CAPHE PHAP-RM

4. AIR QUALITY, EXPOSURE & MONITORING

2016

This work is made possible by National Institute of Health and Environmental Sciences, RO1ES022616, and the Fred A. and Barbara M. Erb Family Foundation. Additional support was provided by the Michigan Center on Lifestage Environmental Exposures and Disease (M-LEEaD), #P30ES017885.

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4 AIR QUALITY EXPOSURE AND MONITORING

This chapter provides an introduction to air quality monitoring and exposure. The following sections describe, for each major pollutants, NAAQS compliance, the monitoring network for that pollutant, and concentration trends based on monitoring data in the Detroit area, and apportionments (for $PM_{2.5}$). Monitoring and exposures of $PM_{2.5}$, O_3 and SO_2 are emphasized, given the importance of these pollutants in the Detroit area.

4.1 Exposures to air pollution and contributing sources

Direct and indirect air pollution exposure. Air pollution exposure can occur directly by breathing pollutants in outdoor air, indoor air, and vehicle cabins. In addition, so-called "indirect" air pollution exposure can occur by ingesting food, water and other materials (e.g., dust) that has been contaminated with air pollutants, and by drinking mother's milk if the mother is exposed to air pollutants. Indirect exposure is important for certain pollutants, e.g., persistent pollutants like lead and other metals, flame retardant chemicals, PCBs, mercury, and DDT.

This resource manual focuses on exposure via the "direct" inhalation exposure pathway. Inhalation exposures depend on the concentration of air pollutants present in each location where spent by an individual, the breathing rate, and the duration in that location. The most important locations, based on the amount of time spent, are generally homes, schools, workplaces, outdoors (often near homes), and in vehicle cabins (car and bus).

Indoor exposure. Exposure from pollutants emitted by industry, vehicles, construction equipment, and other outdoor sources can elevate concentrations in outdoor air. In addition, because pollutants enter buildings and vehicle cabins, indoor and cabin air quality can be affected. For pollutants like O_3 and some PM, indoor concentrations can be lower than outdoor concentrations because these pollutants are unstable or filtered out; for other pollutants, like SO_2, CO, and NO_x, indoor and outdoor levels may be similar since these pollutants are relatively stable gases that are not removed by filters.

Indoor environments and vehicle cabins can contain many pollutant sources, and emissions from indoor sources can seriously degrade air quality and cause levels of some pollutants to exceed outdoor levels. This *Resource Manual* focuses on outdoor sources, but it is important to remove, restrict or ventilate to control indoor pollution sources. Important indoor sources can include cigarette smoke, dust from lead paint, radon gas emanating from subsurface soils, mold on damp or wet surfaces, formaldehyde gas from some carpeting and wood products, scented items (air fresheners, deodorizers, incense, mothballs, etc.,) pesticides, and solvents and fumes (from paint, hair spray, varnish, aerosol sprays, gasoline), among others. Improperly constructed or operating vents, chimneys, heaters, fireplaces, and furnaces can cause very serious air pollutant exposure and possibly death by carbon monoxide poisoning.

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4.2 Air quality monitoring

Monitoring data provides key information regarding current air quality and compliance with air quality standards,[1] including both the primary health protective NAAQS and the secondary welfare protective NAAQS.[2]

In addition, monitoring data can show historical trends indicating whether air quality is changing, as well as information identifying the sources that cause or contribute to air pollution. Monitoring data also are used to quantify health risks, conduct epidemiological studies, and determine whether emission reductions or other actions are needed. The importance of ambient air monitoring data should not be understated. In Michigan, the state's ambient air quality monitoring network and the collected data are described by the MDEQ each year, and this *Resource Manual* draws heavily from the annual Air Monitoring Network Review[3] and the annual Air Quality Monitoring Reports[4] that are published annually.

Monitors are operated and sited to provide different types of information. This includes sites that are selected to: (1) represent population exposure ("population" sites); (2) quantify impacts of major industrial sources ("hotspot" or "source-oriented" sites); (3) quantify impacts of vehicle traffic ("near-road" sites); (4) provide upwind or background concentrations for pollutants that are transported into the area ("background" or "transport-oriented" sites); (5) provide trend or data comparable to national-level assessments; and (6) inform special studies typically lasting from months to years ("research" sites). Many sites have been operated for many years, but the network evolves over time to address EPA rules and meet other demands. The equipment at MDEQ and other monitoring sites varies from location to location, e.g., sites can monitor from one to potentially dozens of pollutants. Most sites have some meteorological instrument, e.g., wind direction and wind speed sensors. The annual costs to equip and maintain a MDEQ or industry monitoring site can range from roughly $75,000 to $250,000, depending on what is measured, the frequency of measurements, and other factors. US EPA provides support for some monitoring operations.

MDEQ monitoring. Many aspects of air quality monitoring, including the number of sites, equipment and procedures, operated by Michigan and other states must meet US EPA guidelines. The monitoring approaches used to determine compliance with air quality standards must be designated meet US EPA rules that designate instrumentation as a Federal Reference Method (FRM) or equivalent. EPA guidelines and rules also specify the minimum number of monitoring sites in an urban region like Detroit, which depend multiple factors including the population size, emissions of certain pollutants (e.g., SO_2), size of roads (e.g., for NO_x), and the recent record of pollutant levels (e.g., $PM_{2.5}$ and O_3). State and federal agencies do not routinely monitor indoor air pollution.

Industry monitoring. Some regions also have high quality fixed site monitoring networks operated by industry and sometimes by industry associations. These vary from single monitors to complex networks. These networks can be either voluntary, or required as part of an air quality permit or court decision. In Michigan, some large

[1] NAAQS Status is shown by county by US EAA at https://www3.epa.gov/airquality/greenbk/anayo_mi.html.

[2] Primary standards provide public health protection, including protecting the health of "sensitive" populations such as asthmatics, children, and the elderly. Secondary standards provide public welfare protection, including protection against decreased visibility and damage to animals, crops, vegetation, and buildings.

[3] Michigan Department of Environmental Quality Air Quality Division. 2015. 2016 Air Monitoring Network Review. Available: http://www.michigan.gov/documents/deq/deq-aqd-toxics-2016_Air_Mon_Network_Review_489490_7.pdf [accessed 2 May 2016]

[4] Michigan Department of Environmental Quality Air Quality Division. 2015. 2014 Air Quality Monitoring Report. Available: http://www.michigan.gov/documents/deq/deq-aqd-amu-2014_Annual_Air_Quality_Report_492732_7.pdf [accessed 2 May 2016]

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landfills and other facilities operate monitoring sites to confirm that dust and other emissions are not excessive. In Detroit, Marathon initiated a monitoring network consisting of four sites measuring SO_2 around the facility. Given the intensity of industry and the magnitude of emissions in southwest Detroit, the lack of monitoring by industry is surprising. For some pollutants, additional sites and measurements of additional pollutants can provide significant information

Low cost monitoring. In recent years, there is considerable interest in using low cost monitors, including those operated by community organizations. This information can be useful, but the quality of the data provided by low cost monitoring approaches can be variable, and these measurements cannot be used to determine compliance or violation of a standard in any "official" capacity.

Additional information regarding monitoring network is described in the sections for each pollutant that follow.

4.3 Ozone

4.3.1 NAAQS Status

The Detroit area (Wayne County) has previously been in non-attainment for O_3: from 1992-1994 under the 1979 1-hr O_3 NAAQS, and from 2004-2008 for the 1997 8-hr O_3 NAAQS. From 2009 to the 2015, all monitors in Southeast Michigan met the O_3 standard, and currently, the area is considered in attainment. However, on October 1, 2015, US EPA established a new health-protective ozone NAAQS of 0.070 ppm (lowering it from 0.075 ppm), measured as the annual 4th highest 8-hr daily maximum averaged over 3 years. O_3 levels in the Detroit area are fluctuating around this level.

MDEQ is currently collecting O_3 data to determine whether the attainment status for Wayne County needs to be changed from attainment to non-attainment, and a recommendation to USEPA is expected in October, 2016. If the area is designated as non-attainment by US EPA, an enforceable air pollution abatement plan must be developed by the MDEQ to bring the area back into attainment.[5] These plans typically involve reductions in emissions of NO_x and VOCs using additional source controls, depending on whether O_3 is NO_x or VOC limited, as and anticipating further reductions in vehicle fleet emissions due to turnover of old vehicles. They may also involve transportation control measures, vehicle inspection programs, restrictions on summer activities emitting VOCs (and possibly NO_x) such as paving bans, and consumer sales of VOC emitting products, such as barbeque lighting fluid.

