Determining Spatial Variability in $PM_{2.5}$ Source Impacts across Detroit, MI

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Abstract

Intra-urban variability in air pollution source impacts was investigated using receptor modeling of daily speciated $PM_{2.5}$ measurements collected at residential outdoor locations across Detroit, MI (Wayne County) as part of the Detroit Exposure and Aerosol Research Study (DEARS) during summer and winter from 2004-2006. Six areas were selected for the residential monitoring in the DEARS to capture impacts from different sources including local industry, motor vehicles, and upwind regional sources. $PM_{2.5}$ measurements were also collected at the Allen Park, MI Chemical Speciation Network (CSN) site for comparison with the residential outdoor sites. Sources impacting $PM_{2.5}$ were quantified using the EPA Chemical Mass Balance Model (CMB 8.2). Published source profiles were used as input to CMB along with a mixed industrial profile and a steel manufacturing profile obtained by applying the EPA Positive Matrix Factorization Model (PMF 4.0) to CSN data from a Midwestern U.S. site with industrial sources similar to Detroit.

Major $PM_{2.5}$ sources impacting the Allen Park and residential monitoring areas during DEARS included motor vehicles (24-36% by mass), secondary sulfate/coal combustion (17-35%), secondary nitrate (16-37%) and organic matter (17-21%). Road dust, steel manufacturing, and mixed industrial sources contributed less than 11% by mass. CMB source contribution estimates for Allen Park during the DEARS generally compared well to CMB estimates from the collocated year-long CSN measurements using the same source profiles. CMB source contributions during DEARS showed similar contributions across the residential monitoring areas for secondary sulfate/coal combustion and secondary nitrate consistent with regional impacts for these sources. Contributions from motor vehicles, steel manufacturing, and mixed industrial sources varied across the DEARS monitoring areas, indicating impacts from local sources within the Detroit airshed that may not be well characterized by the Allen Park monitoring location.

Keywords: Particulate matter; Source apportionment; Chemical Mass Balance; Positive Matrix Factorization; DEARS; Detroit, MI

1. Introduction

Numerous epidemiological studies have shown associations between particulate matter (PM) mass concentrations and increased human mortality and morbidity (Dockery and Pope, 1994; Pope et al., 1995; Samet et al., 2000; US EPA, 2004a; Pope and Dockery, 2006). The United States Environmental Protection Agency (EPA) establishes National Ambient Air Quality Standards (NAAQS) for fine particulate matter ($PM_{2.5}$) to protect the public from the adverse health impacts of $PM_{2.5}$, and Detroit, MI is designated as in nonattainment of both the annual and 24-hr standard. The Detroit airshed is impacted by a complex mixture of local and regional sources, as demonstrated by a number of recent source apportionment studies conducted using Chemical Speciation Network (CSN) $PM_{2.5}$ data for Allen Park, MI (Table 1). These studies indicate the largest $PM_{2.5}$ sources impacting Allen Park include motor vehicles (6-57% by mass), secondary sulfate/coal combustion (27-35% by mass), and secondary nitrate (20-28% by mass). However, there is greater uncertainty in the specific local sources and their relative contributions. Accurate apportionment of PM sources is necessary for developing effective PM control

strategies that target emissions reductions from the various sources contributing to elevated PM levels.

Source apportionment methods are also being used to investigate the relative importance of different PM sources in the observed health effects from PM exposure (Mar et al., 2006; Ito et al., 2006; Sarnet et al., 2008). This approach can provide important information to help focus emission reductions on the sources contributing to the health effects. However, studies using source apportionment results from a single monitoring location may not adequately represent the population variability in exposures to sources, particularly in urban areas such as Detroit with large industrial sources.

A major objective of the Detroit Exposure and Aerosol Research Study (DEARS; Williams et al., 2008) was to assess intra-urban variability in the contribution of different sources to PM exposures by comparing source impacts at a CSN monitoring site (Allen Park) to those at residential locations across the Detroit metropolitan area (Wayne County). During the DEARS, daily speciated $PM_{2.5}$ measurements were collected at six residential exposure monitoring areas (EMAs) across Detroit, as well as at the Allen Park CSN site, during summer and winter for 3 years (2004-2007). The EMAs were selected to capture air pollution impacts from different sources including local industry, motor vehicles, and upwind regional sources.

