

Appendix G

**OVERVIEW OF RECENT DETROIT PM SOURCE
APPORTIONMENT STUDIES
SUPPORT DOCUMENTATION
FOR THE
FINE PARTICULATE SIP**

May 2008

Overview of Recent Detroit PM Source Apportionment Studies

Donna Kenski
Lake Michigan Air Directors Consortium
November 26, 2007

Concentrations of PM_{2.5} in the Detroit metropolitan area currently exceed the National Ambient Air Quality Standard (NAAQS) at 2 of 11 monitoring sites and are within 1 ug of the NAAQS at 4 others (Fig. 1). Modeling studies show that federal controls are expected to bring all but the Dearborn monitor into attainment by 2012(?). Additional local control measures will be needed to achieve the NAAQS at Dearborn. To ensure effective controls, it is imperative that the state and local air programs understand the current composition of PM_{2.5} at each site and also the sources that contribute significant mass to them.

For general background, Fig. 2 shows the chemical components averaged over several years at the speciation trends network (STN) sites in Detroit and upwind. Organic carbon is the largest component of PM_{2.5} on an annual average basis, followed by ammonium sulfate and ammonium nitrate. Concentrations of ammonium sulfate are similar among sites, indicating its regional origin. Organic carbon (OC) and ammonium nitrate, in contrast, have significant site-to-site variability. It is these site differences in concentration, as well as temporal differences, that the source apportionment models use to extract information on the sources that contribute to PM_{2.5} mass.

Six recently published source apportionment studies have examined data from Detroit monitors. These studies are summarized here and a few key findings are drawn from the group as a whole. The studies varied in the number of samples analyzed, the locations of sample collection, the species chosen for study, the source apportionment models applied, and the time periods of sample collection, so conclusions here are necessarily qualitative and somewhat general. Nevertheless, similarities can be drawn despite the variety of approaches and data used. The two most robust studies, Wade et al. (2007) and Gildemeister et al. (2007), both used STN data from the Allen Park and Dearborn sites. The remaining four studies reviewed here collected data independent of the STN network, although one (Brown et al., 2006) used the Allen Park site to collect samples. Figure 3 shows the monitoring sites where data were collected for the studies presented here and Fig. 4 shows the sampling dates for the studies.

Study Summaries

Wade et al. (2007): In the most comprehensive and most recent source apportionment analysis to date, Sonoma Technology examined STN data from

Allen Park (12/2000-12/2006, 662 samples) and Dearborn (5/2002-12/2006, 253 samples). Similar sources were identified at both sites, and contributions were similar for the major sources: secondary sulfate, secondary nitrate, and organic mass. The organic mass factor is described as distinct from elemental carbon (diesel) but is not necessarily only gasoline vehicles. Instead it probably includes some mass from other non-vehicle combustion sources, and is influenced by photochemistry and transport. The two sites are distinguished by the mass allocated to a steel source (1.27 ug at Dearborn vs. 0.05 ug at Allen Park), diesel vehicles (2.84 ug at Dearborn vs. 0.88 ug at Allen Park), and crustal species (1.36 ug at Dearborn vs. 0.62 at Allen Park). Additional mixed industrial factors were identified at each site as well, accounting for about 2 ug. The mixed industrial factors include some sulfate, indicating that local sulfate controls may be effective. Table 1 gives the source allocations for this study and the others, and Figure 5 shows the contributions by source, site, and study authors.

Gildemeister et al. (2007): In a study very similar to Wade et al., Gildemeister et al. examined STN data from Allen Park (12/2000-4/2005) and Dearborn (5/2002-4/2005). PMF was used to distinguish seven sources common to both sites: Secondary sulfate, secondary nitrate, gasoline, diesel, mixed sea/road salt, iron/steel, and soil. A mixed industrial factor was also identified at Dearborn and a biomass burning factor was identified at Allen Park. Contributions to total PM_{2.5} mass are given in Table 1 and Fig. 5. Mass contributions from the secondary sulfate, secondary nitrate, and sea salt were similar at both sites, and also similar to those derived by Wade et al. The influence of local iron and steel industrial sources, mobile sources (gasoline and diesel), and soil was higher at Dearborn than Allen Park. Interestingly, gasoline sources were well correlated but diesel sources were not. The authors suggest that the diesel factor is a combination of sources with both area and point source characteristics. The wind analysis for diesel showed distinct directionality toward the port of Detroit and Ambassador Bridge.

