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SUMMARY OF RECENT AMBIENT AIR QUALITY AND ACCOUNTABILITY ANALYSES IN THE DETROIT AREA

SUMMARY REPORT STI-905317.02-3240

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ABSTRACT

The Detroit metropolitan statistical area (MSA) is nonattainment for PM_{25} and ozone, and is forecast to be residual nonattainment past 2010. To understand the changes in emissions that may be needed to meet attainment goals, the impact of prior control measures on air quality in the area was examined. The primary control measures over the last 10 years have been regional in nature: the Acid Rain Program (targeting SO₂ emissions) and the NO_x SIP Call (targeting summer NO_x emissions to reduce ozone). In addition, ambient trends from 2002 to 2005, which are the most recent years for local emission inventories, were examined at multiple sites by year, season, and source category. Source categories impacting the ambient air were determined using the receptor model positive matrix factorization (PMF). Ambient PM_{2.5} data from multiple sites were investigated to understand how source categories vary spatially and temporally. PMF was applied to SANDWICH-adjusted PM2.5 data to understand how using adjusted PM_{2.5} data impacts the receptor modeling results. The utility of gaseous air toxics data in PMF was explored in two ways: (1) using a combined PM_{25} and gaseous air toxics data set at Allen Park and (2) using a gaseous air toxics only data set at Southwest High School (SWHS). No additional local control measures were implemented during 2001-2006, and minimal interannual changes in most species were observed. A modest downward trend in PM2.5 was observed at some sites over this period. Mobile source air toxics (MSATs) concentrations at one site (SWHS) significantly decreased between 2001 and 2005, but did not decrease at another site (Allen Park).

INTRODUCTION

Detroit is residual nonattainment for particulate matter with a diameter of less than 2.5 micrometers ($PM_{2.5}$) and ozone, and has higher than average risk from air toxics concentrations (**Figure 1**). There are common sources of ozone precursors (volatile organic compounds—VOCs—and NO_x), $PM_{2.5}$ and its precursors, and toxics; and atmospheric processing and transport affect the concentrations of all of these pollutants. A multipollutant approach to resolving air quality problems integrates monitoring and emission controls across pollutants. To continue to expand our understanding of air quality problems in Detroit, this multipollutant accountability analysis was conducted in the Detroit area using routine monitoring data from a number of national monitoring programs, including the Speciated Trends Network (STN), CASTNET, and National Air Toxics Trends Sites (NATTS). The map in **Figure 2** shows the sites from which data were used for this analysis.



Figure 1. Areas with ozone and/or $PM_{2.5}$ concentrations above the National Ambient Air Quality Standards (NAAQS) for 2003 through 2005 and/or with modeled cancer risk estimates from EPA's National Air Toxics Assessment (NATA) 1999 in the top 10% for all counties.

A suite of both accountability and spatiotemporal analyses were conducted. Three sets of analyses were conducted to explore multipollutant trends in the Detroit area and possible responses to emission controls. The primary control measures affecting the Detroit area over the last 10 years have been regional controls: the Acid Rain Program (targeting SO₂ emissions) and the NO_x SIP Call (targeting summer NO_x emissions). SO₂ emissions reductions should lead to a reduction in ambient SO₂ and sulfate concentrations as well as lake acidity and sulfate contributions to visibility impairment. Summer NO_x reductions were imposed to reduce ozone concentrations; ambient NO_x concentrations in 2005 was also investigated. For more information on accountability methods, see Hafner and Roberts (2006), which is included as Appendix A. Additional details on the accountability analyses can be found in Brown (2006), which is included as Appendix B, and in Appendices C and D.

Additional analyses were conducted to understand source categories, spatial and temporal variability, and multipollutant relationships. Spatial and temporal changes in annual averages of

 $PM_{2.5}$ and mobile source related species were examined. PMF was performed on both STN $PM_{2.5}$ data sets and SANDWICH-adjusted data sets at several sites. Details are provided in Rubin et al. (2006), which is included as Appendix E. Gaseous air toxics data were explored using PMF with (1) a combined $PM_{2.5}$ and gas air toxics data set and (2) a gas-air toxics only data set. Details are provided in Appendix F.