In this study, sources impacting $PM_{2.5}$ were quantified for the DEARS summer 2004 and 2005, and winter 2005 and 2006 samples using the EPA Chemical Mass Balance Model (CMB 8.2). In addition to the CMB model, the EPA Positive Matrix Factorization Model (PMF 4.0) was used to generate industrial source profiles from CSN data. Measured source profiles do not exist for local sources in Detroit therefore PMF was used to identify local source profiles. CMB source contribution estimates averaged by EMA and season were compared to investigate the spatial variability in $PM_{2.5}$ source impacts across Detroit during the DEARS.

2. Methods

2.1. $PM_{2.5}$ Data

Daily $PM_{2.5}$ samples collected during the first four seasons of the DEARS were evaluated in this analysis: Season 1, Summer 2004 (July 13 – August 28, 2004); Season 2, Winter 2005 (February 1 – March 19, 2005); Season 3, Summer 2005 (July 12 – August 27, 2005); and Season 4, Winter 2006 (January 24 – March 11, 2006). Samples were collected 24-hrs daily using a personal

environmental monitor (PEM) equipped with either a 37 mm Teflo filter (mass and inorganics) or a quartz filter (elemental and organic carbon), operating at a flow rate of 2 l min^{-1}. Nitrate (particle bound only) was collected using a 0.8 l min^{-1} mini denuder with a quartz filter. Specific details on the DEARS sample collection can be found in Williams et al. (2008). $PM_{2.5}$ PEM samples were collected at the Allen Park, MI CSN site (42.23°N, 83.21°W) and outside of the homes of study participants in six different exposure monitoring areas (EMA; Note: refer to map in Figure 2, Results and Discussion, Section 3).

EMAs were selected based on proximity to point and line air pollution sources in Detroit. An *a priori* source impact type was assigned to each EMA based on information from the National Emissions Inventory (NEI), the Michigan Department of Environmental Quality (MDEQ), direct observations, and other sources as follows: EMA1 (industrial), EMA3 (diesel), EMA4 (traffic/industrial), EMA5 (industrial), EMA6 (highway) and EMA7 (regional background). Residential outdoor samples were collected from several homes in each EMA for approximately 6 weeks during each of the DEARS seasons. Sampling in EMA5 did not begin until Season 3. Further details on the EMAs and participant selection can be found in Williams et al. (2008). The number of valid samples for each EMA by season is provided in Table S1.

The DEARS sample filters were analyzed for mass (gravimetric; Lawless and Rodes, 1999), elemental composition (X-ray Fluorescence, XRF; Dzubay et al., 1998), elemental and organic carbon (Thermal Optical Reflectance, TOR; Birch and Cary, 1996) and nitrate (Ion Chromatography; Demokritou et al., 2001). A correction method was not used for organic carbon (OC) artifacts as OC varies by microenvironment suggesting difficulty in using a correction (Williams et al., 2008; Olson and Norris, 2005).

In addition, CSN $PM_{2.5}$ data from Allen Park, MI was obtained from the EPA Air Quality System database (US EPA, 2007a). The CSN data selected covered January 1, 2004 to December 31, 2006 (1-in-3 day sampling; n = 355 samples) to correspond with the years in which the DEARS samples were collected. CSN $PM_{2.5}$ data from Granite City, IL covering October 3, 2007 to December 27, 2009 (1-in-6 day sampling; n = 126 samples) were also evaluated. This site is located downwind of an integrated steel manufacturing plant and CSN data collection began in October 2007. Species used from both CSN data sets included elements, nitrate, ammonium, potassium ion, organic carbon, and elemental carbon.

2.2. Receptor modeling

Sources contributing to the $PM_{2.5}$ for each sample were quantified using the EPA Chemical Mass Balance Model (CMB 8.2; US EPA, 2004b). CMB is a stand-alone program that quantifies PM sources on a local, urban, and/or regional scale via weighted regression. Input data for this study included elements, nitrate, organic carbon and elemental carbon concentration and uncertainties along with measured source profile concentrations and uncertainties. Prior to running CMB, a reconstructed $PM_{2.5}$ mass (CM) was calculated for each sample using the following formula obtained from Grover et al. (2008):

$$CM(PM_{2.5}) = 2.14\,[Si] + 1.4[Ca] + 1.43[Fe] + 1.2[K] + 1.24[Zn] + 1.8[Cl] + 4.125[S] + 1.29\,[NO_3^-] + \mathbf{X}[OC] + [EC]$$

The factor **"**X" for OC was obtained by plotting mass versus organic carbon and determining the intercept from linear regression. The OC intercept was 1.41 for Allen Park samples and 1.87 for residential outdoor samples. Samples with $PM_{2.5}$ mass measurements greater than 25% of the reconstructed mass were removed from CMB analysis. Across all seasons, less than 1% of the DEARS Allen Park and residential outdoor samples were removed.