4.3.2 Monitoring

Ozone (O_3) is monitored at two sites in Detroit, and at six sites in SE Michigan, shown in Figure 4-1. This number of sites is considered adequate because ozone concentrations tend to be fairly similar across an urban region. In southeast Michigan, the New Haven site, generally downwind of Detroit, has had the highest O_3 concentrations downwind from Detroit, however, in 2009, the highest levels occurred at the Detroit-E 7 Mile site. More recent data (2012-2014) show that Detroit-E 7 Mile, New Haven and Port Huron sites have similar three-year averages. MDEQ suggests that the location of the maximum O_3 concentration has moved about 19 miles closer to the urban center city area, possibly due to changes in the amount, type and location of ozone

[5] MDEQ and DTE Electric Company. 2016. Trenton Channel Power Plant, Proposed permit 227-15 and 125-11C, March 9, 2016.

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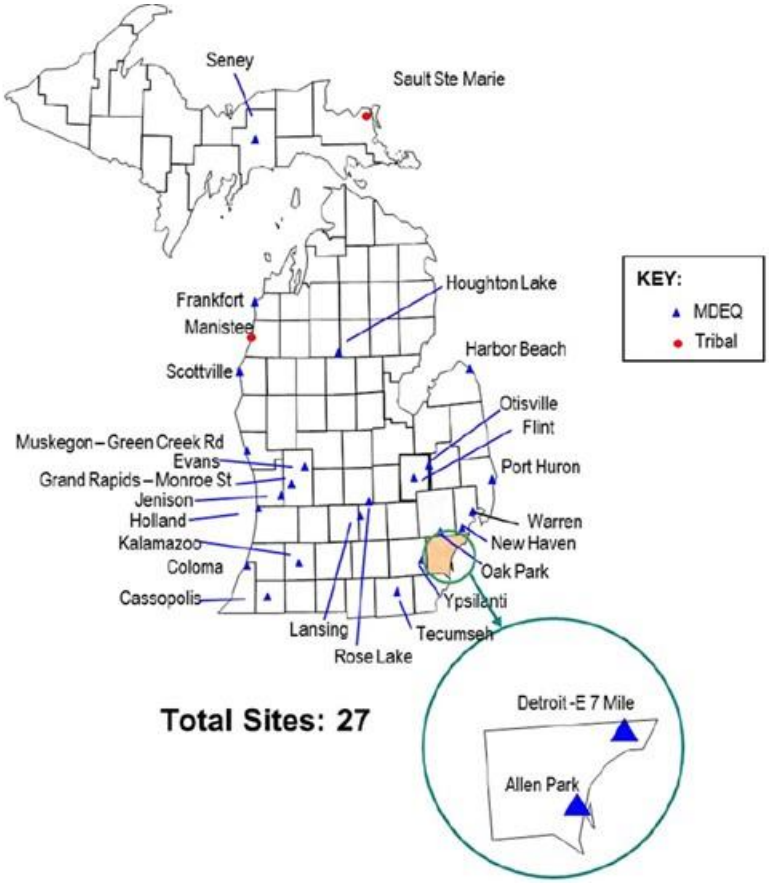
precursor emissions. EPA has indicated that Warren may be becoming the site with the highest O_3 concentration.

Figure 4-1. Location of ozone monitoring sites in Michigan. From MDEQ. http://www.michigan.gov/documents/deq/deq-aqd-toxics-2016_Air_Mon_Network_Review_489490_7.pdf



4.3.3 Trends

Long-term O_3 trends are shown in Figure 4-2 for the Allen Park site, which now has the highest O_3 levels in Detroit. While some decrease in O_3 levels has been seen in Detroit since 2002, current levels are fluctuating around the new NAAQS. Other areas in Michigan have shown greater decreases.

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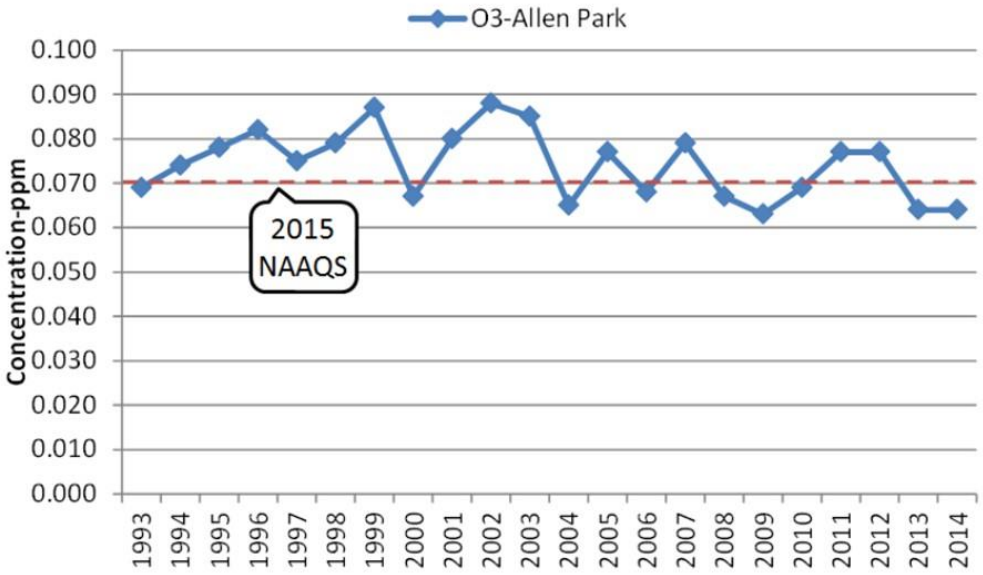
Figure 4-2. Trends in the 4th highest 8-hr concentration monitored at Allen Park. From MDEQ, 2016.[6]



[6] From p. 5, MDEQ, DTE Electric Company, Trenton Channel Power Plant, Proposed permit 227-15 and 125-11C, March 9, 2016

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4.4 Particulate Matter

4.4.1 NAAQS status

Detroit (Wayne County) had previously been in non-attainment with the $PM_{2.5}$ NAAQS: from 2005 to 2012 for the 1997 $PM_{2.5}$ NAAQS; and from 2009 to 2012 for the 2006 NAAQS. Earlier, Wayne County had been in non-compliance from 1992 to 1995 with the PM10 NAAQS. The January 15, 2013 revision to the PM NAAQS lowered the $PM_{2.5}$ annual average concentration from 15.0 µg/m^3 to 12.0 µg/m^3, the 24-hr NAAQS remained at 35 µg/m^3 and is measured as a 98th percentile concentration averaged over 3 years. All sites in Michigan currently meet the $PM_{2.5}$ NAAQS.

4.4.2 Monitoring

Airborne particulate matter (PM) is measured in many ways, the most common of which are:

- Particles less than 2.5 um in diameter, called $PM_{2.5}$. The current health-based NAAQS uses $PM_{2.5}$,which is the emphasis of this report
- Particles less than 10 um in diameter, called PM_{10}. Prior to 1997, the NAAQS used PM_{10}.
- Particles measured as "total suspended particulate (TSP). Prior to 1986, the NAAQS used TSP. These measurements are especially useful for understanding dust fall, including dust fall containing toxic metals and other pollutants.

As for the other pollutants, compliance with the $PM_{2.5}$ NAAQS is based on monitoring data, and US EPA specifies the number and types of monitoring sites required. Locations of $PM_{2.5}$ monitoring sites are shown in Figure 4-3. Currently, monitors with the highest annual average concentration are the Detroit–SWHS (10.7 µg/m^3) and Dearborn (11.6 µg/m^3) sites ("design" values shown); the Dearborn site also has the highest design value (26 µg/m^3) for the 24-hr average value.