Brown et al. (2006): Like Wade et al. and Gildemeister et al., Brown et al. applied PMF to STN data from Allen Park and Dearborn. Seven sources were detected at Allen Park and nine at Dearborn. The allocations to secondary sulfate and nitrate were similar at both sites and also similar to those in Wade and Gildemeister. Mobile sources were about twice as high at Allen Park, but similar at Dearborn. Industrial sources accounted for about 1.3 ug/m³ at Allen Park and 3.5 ug/m³ at Dearborn. A biomass burning source accounted for 0.3 ug/m³ at both sites.

In addition, this study collected samples at Allen Park from Feb. 2004-Feb. 2005 on a 1-in-6-day schedule. These samples were analyzed for speciated organic carbon and elemental carbon in monthly composites and the resulting dataset was analyzed using the chemical mass balance (CMB) method of source apportionment. Eight sources were modeled. The mass apportioned was total organic carbon, rather than PM_{2.5} as in the studies above. Using the organic species allows more precise identification of source contributions from carbon

sources such as motor vehicles. In this study, mobile sources were apportioned to gasoline, diesel, and smoking vehicles. In Detroit, more than half of the OC allocated to mobile sources was attributed to smoking vehicles. Other sources included biomass burning, vegetative detritus, and dirt. Natural gas combustion was included in the model but its contribution was negligible. A significant portion of OC mass during the summer months was not allocated to any source and was presumed to be of secondary biogenic origin. This study is included in Table 1 and Fig. 5 despite the difference in the basis for allocating mass (OC vs $PM_{2.5}$), because the sources it modeled are dominated by OC.

Morishita et al (2006): This study made speciated $PM_{2.5}$ measurements during 4 summers (2000-2003) at the Maybury school near the Ambassador Bridge (see Fig. 3). Maybury school is not a Michigan DEQ site but is close to the West Fort St. site. PMF was applied to 96 samples, using 15 species: S, Se, Mn, Fe, Ni, Zn, Rb, Mo, Cd., Ba, La, Sm, Pb, EC, and OC. Notably, nitrate was excluded from the analysis, although since these were summer samples the nitrate fraction would likely be small. The important crustal species Ca and Si were also excluded, which may have hindered the model's ability to detect a soil or road dust source. Six sources were identified and quantified, as given in Table 1 below: Secondary sulfate/coal combustion, motor vehicles, municipal waste incineration, oil refining/combustion, sewage sludge incineration, and iron/steel manufacturing. This study also evaluated two distinct periods during 2000 more intensively and found that elevated local source emissions, including incinerator and refinery emissions, were associated with adverse health effects during accompanying toxicological studies.

Hammond et al. (2007): Another special measurement study, in which researchers collected speciated $PM_{2.5}$ samples for 11 2-week periods between October 1999 and May 2002. Samples were collected at Maybury School (as in Morishita, above), and also at Keith School in east Detroit. A total of 154 samples from the two sites were used in a PMF analysis. Species included were: PM_{25} mass, OC, EC, La, Sm, Ce, Pb, Al, P, S, V, Cr, Mn, Fe, Ni, Cu, Zn, K, and Se. As in the previous study, nitrate, Ca, and Si were not included. In East Detroit (Keith School) 5 sources were identified: Secondary sulfate/coal combustion, motor vehicles, refinery/oil combustion, automotive electroplating, and a mixed industrial factor including iron/steel manufacturing and waste incineration. At Maybury School, 7 sources were identified. These included the same factors found at Keith School, except the motor vehicles were split into two separate factors distinguished by gasoline combustion and diesel combustion, and an additional sewage sludge incineration source was identified.