Selection of CMB source profiles included profiles from the report "Integration of Results for the Upper Midwest Urban Organics Study" (Brown et al., 2006; referred to as LADCO report). These profiles were selected because they contain elements, ions, carbonaceous species and speciated organic aerosol data. Speciated organic aerosol has been measured in the DEARS samples but is not reported here. The source profiles selected for this analysis provide a consistent set of profiles for a combined inorganic and speciated organic aerosol source apportionment analyses (future analyses). The secondary sulfate and secondary nitrate profiles were obtained from the EPA SPECIATE Database. The road dust profile was obtained from Hildemann et al. (1991) and the gasoline and diesel profiles were obtained from Schauer et al. (2002) and Schauer et al. (1999), respectively. Initial CMB runs could not differentiate between diesel and gasoline contributions therefore a composite motor vehicle profile was developed. Based on the LADCO report, gasoline and diesel contributions to Allen Park for 2002-2004 (estimated by PMF) were 60% and 40% of the total traffic contribution to $PM_{2.5}$ mass, respectively. A weighting factor of 0.60 (gasoline) and 0.40 (diesel) was applied to each specie in the gasoline and diesel profiles to obtain a composite motor vehicle profile. A

biomass combustion profile (Fine et al., 2004) was initially considered however, unreasonable biomass contributions (10-40% by mass) were estimated by CMB using elemental K as a marker for biomass/wood combustion. In personal communication (J.J. Schauer; June 3, 2011), elemental K has been found to be a poor tracer for wood smoke. Major sources of OC are difficult to apportion using only trace elements; organic tracers are ideal. To account for organic carbon sources including gasoline engines, biomass combustion, and secondary organic aerosol, an organic matter source profile was included in CMB with OC equal to 1 and all other species equal to zero. The source profiles used for CMB in this study are provided in Table S2.

Measured source profiles specifically for the Detroit area were not available. Source profiles can vary in different areas; the available profiles may not truly represent sources impacting Detroit, in particular local industrial sources. The EPA Positive Matrix Factorization (PMF 4.0; US EPA, 2009) model was used to obtain more representative local source profiles using CSN $PM_{2.5}$. The PMF model employs a constrained, weighted, least-squares algorithm to generate source profiles and associated uncertainties, and source contributions using species concentrations and uncertainties. Input data for PMF included elements, nitrate, ammonium, potassium ion, organic carbon and elemental carbon concentrations and uncertainty estimates. Initial PMF results indicated that the uncertainties were significantly underestimated as shown by the Q values – Q (robust) value was over twice the Q (theoretical) value. An uncertainty matrix was developed by Dr. Jay Turner (Washington University, St. Louis) using co-located precision data from the Cleveland, OH CSN site (G.T. Craig). More details on the uncertainty matrix can be found in Wade et al. (2008). Cleveland shares many of the same characteristics as the Detroit area in that it is heavily impacted by industry. The uncertainty matrix developed from Cleveland was applied to the Allen Park CSN data for PMF modeling.

In EPA PMF 4.0, the source profile uncertainties or the variability associated with the source profiles (base) were calculated using the classic block bootstrap method. A new method referred to as the Discrete Difference Percentile (DDP; US EPA, 2007b) was used to provide 90% and 95% confidence intervals. This method captures the variability of bootstrap run values as a percent of the base run value and is centered about the base run values.

CMB results were evaluated using fit diagnostics to determine how well the model fit the measured data. In addition, samples were invalidated and removed based on any of the following criteria: collinearity, negative motor vehicle contributions, or zero contribution for all

sources. Calculated sample masses were retained if the mass apportionment was between the acceptable ranges (80-120%; US EPA, 2004b) otherwise the mass apportionment was re-scaled to the measured mass.

2.3. Statistical analysis

Statistical analysis was conducted using SAS software (SAS Institute Inc., Cary, NC). A non-parametric one-way Wilcoxon score test was used to determine spatial variability of source impacts across the EMAs, and to compare source impacts for the EMAs with the Allen Park CSN site. A significance level of 0.05 was used and *p*-values are reported for this study. *P*-values less than 0.05 indicated variability of sources either between EMAs or variability of sources in EMAs compared to Allen Park.