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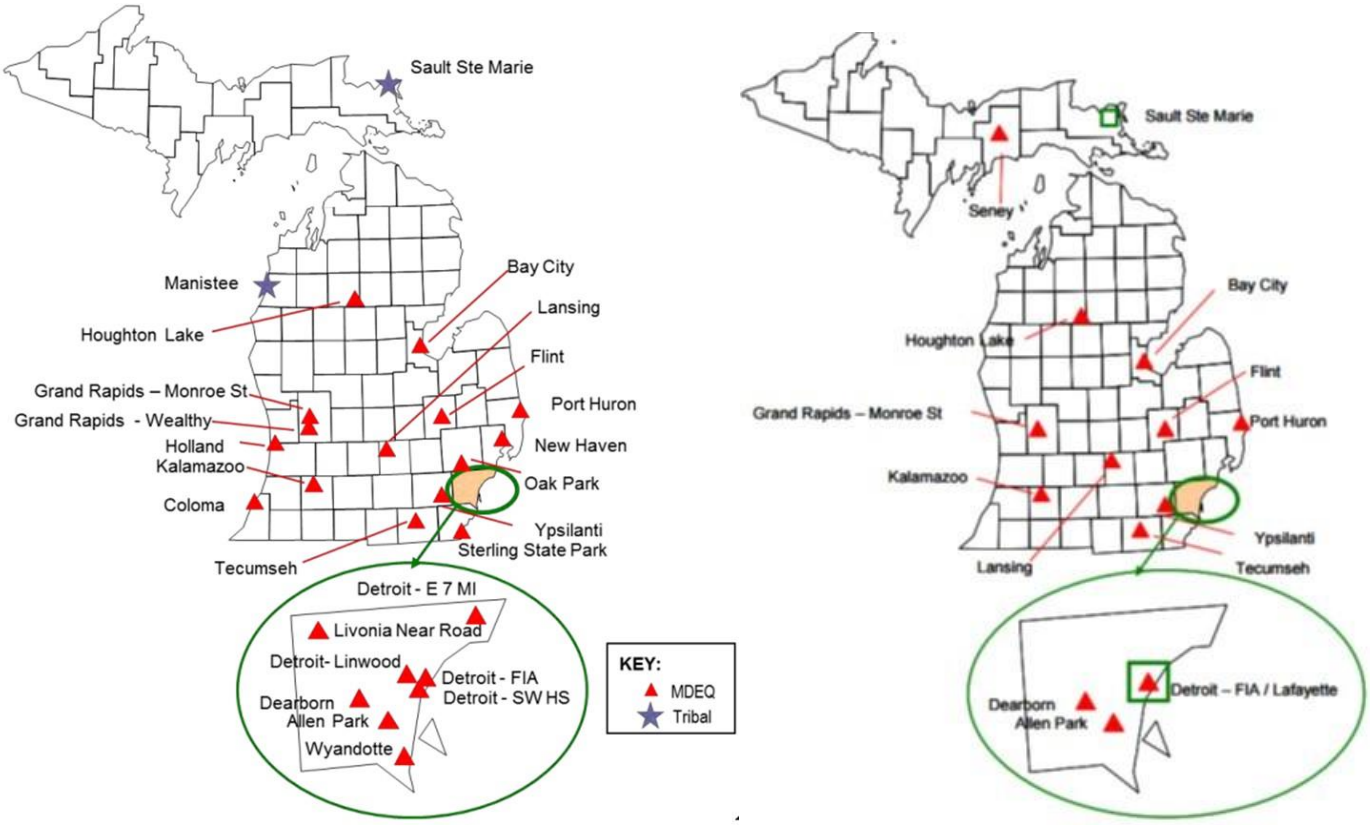
Figure 4-3. Location of $PM_{2.5}$ monitoring sites in Michigan. Left panel shows sites collecting 24-hr samples (FRM monitors). Right panel shows sites collecting continuous (1-hr) samples.[7]



4.4.3 Source apportionments

$PM_{2.5}$ arises from many sources. Secondary PM, largely due to regional or "background" component that drifts from areas distant to Detroit (e.g., Ohio River Valley), is substantial and constitutes roughly 50 to 60% of $PM_{2.5}$ overall (including secondary sulfur and nitrogen compounds). In addition, many local sources emit $PM_{2.5}$, including the point, mobile and area sources discussed in Section 5. These "local" sources can be affected by mitigation strategies such as source control and buffers; these strategies will not greatly alter background levels.

The fraction of PM attributable to different sources can be estimated using source inventories, monitoring data, dispersion modeling, and receptor modeling. A recent analysis[8] of long term $PM_{2.5}$ records at Allen Park using receptor modeling (positive matrix factorization of monitored PM and its composition at this site) provided the following overall apportionment for Detroit (a parallel analysis at a Chicago site was similar): sulfate formed 32 - 33% of $PM_{2.5}$; vehicles contributed 21 - 22%; nitrate constituted 21%; and biomass was 7 - 9%. These four sources represented over 80% of $PM_{2.5}$ concentrations. Crustal (e.g., wind-blown dust) (4 - 8% of $PM_{2.5}$), several

[7] Michigan Department of Environmental Quality Air Quality Division. 2015. 2016 Air Monitoring Network Review. Available: http://www.michigan.gov/documents/deq/deq-aqd-toxics-2016_Air_Mon_Network_Review_489490_7.pdf [accessed 2 May 2016]

[8] Milando C, Huang L, Batterman S. 2016. Trends in PM2.5 emissions, concentrations and apportionments in Detroit and Chicago. Atmospheric Environment: 129, 197-209.

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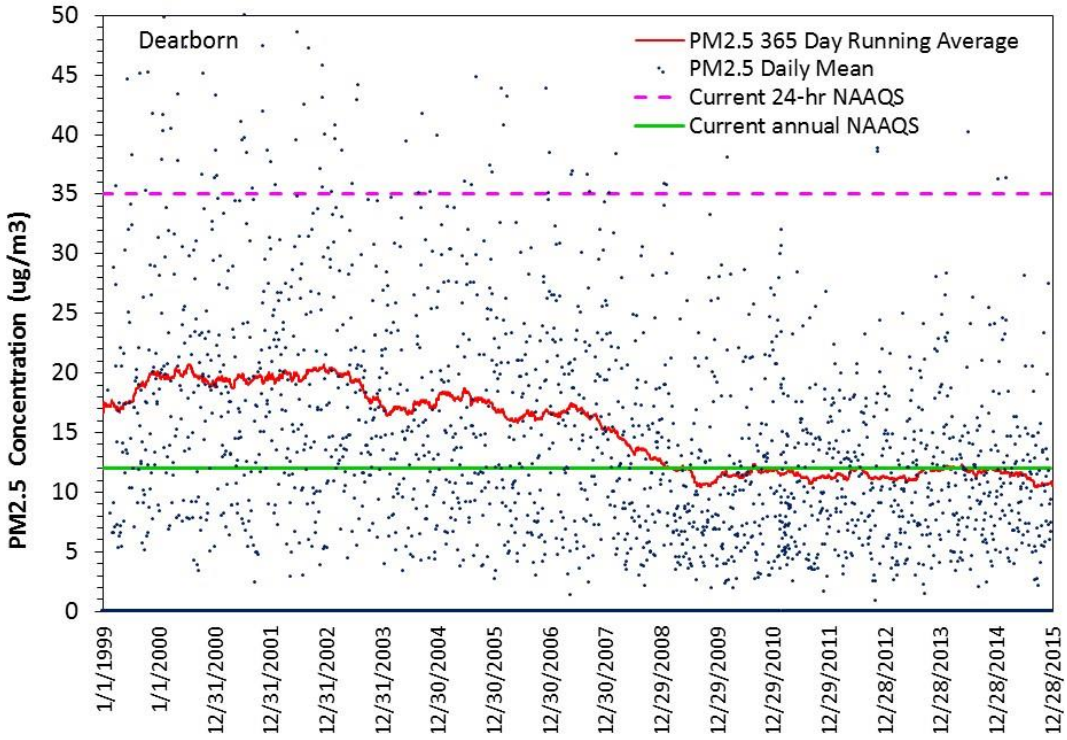
metals (4 - 11%) and Cl/NaCl (2 - 5%) represented the remainder of $PM_{2.5}$. These results were supported by the emissions inventory and the similarity of the secondary contributions (e.g., sulfate and nitrate).

The next section of this Resource Manual uses monitoring data in an approach to separate local and background components of $PM_{2.5}$ in Detroit.

4.4.4 Trends

$PM_{2.5}$ concentrations at many Michigan monitoring sites have shown a general downward trend since 1995. For example, $PM_{2.5}$ levels at Allen Park have decreased by about 5% per year from 2001 to 2015; as mentioned, this was largely driven by decreases in ammonia, nitrate, sulfate and organic carbon.[9] However, results differ from site-to-site, and trends are less apparent in more recent years and at industrial sites like Dearborn. Figure 4-7 displays the 17-year record of $PM_{2.5}$ measurements at the Dearborn site, which used every 3rd day measurements for much of the record, and which currently records some of the highest $PM_{2.5}$ Levels in Detroit. The 365-day running average shows a large decrease from 2006 to 2009; the frequency of very high 1 hour concentrations also fall.