Pere-Trepat et al. (2007): This analysis applied PMF to DRUM samples collected over a 6 week period at the Allen Park site between February and April 2002. The DRUM sampler collects particles in 3 different size modes ($2.5 > D_p > 1.15$, $1.15 > D_p > 0.34$, and $0.34 > D_p > 0.1 \mu m$) and in 3 hour time increments. Each size mode was analyzed for metals, PM mass, and optical

absorption. Carbon and nitrate cannot be quantified from this type of sampler, so a large fraction of PM_{2.5} mass was not represented in the species modeled. Misaligned time stamps plagued the analysis, but once discovered were able to be corrected. Nine factors were resolved with PMF: road salt, a mixed industrial factor with iron and zinc, 2 metal works factors (one with iron in all sizes and Zn, Ti, Cu, and Mn, and the other with intermediate size Fe, small size sulfur, and Zn, Al, Si, and Ca), road dust, and 4 sulfur-dominated sources. The authors suggest that some of the metal-dominated profiles may represent different processes or batch operations at the same facilities, because the wind direction analysis indicated similar origins for each. The sulfur profiles were distinguished by size fraction and temporal behavior and the authors concluded that one was of local origin because of its irregular peaks at random time intervals and one was transported from distant sources long range because of its slowly evolving temporal pattern. Of the other 2 sulfur factors, one may represent dry or wet deposition of sulfate on local soils which are subsequently resuspended, and the other may be associated with industrial activity in the Rouge complex, because it had peaks in the southerly direction. The study did not include quantitative estimates of PM_{2.5} mass associated with each source factor, so it is not included in Table 1 or Fig. 4.

Key Findings and Synthesis:

- The Wade et al., Gildemeister, and Brown studies made very similar allocations to major sources at Allen Park and Dearborn. The data and modeling approach in these 2 studies were almost identical, which no doubt was an important factor in their similar findings.
- The Morishita and Hammond studies differed from Wade, Gildemeister, and Brown in that data were collected at different locations and the species included in the models were somewhat different. Important crustal components Ca and Si were not included as fitting species. Compared to the Wade, Gildemeister, and Brown studies, contributions from vehicles were about the same, secondary sulfate was about twice as high, and industrial contributions were highly variable, ranging from inconsequential at Keith School to a total of 7 ug at Maybury School. The very high allocation to secondary sulfate and low allocation to industry in Hammond et al. may indicate that mass from industrial sources is being assigned incorrectly to secondary sulfate.
- At Dearborn, the source apportionment results indicate that local industrial sources, including steel manufacturing but also other metal industries, likely contribute 2.5-3.5 ug/m³ to annual average PM_{2.5}.
- Dearborn also experiences higher vehicle impacts than Allen Park (1.3 to 1.7 ug greater), and much of the increase is from diesel sources.
- Contributions from secondary sulfate and nitrate do not differ much between Allen Park and Dearborn, evidence that these categories are not being influenced by local sources. Some of the industrial source

fingerprints did include sulfate mass, however, which indicates that local sources of sulfate are present and may be suitable targets for control.

References

1. Brown, S.G., H.R. Hafner, P.T. Roberts, J.J. Schauer, and R.J. Sheesley, Integration of Results for the Upper Midwest Urban Organics Study, Sonoma Technology Report STI-903520-2942-FR (March 2006).
2. Gildemeister, A.E., P.K. Hopke, E. Kim, Sources of fine urban particulate matter in Detroit, MI, *Chemosphere* 69(2007):1064-1074.
3. Hammond, D.M., J.T. Dvornch, G.J. Keeler, E.A. Parker, A.S. Kamal, J.A. Barres, F.Y. Yip, W. Brakefield-Caldwell, *Atmos. Env.* (2007), doi:10.1016 (accepted manuscript).
4. Morishita, M., G.J. Keeler, J.G. Wagner, and J.R. Harkema, Source Identification of ambient PM_{2.5} during summer inhalation exposure studies in Detroit, MI, *Atmos. Env.* 40(2006): 3823-3834.
5. Pere-Trepat, E., E. Kim, P. Paatero, P.K. Hopke, Source apportionment of time and size-resolved ambient particulate matter measured with a rotating DRUM impactor, *Atmos. Env.* 41(2007):5921-5933.
6. Wade, K.S., J.R. Turner, S.B. Brown, J. Garlock, and H.R. Hafner, Data Analysis and Source Apportionment of PM_{2.5} in Selected Midwestern Cities, Sonoma Technology Draft Final Report STI-907018.03-3264-DFR (Nov. 2007).