3. Results and discussion

3.1. Local industrial $PM_{2.5}$ source profiles

Application of EPA PMF 4.0 using the Allen Park CSN data (2004-2006) produced a 7-source solution (Table 1) with approximately 93% of the mass explained. The PMF contributions agreed with previous source apportionment studies that have used different date ranges of Allen Park CSN data (Table 1), although the steel manufacturing contribution was higher and the motor vehicle contribution slightly lower for the date range of this study. Industrial source profiles from PMF (Figure 1) included steel manufacturing (loaded with Fe) and mixed industrial (loaded with Zn). $PM_{2.5}$ zinc has been associated with municipal incinerators (Nagib and Inouye, 2000). In addition, zinc can be emitted from basic oxygen furnaces in steel manufacturing facilities (Sammut et al., 2008).

The Allen Park steel manufacturing and mixed industrial PMF profiles using CSN data were combined with published profiles (motor vehicles, road dust, secondary sulfate, and secondary nitrate) in the CMB model to evaluate sources impacting the DEARS samples. However, the PMF profiles representing steel manufacturing and mixed industrial sources were not clearly identified as demonstrated by poor CMB fit diagnostics. Allen Park is located upwind of the industrial sources in the Detroit area; this site may not be impacted as frequently or strongly as sites located closer to industrial sources to provide adequate source profiles using the 1-in-3 day sampling CSN data. As an alternative, CSN data covering 2007-2009 from a site

in Granite City, IL (Gateway Regional Medical Center; 38.70°N, 90.14°W) located near an integrated steel manufacturing facility was evaluated with PMF to identify a steel manufacturing profile and a mixed industrial profile. This steel facility is considered to be a significant source impacting the St. Louis area and the largest $PM_{2.5}$ source contributor. Two profiles were found (Figure 1) that were similar to measured industrial profiles collected from specific industrial operations in the Granite City area (unpublished results). These profiles are representative of Detroit since both Detroit and the St. Louis area have integrated steel manufacturing facilities and supporting industries such as plating and metal working. These profiles were used along with the published profiles in the CMB analysis of the DEARS samples (Table S2), and the CMB diagnostics showed improved fit of the measured data.

3.2. CMB source contribution estimates for DEARS Allen Park samples

CMB source contribution estimates for DEARS samples collected at Allen Park during Seasons 1 to 4 are displayed in Table 2. Predominant source contributions during all the DEARS seasons included motor vehicles (24-38% by mass), secondary sulfate/coal combustion (19-35%), secondary nitrate (5-35%) and organic matter (17-21%). Significant motor vehicle contributions at Allen Park are expected due to the site's proximity to a major interstate highway. Secondary sulfate contributions were higher during the summer (Seasons 1 and 3) and secondary nitrate contributions were higher in the winter (Seasons 2 and 4), as expected. Road dust contributed 3-5% of the mass across seasons, while steel manufacturing and mixed industrial sources contributed less than 2% for Allen Park during each season.

The relative contribution of sources estimated by CMB for the DEARS Allen Park samples overall compared well with estimates using Allen Park CSN data for 2004-2006 (Table 2). However, road dust and organic matter contributions for the DEARS seasons were about two fold higher compared to the average CSN contributions (over a 2 year time period). Investigating seasonal patterns (Table S3), road dust and motor vehicle contributions were higher in the summer (July to August) compared to winter (January to March) for both DEARS and CSN data. Differences were observed during the winter in which higher steel manufacturing, mixed industrial, and organic matter contributions were higher in DEARS, but summer was higher than winter for CSN data for the same sources. Daily sampling during DEARS versus 1-in-3 day sampling for the CSN data may account for these differences.

CMB results for both the DEARS Allen Park samples and the Allen Park CSN data for 2004-2006 overall were consistent with other source apportionment studies in the Detroit area (Table 1 and 2) except industrial source contributions were lower in the DEARS samples and steel manufacturing was higher in the CSN data.

3.3. CMB source contribution estimates for DEARS residential outdoor samples

CMB source contribution estimates for the DEARS residential outdoor samples averaged by EMA and season are displayed in Table 3. The number of valid samples for these averages generally ranged from 20 to 49 (Table S1). Averaged over all EMAs, the predominant sources impacting the DEARS residential outdoor samples were the same as the DEARS Allen Park samples for each season (as percent of total mass), including motor vehicles (Season 1, 32%; Season 2, 24%; Season 3, 30%; Season 4, 28%), secondary sulfate/coal combustion (Season 1, 32%; Season 2, 17%; Season 3, 35%; Season 4, 17%), and organic matter (Season 1, 18%; Season 2, 21%; Season 3, 21%; Season 4, 20%). Secondary sulfate contributions were higher during the summer and secondary nitrate contributions were higher in the winter, as expected. Organic matter contributions were fairly uniform across the seasons, as for the Allen Park samples. Averaged over all EMAs, road dust contributed 5–10% of the mass across seasons, while steel manufacturing and mixed industrial sources contributed 0.6-2.2% and 0.1-0.2%, respectively across seasons.