Figure 2. Detroit-area monitoring sites used in this analysis.

TRENDS IN PM_{2.5}

 $PM_{2.5}$ has generally decreased according to STN mass. As seen in **Figure 3**, the sum of the major components of $PM_{2.5}$ was lower in 2006 and 2004 than in other years. While the decrease in 2004 is most likely due to meteorology, as it was a relatively cool, wet summer, the decrease in 2006 compared with previous years may indicate a real decrease in emissions. The most notable decrease was at Dearborn, which is located in the heart of Detroit's industrial area. In addition to the decreases in ammonium sulfate and organic matter (OM) seen at all sites, metal oxides have decreased between 2002 and 2006, likely due to a decrease in industrial activity.



Figure 3. Average $PM_{2.5}$ composition by (a) year and (b) season at Ann Arbor (2003-2006), Allen Park (2001-2006), and Dearborn (2002-2006) STN sites. OM (organic matter) is equal to 1.8*blank corrected OC, AmmNO3 is calculated ammonium nitrate from nitrate, AmmSO4 is calculated ammonium sulfate from sulfate, and metal oxides is calculated by the Interagency Monitoring of Protected Visual Environments (IMPROVE) method

(2.2*Al+2.49*Si+1.63*Ca+2.42*Fe+1.94*Ti). Each year had data for all quarters. Average filter mass from collocated Federal Reference Method (FRM) monitors is shown for comparison as asterisks.

GRADIENT ANALYSIS OF PM_{2.5}

By comparing concentrations of $PM_{2.5}$ components between a site outside of Detroit in Ann Arbor to the Allen Park site and to the heavily industrialized Dearborn site, we can better understand the impact of local (i.e., nearby the site) sources in Detroit. We expect Ann Arbor to have relatively low concentrations of $PM_{2.5}$ compared with the Detroit sites. Additionally, we expect a gradient in concentrations between Detroit sites because Dearborn is much closer to point sources than Allen Park is. **Figure 4** shows average concentrations of $PM_{2.5}$ components at Ann Arbor (in grey), average excess concentrations at Allen Park (Allen Park – Ann Arbor, in green), and average excess concentrations at Dearborn (Dearborn – Allen Park, in blue). Consequently, the tops of the green boxes indicate the average concentrations at Allen Park and the tops of the blue boxes indicate the average concentrations at Dearborn.

Ammonium sulfate concentrations are similar at Ann Arbor and Allen Park, confirming its typical regional nature, but there is a small excess at Dearborn compared with Allen Park, possibly caused by local sources. Note that measurement error was not quantified in this assessment. Nitrate is regional, and with a small excess at the Detroit sites compared with Ann Arbor. OM is nearly $1 \mu g/m^3$ higher at Allen Park than at Ann Arbor, and nearly $1 \mu g/m^3$ higher at Dearborn than at Allen Park, due to nearby industrial and mobile sources. Elemental carbon (EC) concentrations are generally higher in Detroit compared with Ann Arbor, similar to other urban areas. As expected, metal oxides are much higher at Dearborn than at either of the other sites due to the local industry. This analysis suggests that nearly $2 \mu g/m^3$ of metal oxides, on average, come from local industrial emissions that do not impact Allen Park.



Figure 4. Average "excess" ammonium sulfate, ammonium nitrate, OM, EC, and metal oxides concentrations at the Dearborn and Allen Park sites compared with the Ann Arbor (Ypsilanti) site, 2003-2006.

SOURCE APPORTIONMENT OF PM_{2.5}

Positive matrix factorization (PMF), described in detail elsewhere (Paatero, 1997; Paatero and Tapper, 1994), is an advanced multivariate receptor modeling technique that calculates site-specific source profiles with time variations of these sources based on correlations imbedded in ambient data. Uncertainty development and data screening methods are described in detail in Rubin et al. (2006).