Three—Year Average PM_{2.5}, 2004—2006

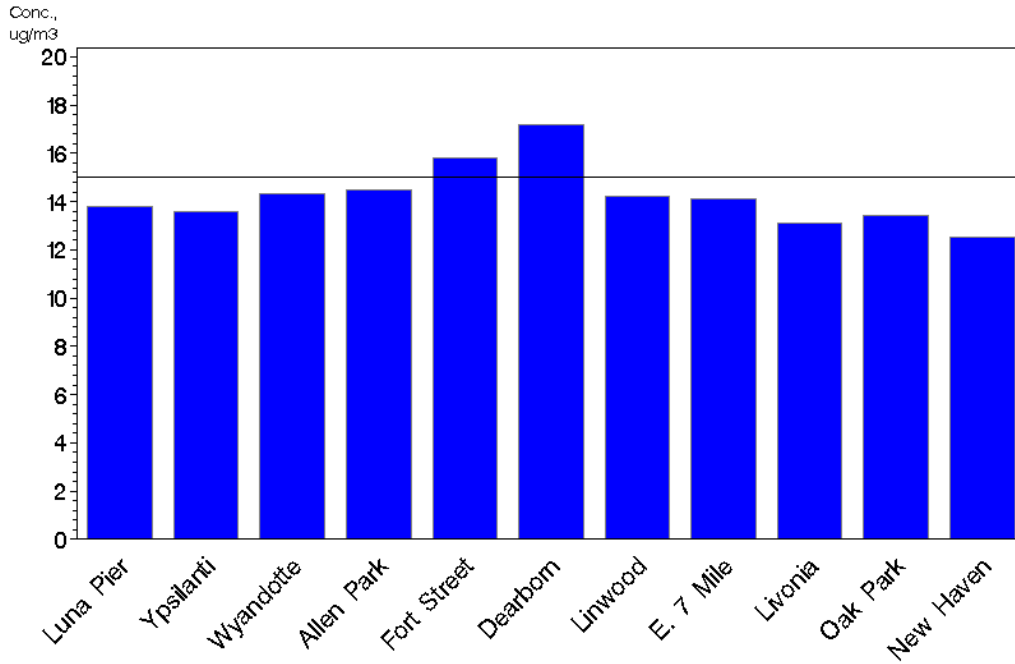


Fig. 1. Current Design Values for Detroit-Area PM_{2.5} FRM Monitors

PM_{2.5} Components — 2005—2006 Average

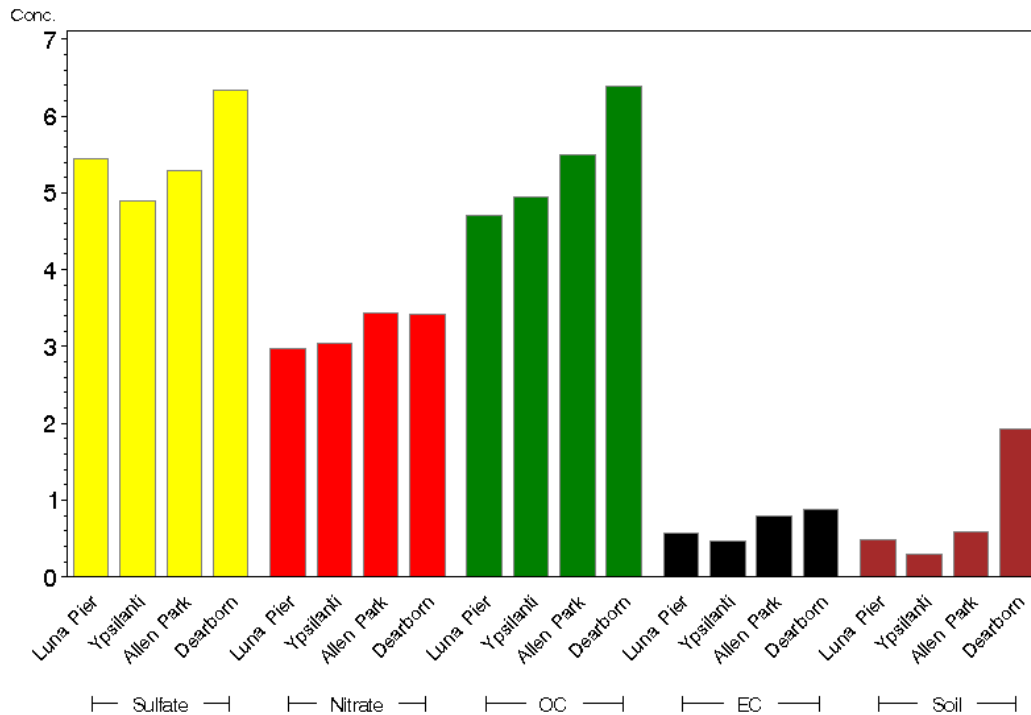