Comparison of the CMB source contribution estimates across EMAs in Table 3 and Table S4 provides support for the source impact type assigned to each EMA prior to the study. The EMA designated as impacted by diesel truck traffic (EMA3) had the highest motor vehicle contributions (4.8-6.6 μg m^{-3}) for all seasons and included neighborhoods in central Detroit within 300 m of the major freeways leading to the Ambassador Bridge – connects Detroit, MI with Windsor, Canada and is the busiest international commercial vehicle crossing in North America (Southeast Michigan Council of Government, 2007). Also, the two EMAs designated as impacted by industry (EMA1 and EMA5) had the highest steel manufacturing (237-923 ng m^{-3}) and mixed industrial contributions (32-84 ng m^{-3}) for all seasons. Both EMA1 and EMA5 included neighborhoods in central Detroit, with EMA1 located to the north of the heavily industrialized Zug Island and EMA5 located closer to automobile manufacturing point sources in Dearborn. Although EMA4 and EMA6 were designated as traffic and highway impacted

respectively, the motor vehicle contribution was generally similar to or less than the EMAs impacted by industry located in central Detroit (EMA1 and EMA5) in both concentration and by percent of mass. However, these traffic-impacted EMAs were located outside of central Detroit, to the northeast and the northwest. These same EMAs (4 and 6) along with EMA7, selected to represent the regional contribution of sources upwind, had the highest percent of the mass from regional sources such as secondary sulfate across all seasons.

3.4. Spatial variability in source impacts

To further examine the spatial variability in source impacts, average CMB source contribution percentages and the combined mass contribution from steel manufacturing and mixed industrial sources (in ng m^{-3}) are shown in Figure 2 for Seasons 3 and 4 when sampling for EMA5 was included in the DEARS. The effect of meteorology and long-range transport on the spatial variability of PM is not included in this discussion as it has been reported by Thornburg et al. (2009) and George et al. (2010). Figure 2 shows that the relative contribution of each source varied between EMAs and Allen Park. EMAs 1 and 5 had higher combined steel manufacturing and mixed industrial contributions (average of 519 ng m^{-3}; 2.7% by mass), indicating that these sites were impacted the most by local industrial activity. On average 50 tons of zinc compounds were emitted per year during 2004-2006 from stationary point sources in Detroit – Wayne County (US EPA TRI, 2009); zinc was identified in Figure 1 with the highest mass loading from the mixed industrial source. Based on the 2005 NEI, industrial metal processing was the highest $PM_{2.5}$ point source emitter (1,853 tons) in Wayne County (US EPA NEI, 2005). EMA3 had higher motor vehicle contributions (average of 5.9 μg m^{-3}; 33% by mass) and the contribution of road dust was somewhat higher for the EMAs located in central Detroit (EMAs 1, 3 and 5; range of 1.0-1.6 μg m^{-3}). EMA4 had somewhat higher contributions from secondary sulfate (average of 5.8 μg m^{-3}; 33% by mass) compared to the other EMAs.

While road dust, steel manufacturing and mixed industrial sources are small contributors to the $PM_{2.5}$ mass across EMAs, species associated with these sources are larger contributors to total metals used in the CMB analysis (Si, Ca, Mn, Fe, Zn and Pb; Figure S1). Iron (Fe) and zinc (Zn) are associated with steel manufacturing and mixed industrial sources, respectively. Industrial impacted sites (EMAs 1 and 5) had the highest Fe concentrations (average of 468 ng m^{-3} compared to 151 ng m^{-3} for EMAs 3, 4, 6 and 7) and Zn concentrations (average of 74.8 ng

m^{-3} compared to 31.9 ng m^{-3} for EMAs 3, 4, 6 and 7). Road dust markers including silicon and calcium accounted for 14-40% of the total metal mass.

Spatial variability of source impacts among the DEARS sampling sites was statistically evaluated via non-parametric one-way Wilcoxon score as shown in Table 4 for all seasons combined. The first column of Table 4 shows the results of the comparison across all EMAs, and the remaining columns display results comparing the individual EMAs to Allen Park (same day only). Across all EMAs, statistically significant differences were found for all the source types with the exception of secondary sulfate ($p = 0.12$) and secondary nitrate ($p = 0.66$). These results indicate intra-urban variations in the different sources contributing to $PM_{2.5}$ at each of the EMAs including road dust, motor vehicles, steel manufacturing, and mixed industrial sources. Secondary sulfate and secondary nitrate contributions were not statistically different between EMAs which is consistent with these sources being primarily due to regional transport.