Figure 4-4. 17 year record of the 24-hr daily $PM_{2.5}$ concentration at Southwestern High School. Plot does not show several measurements above 50 µg/m^3 (highest was 71.5 µg/m^3). Running annual average, current 24-hr and current annual average NAAQS are also shown.



[9] Milando C, Huang L, Batterman S. 2016. Trends in PM2.5 emissions, concentrations and apportionments in Detroit and Chicago. Atmospheric Environment: 129, 197-209.

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To examine recent trends more comprehensively, we used 2009 to 2015 $PM_{2.5}$ data from 12 area monitoring sites around Detroit (each using high quality and comparable Federal Reference Methods), and attempted to separate "background" and "local" sources of $PM_{2.5}$. This analysis shows that $PM_{2.5}$ levels have not changed significantly in the Detroit area over this period, with annual average concentrations averaging 9.9 ±5.8 $\mu g/m^3$ across the 12 sites (the NAAQS is 12 $\mu g/m^3$), and peak 24-hr daily concentrations have remained near or above the NAAQS (35 $\mu g/m^3$). As noted earlier, the area attains the $PM_{2.5}$ NAAQS. Figure 4-5 summaries these data and shows three panels that separate total, background and local contributions.

The top panel of Figure 4-5 shows recent trends in the Detroit area; the green line shows that the long-term average concentration has remained stable. The red dots show the daily 24-hr maximum across the 12 sites. During this period, there were 909 days of valid observations (defined with at least 6 monitors providing values), of which 20 days exceeded 30 $\mu g/m^3$, 12 exceeded 35 $\mu g/m^3$ (the current NAAQS), and 4 exceeded 40 $\mu g/m^3$.

The center panel of Figure 4-5 shows estimates of "background" concentrations, defined as the lowest or second lowest observation in the network when at least 6 sites reported valid data. While there are significant fluctuations, the long term average (green line) is relatively flat, indicating little change over the 5-year period. The lowest and 2nd lowest averaged 8.0 ± 5.2 and 8.8 ± 5.5 $\mu g/m^3$, respectively.

The lower panel of Figure 4-5 shows estimates of the "local" increment, defined as the maximum 24-hr daily concentration minus the 2nd lowest 24-hr daily concentrations, again when at least 6 sites reported valid data. The 2nd lowest is used, rather than the lowest, to be more robust in the case of monitoring anomalies. This plot, using a log scale, also shows no consistent trend, with the average local increment being 3.9 ± 2.8 $\mu g/m^3$. These results suggest that at the most impacted sites (e.g., Dearborn), local sources contribute about 30% of the $PM_{2.5}$. This result is somewhat lower than suggested by receptor modeling, discussed above, probably because the lowest or 2nd lowest observation includes contributions from local sources.

Overall, this analysis shows that both long term (e.g., annual) and short-term peak (e.g., 24-hr) average levels of $PM_{2.5}$ in Detroit have changed little over the past 6 years.

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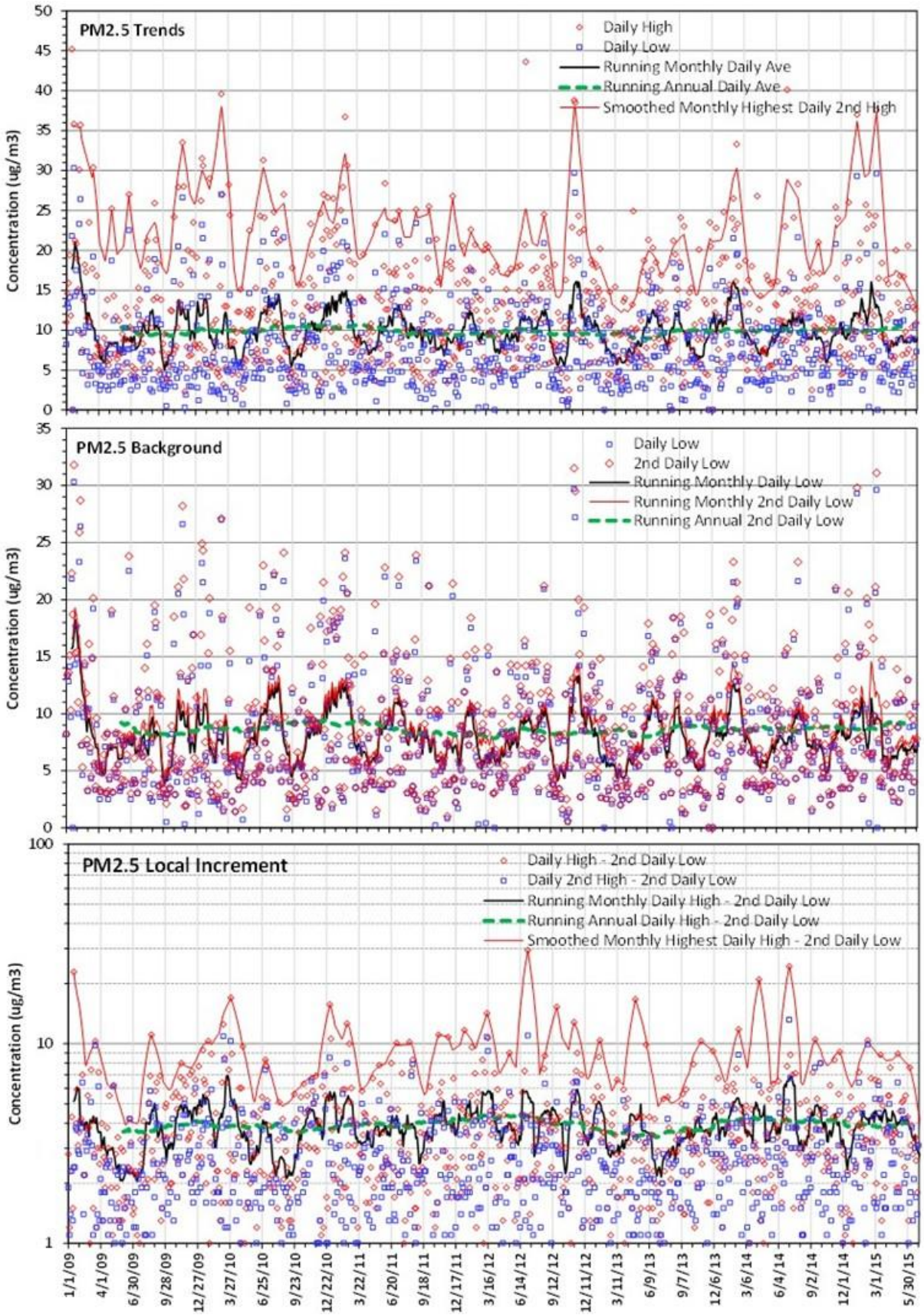
Figure 4-5. Trends of $PM_{2.5}$ at Detroit area monitoring sites. 2009 to 2012 data at FRM sites.



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4.5 SO_2

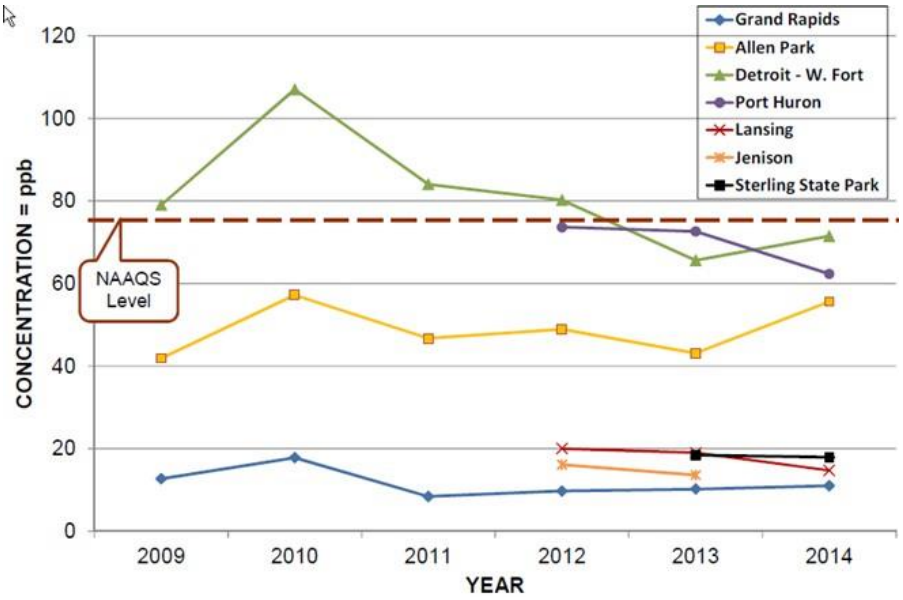
4.5.1 NAAQS Status

SO_2 levels have fallen from very high levels seen in the 1980s, as discussed later. Still, prior to 2010, Wayne County had always been in attainment with the SO_2 NAAQS prevailing at the time.