Fig. 2 Chemical Composition of PM_{2.5} at Speciation Trends Network Sites

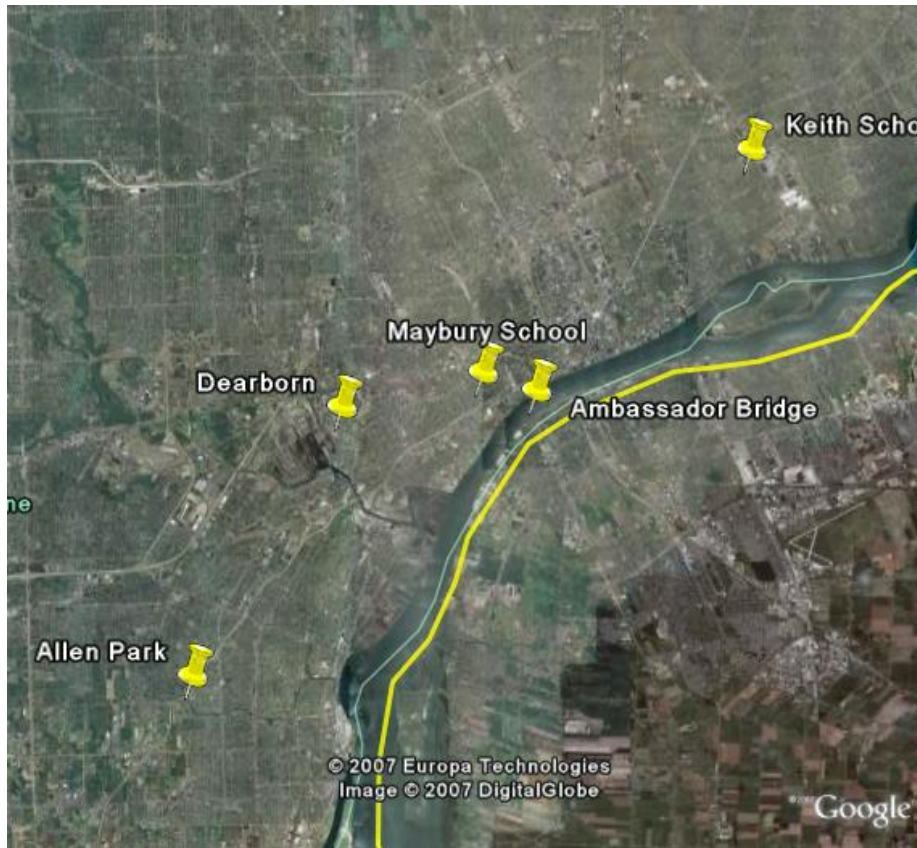


Fig. 3 Monitoring Sites in Detroit Where Source Apportionment Studies Have Been Performed