Results from the comparisons of source contributions for each EMA versus Allen Park in Table 4 provide further information on the spatial variability in source impacts. Allen Park is located near a major highway (I-75) which is characterized by a mixture of gasoline and diesel vehicles, and is approximately 28 km southwest of central Detroit. Although the contribution of motor vehicles was statistically different when compared across all EMAs, some EMAs were not statistically different from Allen Park (EMA1, EMA3, and EMA5). EMAs with statistically different motor vehicle contributions compared to Allen Park including EMA4, EMA6 and EMA7, were the farthest away (31.4 km northeast, 17.7 km north and 23.2 km west, respectively). Significant differences ($p < 0.01$) were observed for road dust contributions for the three EMAs located in central Detroit (EMA1, EMA3, and EMA5) compared to Allen Park. Contributions from steel manufacturing and mixed industrial sources for EMA1, EMA4 (steel manufacturing only), EMA5, EMA6 and EMA7 also differed from Allen Park. Secondary sulfate and secondary nitrate contributions were not different between Allen Park and any of the EMAs which is again consistent with regional transport for this source.

4. Conclusions

This study demonstrated that sources of $PM_{2.5}$ can be quantified for human exposure studies such as the DEARS using a combination of receptor modeling techniques. Application of the CMB model using PMF-generated source profiles for local sources without measured profiles provided reasonable estimates of the major source contributions when the profiles were

generated based on CSN monitoring data routinely impacted by similar local sources. The CMB results were fairly consistent with past source apportionment studies for Detroit, with the exception of lower industrial contributions.

A major goal of DEARS was to determine if a central monitoring site (Allen Park) is sufficient to represent residential or personal exposures to $PM_{2.5}$ sources for an urban industrial area such as Detroit. This source apportionment analysis provided confirmation that the residential monitoring areas selected for the DEARS were differentially impacted by localized PM sources including motor vehicles, road dust, steel manufacturing, and mixed industrial sources. Therefore, the proximity of an individual's residence to different PM sources may be an important factor for how representative the Allen Park monitoring location is. Allen Park may adequately represent areas of Wayne County upwind of the major industrial sources in Detroit (such as EMA6 and EMA7), but not areas in close proximity to them (such as EMA1 and EMA5) or to a major local diesel traffic source (such as EMA3). Industrial source profiles generated from PMF using the Allen Park CSN data were also not able to characterize sources sufficiently in CMB for the DEARS samples.

Several limitations of this study are noteworthy for informing future studies. The lack of measured source profiles for the major local industrial sources in Detroit required significant efforts to develop appropriate profiles for input to CMB. Source-specific profile measurements are needed for local sources in Detroit to improve source apportionment. Furthermore, traditional 24-hr data may not capture variability in contributions especially from industrial sources. More recently, high-time resolution measurements (1-hr or less) have been investigated using the Semi-continuous Elements in Aerosol Sampler (SEAS; Pancras and Landis, 2011). Collection of these data in human exposure and source apportionment studies may provide more reliable source contribution estimates for local industrial sources. However, evaluating the use of SEAS data in receptor models is a current research need as high-time resolution data is noisier and source profiles may be more transient.

Concerning nitrate data, during the DEARS, only particle-bound nitrate was collected using a mini denuder. Collection of both particle-bound and gaseous nitrate in the DEARS would have allowed for better comparison to CSN data which represents both forms of nitrate. Personal monitors that collect both forms of nitrate should be developed and implemented in human exposure studies such as the DEARS. Another limitation of the DEARS was quantifying

biomass burning contributions using the available elemental potassium data. The DEARS samples were not analyzed for potassium ion concentrations which may have provided improved source apportionment. Many studies have suggested that water soluble organic carbon is a sufficient marker for biomass burning and secondary aerosol (Sullivan et al., 2011; Sullivan et al., 2006). Human exposure and source apportionment studies should consider measuring potassium ion and water soluble organic carbon concentrations to help resolve biomass burning contributions. The lack of an OC correction methodology was another constraint in this study. Excessive OC artifact on personal samples may have resulted in higher organic matter contributions. Development of a standardized OC correction method would be useful for future human exposure studies. Lastly, an organic matter source profile was included due to the lack of distinct marker species for organic sources. Speciated organic aerosol data is available for the DEARS samples and these data will be used in receptor models to explore the relative contribution of gasoline, diesel and biomass combustion sources impacting Detroit.