On June 2, 2010, the EPA revised the health protective SO_2 NAAQS by changing from 24-hour and annual average concentration standards to a 1-hour, 99th percentile measurement averaged over 3 years, set at 75 ppb. Based on air monitoring data, the SO_2 NAAQS was not met in Wayne County. Because MDEQ has not completed an air pollution abatement plan, a portion of Wayne County was designated as non-attainment for SO_2 from 2013 to the present. This region was defined by MDEQ as a corridor that runs from the southern border with Monroe County, along I-75, M-39, M-94 and US-12 and extending east to the Detroit River. Several major SO_2 sources are located in this corridor.[10] A proposed State Implementation Plan (SIP) for SO_2 was released by MDEQ in August, 2015.[11] SIPs are designed to bring areas into compliance with the NAAQS.

Air quality monitoring data are used to determine NAAQS status for SO_2 (and other pollutants). Trends of concentration statistics that follow the NAAQS definition for the past 5 years are shown in Figure 4-6.

Figure 4-6. SO_2 levels in Michigan from 2009-2014 showing 1-hour 99th percentile concentration commensurate with the NAAQS. From MDEQ.[12]



[10] Michigan Department of Environmental Quality. 2016. Public Participation Documents for DTE Electric Company Trenton Channel Power Plant, March 9, 2016. Available: http://www.deq.state.mi.us/aps/downloads/permits/PubNotice/227-15/227-15and125-11CFactSheet.pdf [accessed 2 May 2016]

[11] Michigan Department of Environmental Quality. 2015 Proposed Sulfur Dioxide One-Hour National Ambient Air Quality Standard State Implementation Plan, August 20, 2015.Available: http://www.deq.state.mi.us/aps/downloads/SIP/SO2SIP.pdf [accessed 2 May 2016]

[12] Michigan Department of Environmental Quality Air Quality Division. 2015. 2016 Air Monitoring Network Review. Available: http://www.michigan.gov/documents/deq/deq-aqd-toxics-2016_Air_Mon_Network_Review_489490_7.pdf [accessed 2 May 2016]

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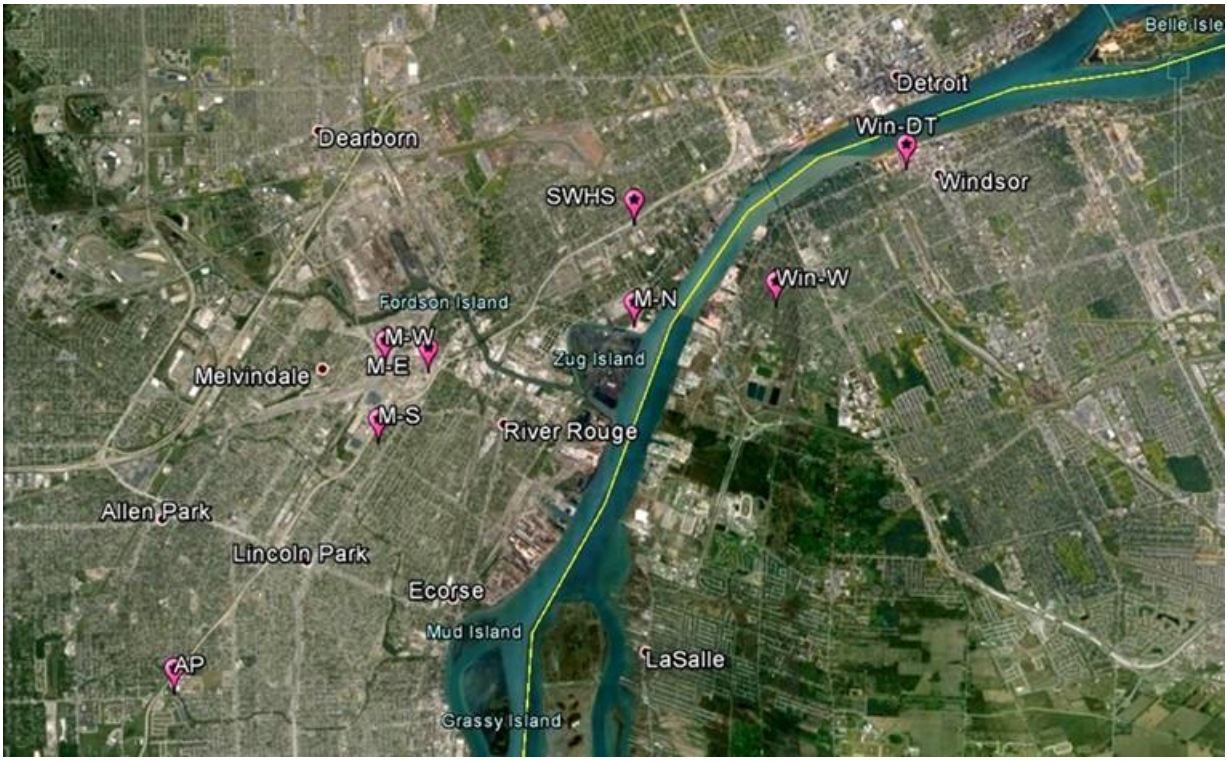
As discussed later, the spatial coverage of SO_2 monitoring in Detroit is sparse and likely misses a number of SO_2 hotspots. (Our analysis below adds the Marathon and Canadian sites to what has been discussed by MDEQ.) In particular, our dispersion modeling suggests that a larger region may not be in attainment, however, there are few monitoring sites that can confirm dispersion modeling results.

4.5.2 Monitoring sites

SO_2 has been monitored at Detroit area locations using EPA-approved methods since 1971, initially by the Wayne County Air Quality Management Division, and then by the MDEQ after 2002. Since 2009, SO_2 has been continuously monitored at 3 locations in Michigan (Southwestern High School on Fort Street in Detroit, Allen Park in Detroit, and in Grand Rapids). Other sites in the region include Port Huron, Sterling State Park (in Monroe County, and West Olive near Lake Michigan.

For portions of the 2009-2015 period evaluated here, SO_2 has been monitored at 9 additional locations in the Detroit area. These include 4 locations surrounding the Marathon Refinery (designated as Marathon North, West, East and South) that started on Jan. 1, 2012. In addition, SO_2 is monitored using EPA-type instrumentation at two sites in Windsor, Canada, designated as Windsor Downtown (DT) and Windsor West (W). SO_2 is monitored continuously and reported as a 1-hr average on the EPA and Canadian sites, commensurate with the current form of the National Ambient Air Quality Standard (NAAQS), which is currently 75 ppb calculated as the 3-year average of the annual 99th percentile 1-hr concentration. The locations of the 8 Detroit area monitoring sites are shown in Figure 4-7. The Windsor downtown site is essentially just across the Detroit River from downtown Detroit.

Figure 4-7. Locations of current SO_2 monitoring sites in the Detroit area. SWHS is Southwestern High School, AP is Allen Park, M is Marathon (North, East, West, South), Win-DT is Windsor Downtown, Win-W is Windsor West. Uses Google maps.



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The number of sites in the Detroit area does not necessarily reflect the complexity of spatial pattern of SO_2 concentrations. Based on modeling, the maximum 1-hr SO_2 concentrations occur near but not exactly at the location of the Southwestern High School monitor. There are also localized "hotspots" that may occur closer to large SO_2 emission sources with poor dispersion (i.e., low stacks), such as Carmeuse Lime, US Steel and AK Steel. (Figure 4-11, discussed later, provides a map showing predicted locations of maximum impact.)

4.5.3 Trends

Data summary

Hourly SO_2 data from 1980 through the present were obtained from the EPA and Canadian web sites and collated. Missing data was ignored. Because the NAAQS focuses on 1-hr peak concentrations, our analysis also emphasizes this statistic. The daily 1-hr high was calculated for each day if any SO_2 data were present on that day. (Results did not change in any noticeable way if 75% or more of the hourly observations were required on each day to calculate the daily 1-hr high.)