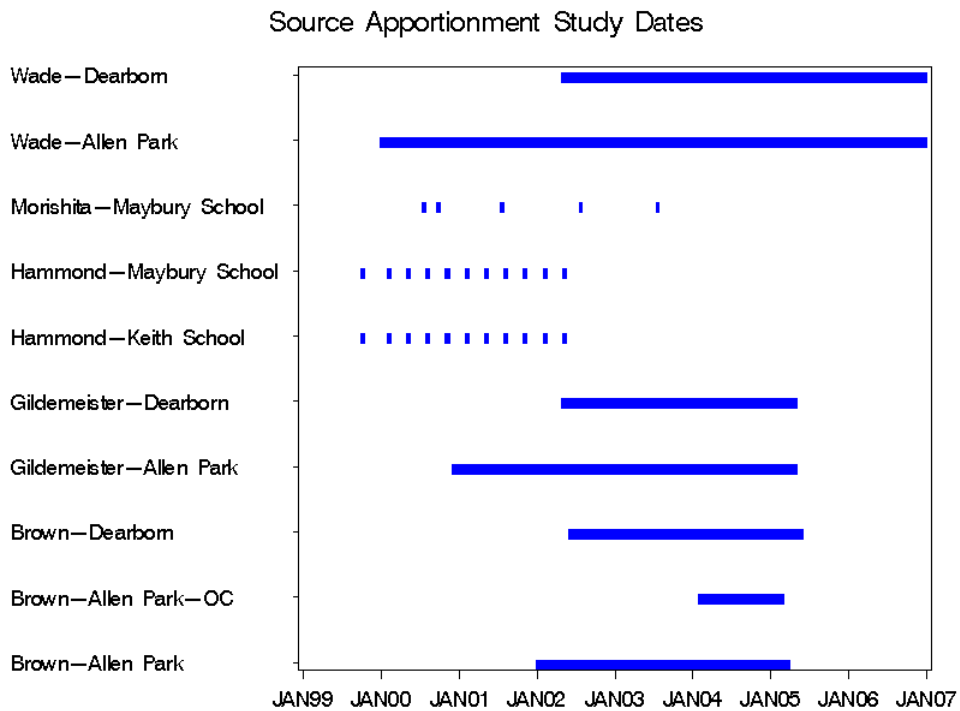


Fig. 4 Dates of Source Apportionment Studies

Summary of Source Apportionment Results at Detroit Sites

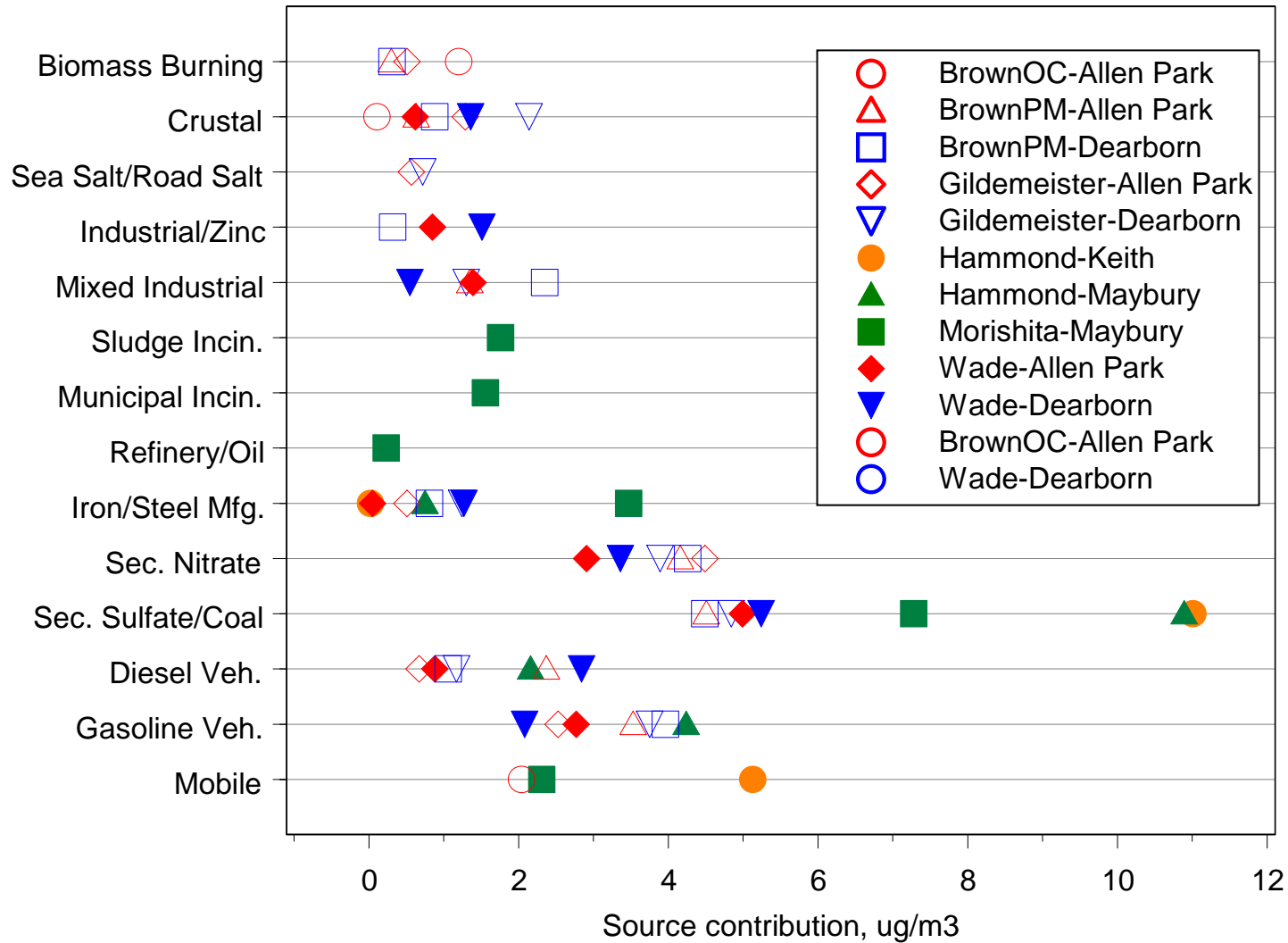


Fig. 5 Summary of Source Contributions from Various Studies and Sites (contributions less than 0.05 ug/m³ are not plotted). Unique symbols are used for each study and site; colors indicate sites—i.e., red=Allen Park, blue=Dearborn, orange=Keith School, green=Maybury School.

Table 1 Summary of Source Contributions to PM_{2.5} by Study and Site

Source Category	Wade et al.		Gildemeister et al.		Brown et al. ^a			Morishita et al. ^b	Hammond et al.	
	Allen Park	Dearborn	Allen Park	Dearborn	Allen Park(OC)	Allen Park(PM)	Dearborn (PM)	Maybury School	Maybury School	Keith School
Vehicles					2.04			2.31		5.13
Gasoline	2.77	2.08	2.53	3.75		3.53	3.96		4.24	
Diesel	0.88	2.84	0.67	1.17		2.37	1.06		2.16	
Secondary sulfate/coal	4.99	5.24	4.99	4.84		4.51	4.49	7.28	10.89	11.01
Secondary nitrate	2.91	3.36	4.49	3.89		4.16	4.26			
Industrial						1.35	2.35			
Iron/steel mfg.	0.05	1.27	0.51	1.24			0.81	3.47	0.75	0.02
Mixed industry/zinc	0.85	1.51		1.30			0.32			
Mixed industry/lead	1.39	0.55								
Municipal incinerator								1.56		
Sludge incinerator								1.76	0.02	
Refinery/oil combustion								0.23	0.06	0.06
Electroplating									0.03	0.03
Sea/road salt			0.57	0.72						
Crustal/soil	0.62	1.36	1.29	2.14	0.11	0.63	0.88			