For three sites, Luna Pier, Dearborn, and Allen Park, PMF was applied to apportion the speciated PM_{2.5} data through 2005. Some factors were similar at all three sites: ammonium sulfate, ammonium nitrate, soil, and mobile sources. Silicon/calcium and nickel/chromium factors were identified in addition to a second calcium factor at Luna Pier. The identification of two industrial factors at Luna Pier may be attributed to the proximity of this site to both Toledo and Detroit. Of all three sites, Dearborn had the most factors resolved. This is expected due to the complexity of sources around the site. Results are shown in **Figure 5**. Wind roses and emission inventory information were useful in corroborating the industrial factors. Although overall concentrations decreased at all sites in 2004, likely due to meteorology, no trend across source contributions was seen from year to year (**Figure 6**). Additional information on this work is available in Rubin et al. (2006). NOTE: Copper at Dearborn and Allen Park may be coming from co-located high volume sampler that uses copper brushes (on-site inspection showed worn brushes).



Figure 5. Average PMF results for (a) 8-factor solution at Luna Pier for STN data (May 2002 through December 2005); (b) 9-factor solution at Allen Park for STN



data (2000 through 2005); and (c) 10-factor solution at Dearborn for STN data (May 2002 through December 2005).

Figure 6. Average PMF results by year for (a) an 8-factor solution at Luna Pier for STN data (May 2002 through December 2005); (b) a 9-factor solution at Allen Park for STN data (2000

through 2005); and (c) a 10-factor solution at Dearborn for STN data (May 2002 through December 2005).

SOURCE APPORTIONMENT OF SANDWICH-ADJUSTED PM_{2.5}

While STN measures PM_{25} mass and the species that comprise the mass, the measurements are often slightly different than the FRM PM2.5 mass measurements, which are the metric for regulations. To translate the STN measurements into "FRM equivalent" measurements, the Sulfate, Adjusted Nitrate, Derived Water, Inferred Carbonaceous mass and estimated aerosol acidity (H+) material balance approach (SANDWICH) was developed (Frank, 2006). PMF was performed on SANDWICH adjusted data from the Detroit area sites to explore any differences in apportionment between a standard STN data set and a SANDWICH adjusted data set. The ambient concentrations and PMF results using SANDWICH data were very similar to STN results as shown for Allen Park in Figure 7. In the SANDWICH PMF results, a larger fraction of the mass is attributed to ammonium sulfate and less to ammonium nitrate, consistent with ambient data. Better mass recovery was achieved using the SANDWICH data set, mostly due to the difference in sulfate mass. With respect to the number of factors, Allen Park was the only site at which the SANDWICH and STN data sets did not agree. Using the SANDWICH data, PMF was able to split the carbon into a mobile and a diesel source, which was not achieved with the STN data. However, neither the wood burning nor the steel source factor was identified with the SANDWICH data. On a daily basis, the SANDWICH PMF results can be different than the STN PMF results, but these differences are nearly all due to the differences between SANDWICH and regular STN data (i.e., carbon, nitrate, and sulfate concentrations are already different between the two data sets). Additional information on this work is available in Rubin et al. (2006).



Figure 7. PMF results and ambient mass composition for both STN and SANDWICH data sets at Allen Park (2000 through 2005).

EXPLORATORY SOURCE APPORTIONMENT OF PM2.5 AND AIR TOXICS

PMF runs were conducted using 8 to 11 factors for a combined STN PM_{2.5} and gaseous air toxics data set at Allen Park. Fractional uncertainties were used for the gaseous species (Wade et al., 2007). Over all runs conducted, OC and EC were not split into separate factors. Benzene, o-xylene, ethylbenzene, and toluene were grouped with the steel source (iron and chromium), while formaldehyde and acetaldehyde were grouped with the general mobile source (OC/EC) in all runs conducted. One of the expectations of using the gaseous air toxics data with STN PM_{2.5} data was that the additional species would help separate the mobile sources into gasoline and diesel factors. At Allen Park, though, no additional insight into the split of mobile sources was obtained. The distribution of gaseous air toxics (**Figure 8**) suggests that a large fraction of the OC may be secondary, because the aldehydes are associated with that factor. Overall, the inclusion of air toxics resulted in no significant difference in how PM_{2.5} was apportioned with PMF. However, the data set was limited in total samples (N=153), toxics used (many were below detection), and uncertainty information. Additional information on this work is available in Rubin et al. (2006).