During the 2009-2015 period, the single highest 1-hr concentrations at the eight sites reached 500 ppb at the Marathon N site and 160 ppb at the SWHS site. During this period, the maximum 1-hr concentration exceeded or reached the NAAQS concentration of 75 ppb at all sites, though this does not constitute violation of the NAAQS since the NAAQS is determined using a 3-year running average of the 99th percentile daily 1-hr concentration. Higher 1-hr concentrations have been measured prior to 2009, e.g., concentrations at the SWHS site reached 172 ppb in 1999, 224 ppb in 2001, and 832 ppb in 2002; concentrations at the Allen Park site reached 99 ppb in 2008.

A summary of available data at the 8 Detroit area monitors is shown in Table 4-1.

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Table 4-1. Summary of highest 1-hr daily SO_2 concentrations at the Detroit area monitoring sites (ppb). SWHS is Southwestern High School, AP=Allen Park, M is Marathon (North, East, West, South), Win-DT is Windsor downtown, Win-W is Windsor west. Covers 2009 to 2015 (2015 is incomplete; 2015 data for Canada is not available.)

Statistic	SWHS	AP	M-N	M-W	M-E	M-S	Wind-DT	Wind-W
No. Obs.	2326	2335	1328	1328	1332	1324	2185	2149
Mean	13.1	6.8	7.2	6.5	7.5	7.7	12.2	12.2
SD	18.7	10.0	16.1	8.9	9.2	10.9	11.3	11.3
Minimum	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-0.2
10th Percentile	0.7	0.4	1.0	1.0	1.0	0.0	1.7	1.0
25th Percentile	1.7	0.9	2.0	1.0	2.0	1.0	3.8	3.0
50th Percentile	4.5	2.5	4.0	3.0	4.0	3.0	9.0	9.0
75th Percentile	16.5	8.4	8.0	8.0	9.0	10.0	18.0	18.0
90th Percentile	40.0	19.2	16.0	17.0	18.0	21.0	28.0	27.7
95th Percentile	54.4	27.2	24.0	24.0	24.0	27.0	34.0	34.5
Maximum	160.0	87.8	500.0	88.0	108.0	107.0	82.0	75.0

Temporal trends

First, we show the 35 year record of the highest 1-hr daily concentrations measured at Southwestern High School in Figure 4-7. This site has the longest complete record in Detroit, and some of the highest SO_2 concentrations. The red line shows a 365 day running 99th percentile trend. This plot is designed to show how peak levels have been changing. It is largely comparable to the NAAQS statistic, except that the NAAQS uses a calendar year period. However, the current NAAQS would not apply prior to 2010. If it had, Detroit – and most other areas with large coal-fired facilities – would be in "severe" non-attainment. Figure 4-7 shows that peak levels have declined considerably from the 1980s and mid-2000s, although highest 1-hr daily levels at this site still approach or exceed the current NAAQS in recent years.

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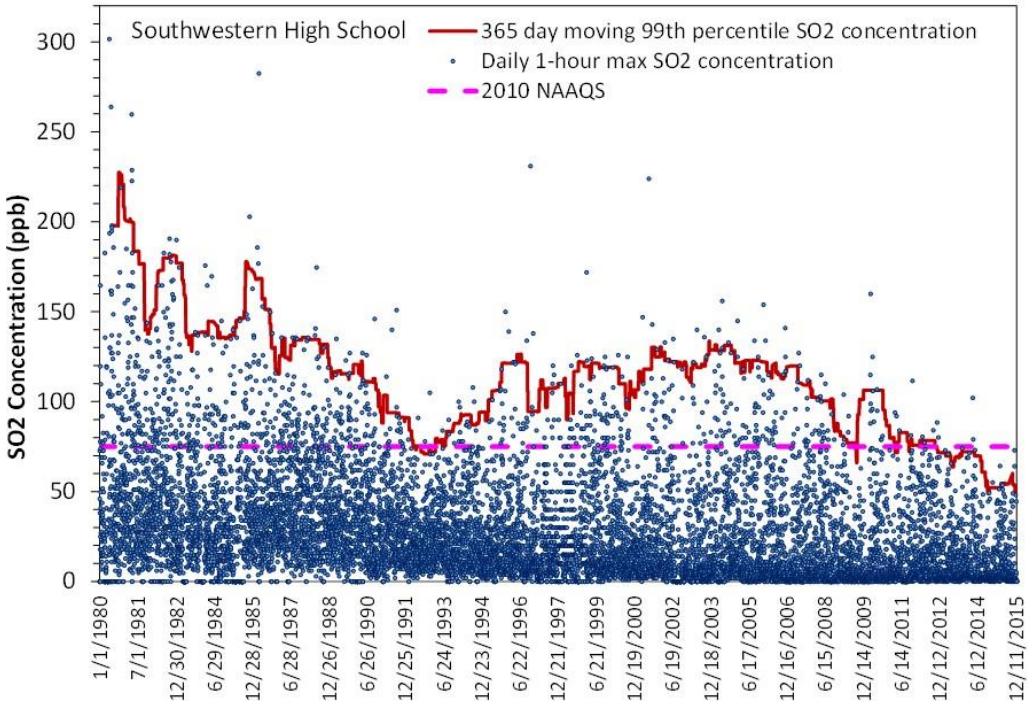
Figure 4-8. 35 year record of the highest 1-hr daily SO_2 concentrations at Southwestern High School and the current NAAQS. Plot does not show measurement of 832 ppb on 9/16/2002.



A second plot of trends is shown in Figure 4-9 again using the daily 1-hr high, but with more recent data at the 8 Detroit area sites (Southwestern High School, Allen Park, the group of monitors surrounding Marathon, and the two Windsor sites). For the four Marathon sites, the analyses uses the daily 1-hr high across the four sites. For the two Windsor sites, the analysis uses the daily 1-hr maximum across the two sites. Analysis of 1-hr data is somewhat complex as these concentrations are highly variable. To observe trends that are potentially more relevant to health effects, e.g., exacerbation of asthma, the following variable are plotted:

- Daily 1-hr high concentrations (shown as individual points).
- Smoothed running weekly daily 1-hr high concentration (shown as the red line). This is calculated as the highest 1-hr daily concentration over the week, with two iterations of a smoother, each using a weekly running average. This shows the trend of 1-hr high concentrations at the site.
- Smoothed running weekly average of the daily 1-hr high concentration. This takes the average 1-hr concentration over the week at the site, and applies two iterations of the same smoother described above. This shows average peak levels over the week. This statistic is of secondary interest.
- Running seasonal daily 1-hr average. This takes the 90-day average of the daily 1-hr high concentrations. It mainly shows long term (seasonal) trends.

This analysis is designed to indicate trends of peak concentrations that are relevant to health impacts from SO_2 (not NAAQS compliance). Because a log scale is used, small excursions at the top of the plot can be meaningful.

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The following are some key results of the trend analysis:

- The highest monitored concentrations occurred at Marathon in 2012 when a concentration of 500 ppb was noted for a single hour. With this exception, the highest concentrations occurred at the Southwest High School in 2010 when a 1-hr concentration reached 160 ppb, and three daily 1-hr concentrations exceeded 100 ppb.
- No strong long-term (across years) trends are apparent. This applies to both the peak and average 1-hr concentrations. Towards the end of the available record (fall 2015 onward), a small decrease is apparent, but this could also just reflect the variability in the data.
- Seasonal effects are shown at the Allen Park monitoring site, with higher concentrations in summer, likely due to prevailing wind directions in the direction of sources. Seasonal averages at the Canadian sites also show seasonal effects, though less strong that those at Allen Park. The other sites do not show seasonal trends.

Figure 4-9. Trends of daily 1-hr SO_2 concentrations at Detroit area monitors. Panel 1: Southwestern High School; Panel 2: Allen Park; Panel 3: Maximum of 4 Marathon Refinery Sites; Panel 4: Maximum of 2 Windsor Sites.

