind were above analytical detection limits for both sample filters. Concentration of all analyzed metals more than doubled. An increase of 788% in Fe produced the greatest amount of PM_{10} concentration increase in the downwind filter. Iron accounted for nearly 20% of the sample weight gain between upwind and downwind filters, and if all that iron was bound in rust particles it would then account for nearly 30% of the weight gain (accounts for weights of other atoms to the iron atom, that comprise a rust molecule).

Analysis of Potential Sources

Converting the concentrations to parts per million by weight (ppmw) allows comparisons to some potential PM_{10} sources in the area (wind-blown soils and road salt)(see Table B4). Parts per million by weight was calculated by dividing the laboratory determined mass for each metal in micrograms (µg) by the total PM_{10} sample mass (µg) and multiplying by one million.

For this assessment, only Filter Sets 2 and 3 were chosen because of their clear upwind to downwind wind conditions. Iron in both filter sets was significantly higher than in either soil or road salt and similar results were found with Cr, Cu, Pb, and Zn. Aluminum, however, was lower than average soil content and higher than that in road salt.

Table B4: PM_{10} Metal Concentration Changes Compared to Soil and Salt (ppmw)

(ppm)	**Filter Set 2**	**Filter Set 3**	**Average Soil**	**Road Salt**
Aluminum (Al)	4,808	10,289	72,000	150
Chromium (Cr)	221	562	54	ND
Copper (Cu)	649	620	25	ND
Iron (Fe)	58,173	194,767	26,100	160
Lead (Pb)	490	1,337	19	ND
Zinc (Zn)	6,250	31,977	60	ND

References for source composition information are located in Appendix C.

Another analytical methodology using ratios of metal content in each collected filter sample was applied to the sample set metals data. Tracking how concentrations of metals in each sample set change with regard to each other can also produce useful source identification information. Many potential sources consist of its elements in a certain ratio, much like individual ingredients in a cooking recipe (i.e., there can be some minor variation in the amounts of the ingredients and/or the inclusion or exclusion of other ingredients, but the essence of the product usually falls into a normal range that identifies it). In the case of this study, potential sources such as soils, salts, and oils are the products of their ingredients (including metals). DES reviewed publications of analyses for relative ratios of metals in each source type of interest and determined the high, low and average relative content of certain metals to key metals (iron and aluminum). If a sample were dominated by wind-blown soil, one would expect the ratio of aluminum to iron (Al/Fe) of that sample to approximate that of soils tested in the literature.

Table B5 compares the three filter sets analyzed for metals to average literature ratios for aluminum to iron. Each filter set was found to be too iron-rich to be primarily composed of soil or road salt. Further, the sample sets were also too iron-rich to be primarily composed of car, truck, or ship exhaust, which is typically below detection limits for iron.

Table B5: PM_{10} Metal Concentration Change Ratios (upwind to downwind) Compared to Soil and Salt

	Filter Set 1	Filter Set 2	Filter Set 3	Average Soil	Road Salt
Al/Fe	ND	0.08	0.05	2.77	0.94
Cr/Fe	0.017	0.004	0.003	0.001	~0
Cu/Fe	0.034	0.01	0.003	0.002	~0
Pb/Fe	ND	0.008	0.007	0.0007	~0
Zn/Fe	ND	ND	0.16	0.002	~0

Notes:

1. *Source chemical ratios calculated from data provided by USGS, EPA, and PA Department of Environmental Protection – See Appendix C.*
2. *Ranges in data are considered in the analyses, but only the average value is presented in the table.*
3. *Emission ratio references for gasoline, diesel and fuel oil are not included in Table B5 because the iron content in related emission sources is nearly zero.*

Analytical Method

Preservation of Samples

Sample collection filters made of Teflon (PTFE) were stored in sealed clean Petri dishes and further sealed in zippered storage bags before and after sample collection. After exposure, the sealed filters were promptly placed into refrigerated storage at 1 - 4ºC until the laboratory was ready for analysis.

Laboratory Process Description

For each sample run, sets of filters (upwind and downwind) were exposed to sample collection in order to analyze samples for differing content. Analytical techniques have inherent abilities and limitations regarding what chemical species can be detected and to what degree. For this study, selected metals were analyzed by the NHDES laboratory through inductively coupled plasma mass spectrometry (ICPMS). Like other analytical devices, ICPMS has a minimum sample concentration which can be reliably measured and is reported as the detection limit. These detection limits are reported in Table B1 above.

Each filter was analyzed for metal species including aluminum, chromium, copper, iron, lead, and zinc**.** These metals were selected due to their applicability in identifying emission source type.

Filter preparation for ICPMS included digestion of metals with 22.75 mL of nitric acid and 83.75 mL of hydrochloric acid. The digestive acid was then brought to a final volume of 500 mL with ultrapur deionized (DI) water. All digestion tubes and caps were rinsed with ultrapur DI water prior to use. Before sample digestion, the outer support rings of the PTFE air filters were removed using a scalpel and glass ceramic cutting plate. A separate location on the cutting plate was used for each filter to prevent contamination between filters. The filters were placed in digestion tubes. 25 mL of digestion acid was added to each tube and then the tubes were heated

for one hour with a heating block at 85ºC. After one hour the samples were brought to 50 mL with ultrapur DI water. The samples were again heated until the volume was 25 mL. The samples were cooled then brought to 50 mL final volumes with ultrapur DI water. A 0.45 µm filter disc and syringe for each digested sample was pre-rinsed with ultrapur DI water. 2.0 mL of each digestate was pushed through the syringe filter to waste prior to filtering approximately 10 mL into a test tube pre-rinsed with ultrapur DI water. Each sample was then diluted 2 fold with ultrapur DI water into a pre-rinsed test tube. The pipette tips were also pre-rinsed with DI water.

The analyses were performed by ICPMS using collision cell in Helium mode.

For quality control purposes as well as accounting for sample process background levels of materials on the filters, several blanks were analyzed. These included filter blanks (clean and unexposed PTFE filters), process blanks (PTFE filters that follow the entire sample filter process except were never exposed for sampling), and three laboratory blanks without filters including a Laboratory Reagent Blank (LRB), a Laboratory Fortified Blank (LFB), and an Independent Calibration Verification (ICV).

The sample blanks were then processed and analyzed for metals as described above with the following additional steps:

- (metals) The LFB samples (with and without filters) were spiked at 10 ppb after adding digestion acid.
- (metals) The ICV samples were spiked at 25 ppb after adding digestion acid.

When sample blanks showed content above the analytical detection limit for a metal, study samples were corrected by subtracting the blank sample mass from the study sample.

Appendix C - Source Chemical Content References:

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