Figure 8. Apportionment of each species (% of species) by PMF factor for air toxics included in the apportionment of $PM_{2.5}$ at Allen Park (April 2001-November 2005, N=153).

ACCOUNTABILITY: DECREASES DUE TO THE ACID RAIN PROGRAM

 SO_2 is both a local and regional pollutant, so intra-urban differences in ambient concentrations are expected. If local sources are close to monitors, they may obscure long-term regional trends. Continuous SO_2 data for 1993-2005 are available from the EPA's Air Quality System (AQS) for five sites in the Detroit area. National SO_2 emission trend estimates are available from 1993-2002,¹ and power generating facility emissions are available from 1995-2005. In addition to SO_2 , sulfate aerosol, visibility extinction from sulfate aerosol, and acid deposition should be impacted by the Acid Rain Program. To understand the multi-media effect of SO_2 regulations, 1993-2005 data for ambient sulfate aerosol concentration, sulfur deposition, and light extinction due to sulfate aerosol were obtained from the Ann Arbor, Michigan, CASTNET site.

Between 1993 and 2002, national SO_2 emissions reductions were gradual. Emissions from power generating facilities in Michigan and regionally showed a large decrease in concentrations from 1998-2001. Specific dates and locations of local SO_2 controls in the Detroit area are not known; regional controls may impact concentrations in the Detroit area.

Overall, all sites showed a decrease in ambient SO_2 concentrations from 1993 to 2005 (**Figure 9**). Three-year averages were used for most of this analysis to reduce year-to-year variability. A large decrease (about 30%) in year-to-year SO_2 concentrations is evident between 1994 and 1995, corresponding to the largest decrease in year-to-year emissions nationally (28%). Changes noted include a

- 14% decrease in Michigan SO₂ emissions from power generation (1995-1997 to 2003-2005);
- 26% region-wide decrease in SO₂ emissions from power generation (1995-1997 to 2003-2005);
- 26% decrease in average SO₂ concentrations in Detroit (1993-1995 to 2003-2005);
- 24% decrease in sulfate concentrations in Ann Arbor (1991-1993 to 2003-2005);
- 7% decrease in sulfate concentrations in Allen Park (2001-2003 to 2003-2005);
- 26% decrease in total sulfur deposition in Ann Arbor (1991-1993 to 2003-2005); and
- 17% decrease in light extinction due to sulfate (1991-1993 to 2003-2005).

Additional details on this analysis are available in Appendices B and C.

¹ National Emission Inventory; <http://www.epa.gov/ttn/chief/trends/>.



Axis note: Light extinction calculated from $b=(3)ft(RH)[SO_4^-]$, where RH is relative humidity.

Figure 9. Annual total SO_2 emissions in Michigan and the regional area (black and blue lines); three-year averaged concentrations of sulfur species in Michigan (final year of three-year average is indicated on the x-axis).

ACCOUNTABILITY: INITIAL EVALUATION OF THE NOX SIP CALL

 NO_x is both a locally and regionally emitted and distributed pollutant. Intra-urban differences in NO_x concentrations are likely, and mobile sources typically produce the most NO_x in urban areas. NO_x from power generation (the target of the NO_x SIP Call) constitutes about 30% of total NO_x emissions in the Detroit area (U.S. Environmental Protection Agency, 2004), so changes in NO_x emissions from other sources (such as mobile sources) could confound how NO_x concentration trends (or lack of trends) are interpreted. In addition, NO_x data are only available from two sites in the Detroit area for 2002-2005, and regulations in Michigan to reduce NO_x were not implemented until 2004. Decreases in NO_x concentrations in Detroit because of these regulations are probably not large enough to be noticeable with such a short data record. Ozone concentrations are expected to decrease corresponding to a decrease in NO_x concentration is only in effect during summer months; when nitrate formation is minimal and the nitrate contribution to $PM_{2.5}$ mass is very small.