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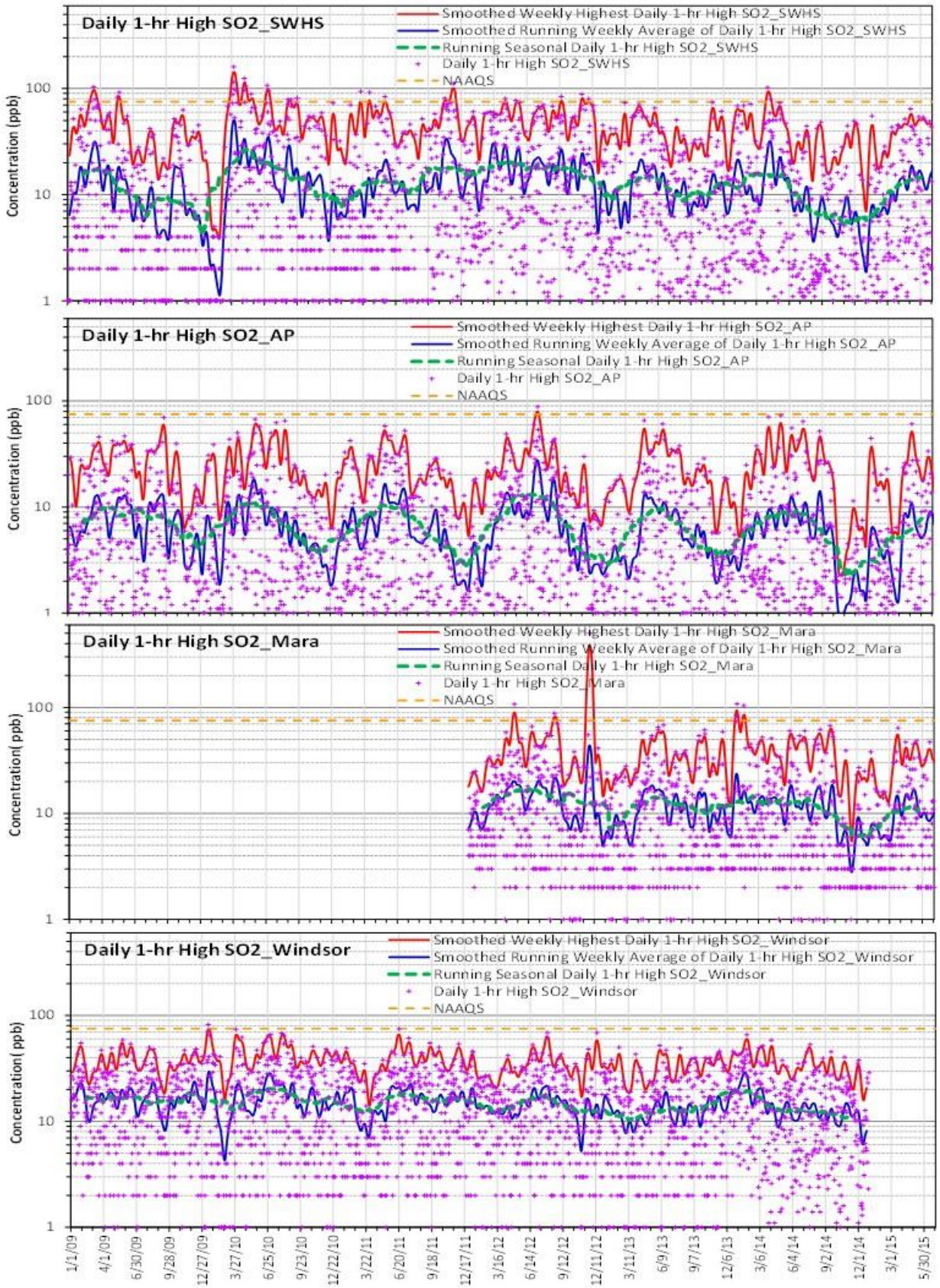

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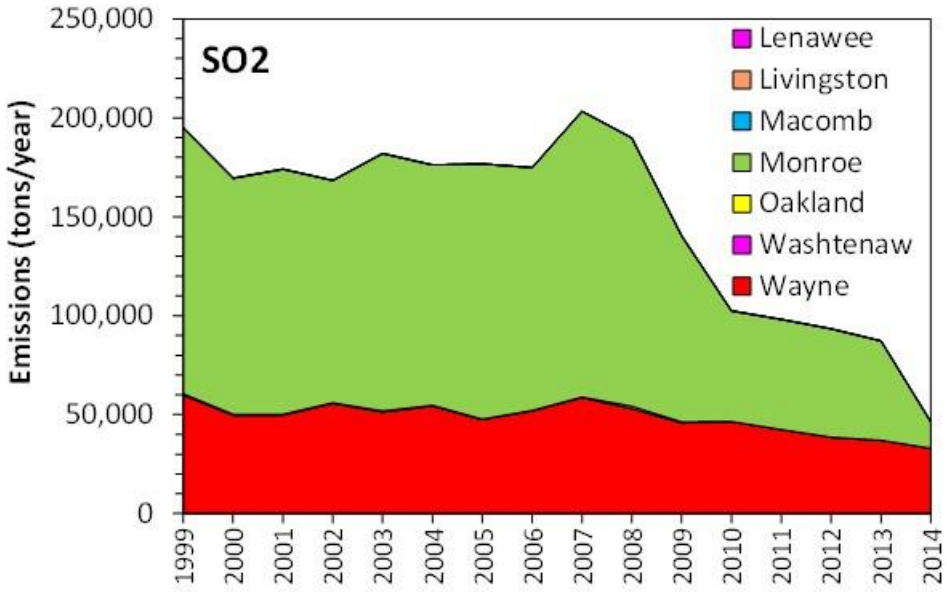
The lack of large trends in recent 1-hr concentrations is noteworthy given the gradual decrease in reported SO_2 emissions in Wayne County over 2010 to 2014 and earlier (shown in Figure 4-10), and the larger decrease in Monroe County emissions from 2013 to 2014. Examination of daily 24-hr average concentrations, rather than daily 1-hr high concentrations shows comparable results, i.e., no strong long-term trends (plots not shown). This suggests that the smaller sources in Detroit, rather than the larger sources that are responsible for the bulk of SO_2 emissions, produce the "hotspots" recorded by the Detroit monitors.

By comparison, the only other SO_2 monitor with long term records located in Michigan (in Grand Rapids), shows a long-term trend of decreasing SO_2 concentrations over this period, although concentrations are much lower (rarely exceeding 10 ppb, as compared to 100 ppb in Detroit).

Figure 4-10. Trends of SO_2 emissions from point sources from 1999 to 2014 by county. Based on MAERS data.



4.5.4 Spatial patterns

Most SO_2 is emitted by a relatively small number of large point sources, and the areas affected by SO_2 tend to reflect local source influences. Areas with the highest concentrations are called "hotspots."

SO_2 "hotspots" are depicted in Figure 4-11, which shows the 4th highest 1-hr daily concentration predicted using MDEQ and EPA approved models (AERMOD), emission parameters used by MDEQ, and 2012 meteorology. The figure shows predicted concentrations over a larger area than the modeling performed by MDEQ in the 2015 proposed SO_2 SIP. The areas potentially impacted by SO_2 clearly extends beyond the SIP non-attainment zone.

As noted earlier, the SO_2 monitoring network in Detroit includes only two sites with long term records (Southwestern High School and Allen Park). This report utilizes all available SO_2 data, and incorporates data from 6 additional sites (locations shown earlier in Figure 4-7). Even with these 8 sites, the existing monitoring network does not provide adequate spatial coverage of SO_2 concentrations. In particular, existing monitoring