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Figure 1

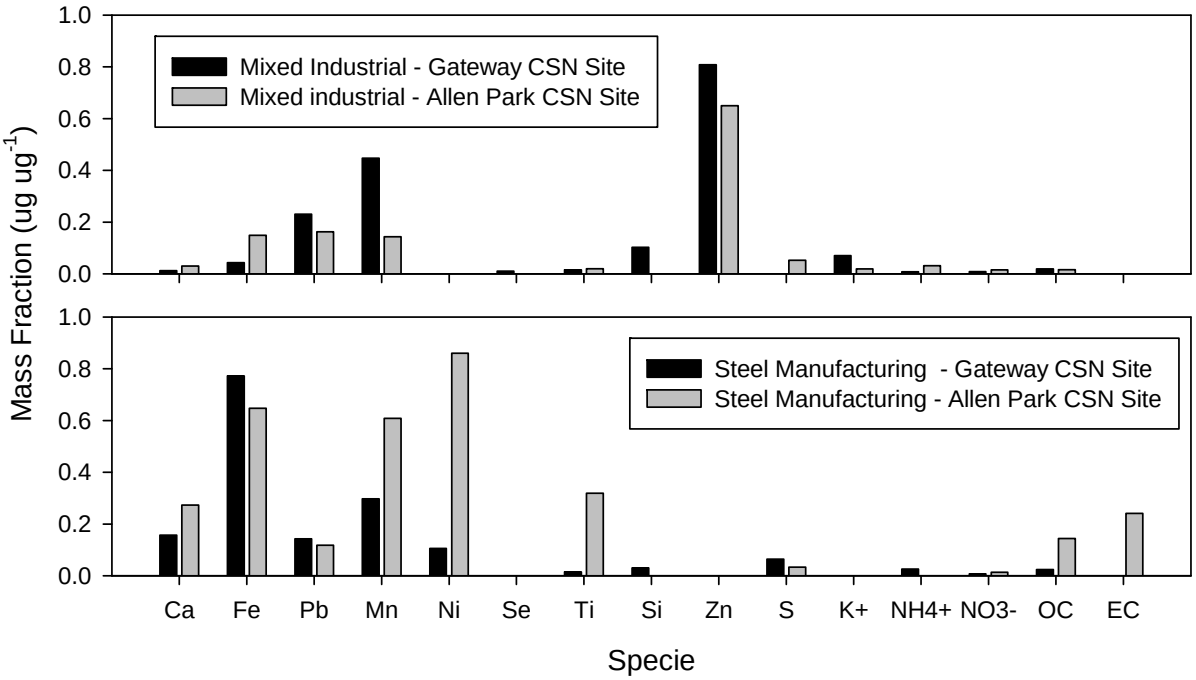

Mixed Industrial - Gateway CSN Site
Mixed industrial - Allen Park CSN Site
Steel Manufacturing - Gateway CSN Site
Steel Manufacturing - Allen Park CSN Site
Mass Fraction (ug ug-1)
1.0
0.8
0.6
0.4
0.2
0.0
Ca
Fe
Pb
Mn
Ni
Se
Ti
Si
Zn
S
K+
NH4+
NO3-
OC
EC
Specie

Figure 2 (Color Figure)