When summer-only yearly box whisker plots were examined for the two Detroit NO_x measurement sites, East 7 Mile and Linwood, no consistent change in concentrations across sites after 2004 was seen. At East 7 Mile, NO_x concentrations decreased in 2004, followed by an increase in 2005 (**Figure 10**). This change in ambient NO_x concentrations was not observed at the Linwood site, even though it is closer to NO_x point sources. Differences between the NO_x concentrations at these two sites are likely due to differences in the proximity of both mobile and point NO_x sources to the monitors. Concentrations were segregated by hour to examine rushhour (i.e., mobile source-dominated) versus non-rush hour concentrations, nighttime hour (lowest mobile source contribution) concentrations, and daytime hour concentrations, but no consistent trend was evident. Because mobile source activity is lower on weekends but power generation activity generally is not, ambient NO_x concentrations were also segregated by day of week and hour to determine whether examining periods when mobile source emissions are low could reveal trends from power generation sources. Again, no consistent trend was observed at sites from which data were available.

Because the large mobile source contribution to NO_x may confound any changes in Detroit urban NO_x concentrations due to the NO_x SIP Call, wind direction analysis was also performed to isolate NO_x point sources in the ambient data record. Data were divided by wind direction into three groups: (1) 180-225 degrees, expected to be dominated by point sources, (2) winds from the Detroit area—mobile-dominated, and (3) winds from Canada—no emissions information available. Concentrations were significantly higher at East 7 Mile and Linwood when the wind was from 180-225 degrees, supporting the hypothesis that large NO_x point sources in this direction impact ambient concentrations. However, no significant year-to-year change in concentrations from this sector was evident at either site. Data were divided by hours to further isolate the point source-versus-mobile source contribution, but no consistent change across years was seen with morning hourly data only or nighttime hourly data only.

Ratio analysis was also conducted using ratios of NO_x and mobile source-dominated pollutants. If the mobile source species (benzene and total hydrocarbons) do not change with time, a change in their ratios to NO_x could indicate a change in the point source contribution. However, no consistent year-to-year change was seen in these ratios at either site (e.g., see Figure 9). Additional details on this analysis are available in Appendices B and C.



Figure 10. Notched box plots of concentrations of (a) NO_x (ppb) and (b) the total nonmethane organic compounds (TNMOC): NO_x ratio at the East 7 Mile site; summer of 2002-2005 data used.

ACCOUNTABILITY: HOW DO PEAK EMISSIONS IMPACT OZONE?

An accountability analysis to examine the connection among weather, peak emissions, and resulting air quality (e.g., electric generating unit [EGU] SO₂ peak emissions and PM_{2.5}; EGU NO_x peak emissions and ozone) was performed for 2005. The year 2005 was selected because air quality was worse in 2005 than in 2004, and ambient NO_x plus daily emissions data were available for 2005. Peak emissions were defined as emissions from facilities that operated for less than 1,000 hours during the 2005 ozone season, i.e., facilities that were only operated when demand was highest. However, as seen in **Figure 11**, several large power plants in the Detroit area (including Monroe and J H Campbell) are not considered peak emitters and typically account for almost all of the NO_x emissions; therefore, peak emissions were not a large fraction of total NO_x emissions in this area. Additional details on this analysis are available in Appendix D.



Daily temperature is daily max temperature for the Detroit MSA (source: AQS) AQI is based on daily max 8-hour OS values for Detroit MSA (source: AQS) Output is total daily output for the Monroe Power Plant (source: EPA Clean Air Markets; http://cipub.opa.gov/gcim/index.clm?fuseection-emissions.wizard) Emissions are from all facilities in Michigan Peak NOx emissions are from facilities that operated for <1000 hours during the 2005 O3 season (source: EPA Clean Air Markets; http://cipub.opa.gov/gcim/index.clm?fuseection-emissions.wizard) Base NOx emissions are from facilities that operated for <1000 hours during the 2005 O3 season (source: EPA Clean Air Markets; http://cipub.opa.gov/gcim/index.clm?fuseection-emissions.wizard)

Figure 11. Daily ozone Air Quality Index (AQI), maximum daily temperature, EGU output (1000 MWh), and peak and base NO_x emissions during the 2005 ozone season (April through September). Peak emissions are from facilities that operated for less than 1,000 hours during the 2005 ozone season.