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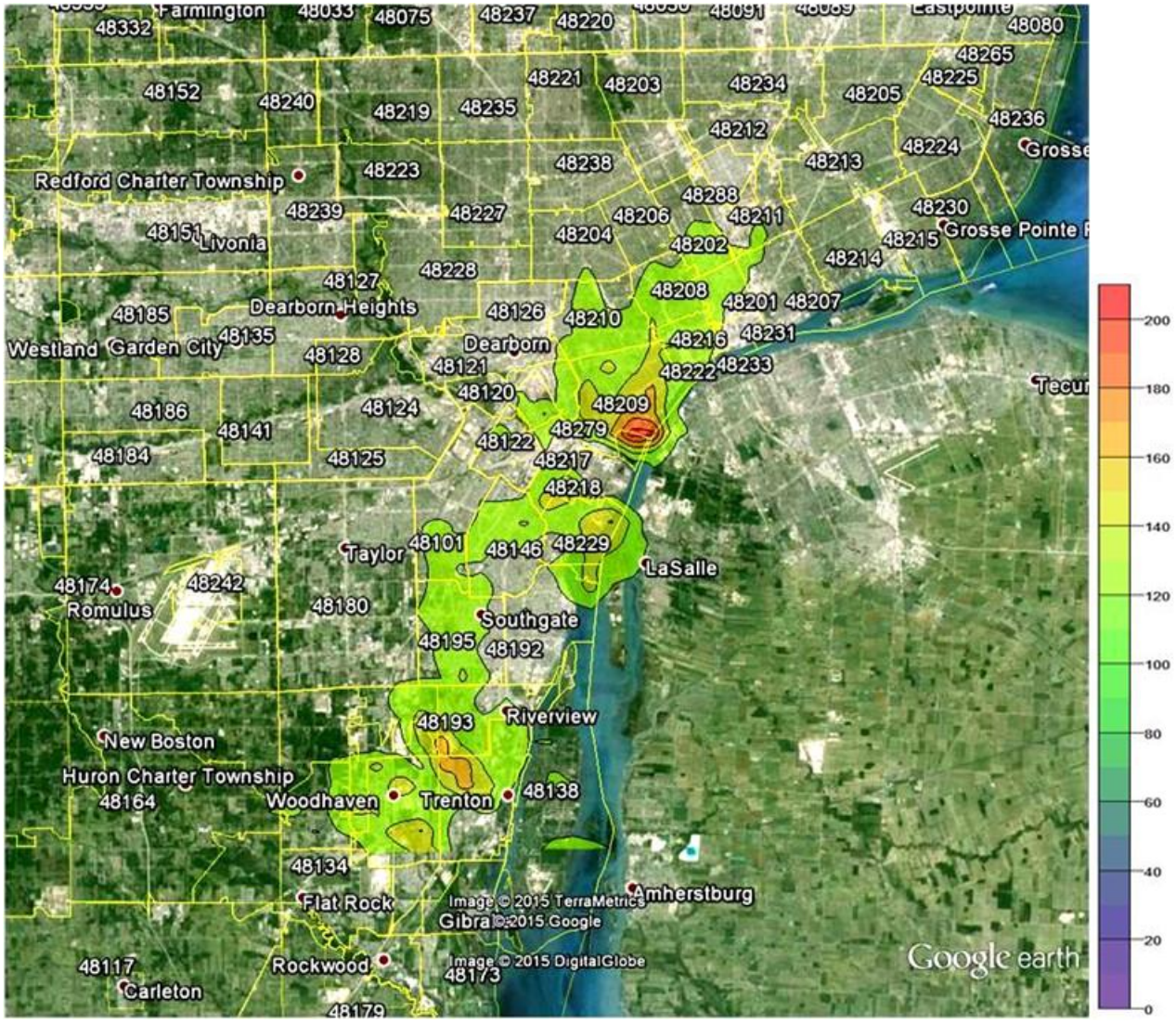
sites are not at the hotspot locations with the highest predicted SO_2 concentration. The Southwestern High School monitor site is closest to the predicted hotspot, but depending on the modeling assumptions, the predicted hotspot can be closer to or further from major sources, and the resulting concentrations can vary substantially.

Figure 4-11. Predicted SO_2 concentrations (µg/m3) across the Detroit region. Shows 4th highest daily 1-hr concentration predicted from major Detroit area sources, including DTE-Trenton, DTE-River Rouge, DTE-Monroe Facilities, and US Steel. Based on AERMOD, 2012 meteorology, 1000 m grid, and no background. (157 µg/m3 is the equivalent of 75 ppb, the current 1-hr NAAQS concentration.



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4.6 Nitrogen oxides

4.6.1 NAAQS status

EPA has set both primary and secondary standards for NO_2 at 0.053 parts per million (53 ppb), averaged annually, and also established an additional 1-hour primary standard at 100 ppb. Since 1978 no areas in Michigan have exceeded the annual NO_2 NAAQS. In addition, no monitoring site has exceeded the 1-hour standard. However, if the region becomes non-attainment for O_3 (see Section 4.3), there will be considerable attention to NO_x emissions and monitoring.

4.6.2 Monitoring

Monitoring for nitrogen oxides (NO_x) by MDEQ using EPA-approved methods provides essentially simultaneous and hourly measurements of nitrogen dioxide (NO_2) and nitric oxide (NO). Most sources emit primarily NO, which is quickly oxidized in the atmosphere into NO_2. The NAAQS health-based limits use NO_2.

Monitoring of NO_x and NO_x trends are important due to the potential for health effects from NO_2 (and NO) exposure directly, but also for two other important reasons: (1) NO and NO_2 can react with volatile organic compounds (VOCs) in the presence of sunlight to produce ground-level ozone (O_3), a widespread and important pollutant affecting health in Detroit and numerous other urban and rural areas. (2) NO_x can form nitrate aerosols that contribute to "secondary" $PM_{2.5}$.

Overall, NO_2 concentrations are decreasing across Michigan. The percent reduction in annual mean NO_2, for the period 2002 to 2011 recorded at Detroit was 33 percent.

Trends suggested by analyses of data in Detroit and elsewhere suggest that the relative contribution of nitrogen-associated secondary PM fraction of total $PM_{2.5}$ is increasing, a result of decreases concentrations of sulfate aerosol and potentially growing importance of other secondary aerosols, including those formed from NO_x emissions.[30] Major emission sources of NO_x include motor vehicle exhaust, electric utilities and industrial boilers.

4.7 Carbon Monoxide

4.7.1 NAAQS Status

At present, all Michigan areas are designated in attainment of the 1-hour and 8-hour standards. There have been no exceedances of the 1-hour and 8-hour CO NAAQS since 1991. The 1-hr standard of 35 ppm has not changed since 1971; the 8-hr standard is 9 ppm. Monitored levels fall well below the NAAQS, e.g., levels have been below 5 ppm at the four Detroit area sites since 2002.

4.7.2 Monitoring

CO is monitored at four sites in Detroit. Two are near-road sites, within 50 m (Livonia, and Eliza Howell #1); the two others are within 200 m (Allen Park, Eliza Howell #2).

Vehicle emissions are typically the largest emitter of CO, and CO "hotspots" can occur near major roads and intersections.

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4.8 Toxics

A variety of monitoring sites measure air toxics, including metals and organic compounds. The number of sites measuring toxics is limited, in large part due to the cost of monitoring.

Air toxics represent a large and diverse group of substances, including compounds that are persistent, bioaccumulative and toxic (PBT). There are no health-protective standards, but typically a risk-based approach is used; MDEQ uses short- and long-term screening levels and health benchmark levels that focus on the direct inhalation pathway. While data are collected, there has been few comprehensive analyses of toxics data. On an intermittent basis, several special studies have been conducted that increased monitoring and analysis of toxics, the most recent being the Detroit Area Toxics Imitative in 2005-6. More recently, MDEQ notes that formaldehyde levels in southeast Michigan are very heterogeneous, and that historical concentrations at River Rouge are elevated.[13]

Metals

Currently, metals are measured at the following sites:

- Manganese, arsenic, cadmium and nickel (Mn, As, Cd, and Ni) are measured on TSP (total suspended particulate) samples at 5 area sites (Southwestern HS, Dearborn, Delray/Jefferson, River Rouge, and Allen Park). These samples are collected every 6 or 12 days.
- Lead (Pb) is measured on TSP samples at 2 sites (Allen Park and Dearborn)
- Other metals on TSP samples: Dearborn also measures a large suite of additional metals (beryllium, vanadium, chromium, manganese, nickel, cobalt, copper, zinc, arsenic, molybdenum, cadmium, barium, lead, and iron)
- Many metals are measured on $PM_{2.5}$ samples at three sites (Dearborn, Allen Park, and Fort Street). These samples are collected every 6 days (every 3 at Allen Park).

The spatial coverage of the metals network is limited vis-à-vis the potentially large emission from the steel, coke and other industries in southwest Detroit.

Organics

Two site currently measure organic species

- Fort Street measures VOCs and carbonyls (formaldehyde and acetaldehyde) every 12 days
- Dearborn measures VOCs, carbonyls and PAHs, as well as EC and OC, every 6 days.

In addition, Dearborn and Allen Park use aethalometers to measure carbon black, and indicator of soot and diesel exhaust.

[13] 2016 Air Monitoring Network Review, Michigan Department of Environmental Quality Air Quality Division. June 29, 2015, http://www.michigan.gov/documents/deq/deq-aqd-toxics-2016_Air_Mon_Network_Review_489490_7.pdf

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