Biomass burning			0.51		1.20	0.30	0.31			

^aBrown et al. apportioned PM_{2.5} using STN data and organic carbon mass using speciated organic data.

^bMorishita data are averaged over 5 different sampling periods and weighted by number of samples.

Table 1 (Alternate version) Summary of Source Contributions to PM_{2.5} by Study and Site

	Allen Park				Dearborn			Maybury School		Keith School
	Wade	Gildemeister	Brown(PM) ^a	Brown(OC)	Wade	Gildemeister	Brown(PM)	Morishita ^b	Hammond	Hammond
Vehicles				2.04				2.31		5.13
Gasoline	2.77	2.53	3.53		2.08	3.75	3.96		4.24	
Diesel	0.88	0.67	2.37		2.84	1.17	1.06		2.16	
Secondary sulfate/coal	4.99	4.99	4.51		5.24	4.84	4.49	7.28	10.89	11.01
Secondary nitrate	2.91	4.49	4.16		3.36	3.89	4.26			
Industrial			1.35				2.35			
Iron/steel mfg.	0.05	0.51			1.27	1.24	0.81	3.47	0.75	0.02
Mixed industry/zinc	0.85				1.51	1.30	0.32			
Mixed industry/lead	1.39				0.55					
Municipal incinerator								1.56		
Sludge incinerator								1.76	0.02	
Refinery/oil combustion								0.23	0.06	0.06
Electroplating									0.03	0.03
Sea/road salt		0.57				0.72				
Crustal/soil	0.62	1.29	0.63	0.11	1.36	2.14	0.88			
Biomass burning		0.51	0.30	1.20			0.31			

^aBrown et al. apportioned PM_{2.5} using STN data and organic carbon mass using speciated organic data.

^bMorishita data are averaged over 5 different sampling periods and weighted by number of samples.