TRENDS IN ANNUAL AVERAGES OF MOBILE SOURCE RELATED SPECIES

To explore whether the ambient data indicate a change in source contributions over time, annual average concentrations of mobile source related species OC, EC, 1,3-butadiene, and benzene) were examined at Allen Park and Southwest High School. Data were investigated using both a t-test, which is used to detect a significant difference between two years of data, and an f-test, which is used to detect whether the slope of average concentrations by year is significantly different than zero. In both cases, a p-value of less than 0.05, corresponding to a 95% confidence level, was considered significant. Benzene and 1,3-butadiene did not have significant trends at either site (**Figure 12**). Only 1,3-butadiene at Southwest High School had a significant change from 2004 to 2005 (p-value <0.01). OC and EC had significant trends at Allen Park; however, this may be misleading because 2002 was the only year that was significantly different than other years. Additional years of data are needed to confirm this trend. Weekday versus weekend and seasonal differences were also examined for these pollutants. Benzene and 1,3-butadiene had no significant differences by day of week or season at either site.

EC at Allen Park was significantly lower in the spring and winter months compared with the rest of the year as well as on weekends compared with weekdays. The lower concentrations in the cooler months is most likely due to less atmospheric mixing, but the lower concentrations on the weekends implies that EC is dominated by diesel emissions, which are reduced on weekends. OC was significantly higher in the summer months but had no difference in concentrations on weekends compared with weekdays. Higher concentrations in the warmer months are most likely due to increased photochemistry.



Figure 12. Annual average concentrations of mobile source-related compounds at Allen Park and Southwest High School.

EXPLORATORY APPORTIONMENT WITH GASEOUS AIR TOXICS DATA

To identify sources of ambient air toxics to further understand the relationships among source types and air pollutants, gaseous air toxics data from the SWHS site were explored using PMF. Samples were collected during 2001 to 2006; 150 samples were suitable for PMF and 20 species were available and had sufficient data above detection. Uncertainty estimates were developed using duplicate samples from the Environmental Laboratory of the Michigan Department of Environmental Quality. Because multiple minimum detection limits (MDLs) were reported for each species, the mode MDL was used to prevent introducing a false signal if many of the data are below detection. Data below the detection limit were substituted with MDL divided by 2 and given uncertainties of 5/6 times the MDL. Missing data were replaced with the median and given an uncertainty of 4 times the median. Three- to eight-factor solutions were explored. The four-factor solution was chosen as the final solution. Factors included chlorinated compounds, acetonitrile, secondary formation (including acetaldehyde and formaldehyde), and mobile exhaust (including benzenes, xylenes, and toluene) (**Figure 13**). Additional factors could potentially be resolved using additional species above detection, species that are unique source tracers, and more samples. For example, no biogenic tracer was available for these analyses, therefore no biogenic factor could be resolved even though biogenic emissions are expected to be an important contributor to VOCs.



Figure 13. Percent of species attributed to each factor by PMF; Southwest High School, 2001-2006, n = 150.

Annual average source contributions were examined for significant year-to-year differences (**Figure 14**). The mobile source exhaust factor was the only factor to have a significant decreasing trend (based on F-test, p-value < 0.001). Secondary formaldehyde decreased significantly in 2005 compared with 2004 (t-test, p-value = 0.01). Acetonitrile had no significant year-to-year changes in concentration, but did increase significantly in 2004 compared with 2002 (t-test, p-value = 0.03). Mobile source emissions are a significant contributor to the gaseous air toxics explored in this analysis.



Figure 14. Average PMF contribution of factors resolved for SWHS gaseous air toxics data; all values are normalized to 2001 except the acetonitrile factor which was zero in 2001; therefore, acetonitrile averages are normalized to 2002.

CONCLUSIONS

Several methods were applied to multipollutant data sets in the Detroit area to better understand trends over time and relationships to emissions controls. The influence of the largest regional control affecting $PM_{2.5}$ concentrations, the Acid Rain Program, was observed in the ambient sulfur and sulfur-related data. Impacts of the NO_x SIP Call were not observed in the ambient urban NO_x data, but data were limited and the sites were dominated by mobile source emissions. Results from a range of ozone, NO_x, $PM_{2.5}$, and air toxics analyses indicate little impact from local controls (if any were implemented) and few relationships among pollutants through mobile source emissions. Trends and source apportionment analyses can be enhanced as additional data become available.

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