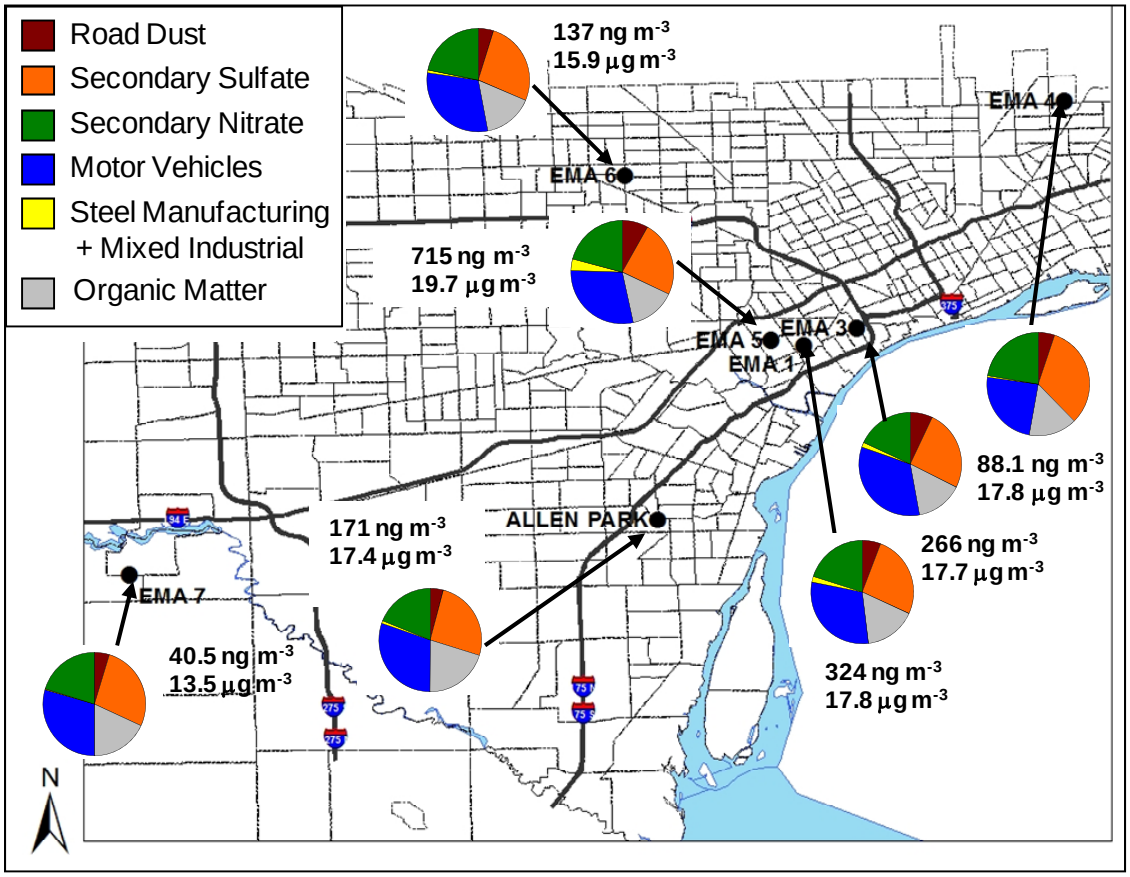


Table 1. Previous Source Apportionment Results (in %) for the Allen Park, MI CSN Site

	2000-2005 (Hopke, 2007)	2000-2005 (Gildemeister et al., 2007)	2002-2004 (Brown et al., 2006)	2002-2005 (Buzcu et al., 2007)	2001-2006 (Wade et al., 2008)	2004-2006 (PMF – this study)	2004-2006 (CMB – this study)
Gasoline	18	15	21	21	-	22*	40*
Diesel	10	42	14	14	6.0	-	
Biomass Burning/ Wood Combustion	2.3	3.2	1.8	2.0	-	2.0	-
Organic Matter	-	-	-	-	19	-	12
Secondary Sulfate/Coal	29	31	27	27	35	33	26
Secondary Nitrate	25	28	25	25	20	23	19
Soil/Road Dust	5.7	8.0	3.7	4.0	4.0	8.4	2.2
Iron/Steel Manufacturing	3.4	3.2	-	-	< 1.0	7.6	0.55
Mixed Industrial	3.5	-	4.7	-	10	4.3	0.08
Industrial Zinc	-	-	-	5.0	6.0	-	-
Metal Plating	-	-	3.3	3.0	-	-	-
Aged Sea and Road Salt	4.0	4.0	-	-	-	-	-

* Includes gasoline and diesel

Table 2. Average CMB Source Contribution Estimates in μg m^{-3} (% of mass) for the DEARS Allen Park Samples.

	Season 1 Summer 2004	Season 2 Winter 2005	Season 3 Summer 2005	Season 4 Winter 2006	Combined Seasons 1 to 4	CSN Data 2004-2006
Road Dust	0.86 (5.4)	0.51 (2.5)	0.87 (4.6)	0.62 (4.4)	0.70 (4.0)	0.34 (2.2)
Secondary Sulfate	5.3 (34)	3.8 (19)	6.7 (35)	2.6 (19)	4.6 (26)	3.9 (26)
Secondary Nitrate	0.76 (4.8)	7.0 (35)	1.1 (5.8)	3.9 (27)	3.4 (20)	2.9 (19)
Motor Vehicles	5.9 (38)	4.7 (24)	6.4 (34)	4.3 (30)	5.3 (30)	6.1 (40)
Steel Manufacturing*	74 (0.47)	131 (0.65)	111 (0.58)	197 (1.4)	150 (0.86)	84 (0.55)
Mixed Industrial*	15 (0.10)	24 (0.12)	16 (0.09)	16 (0.12)	22 (0.12)	12 (0.08)
Organic Matter#	2.7 (17)	3.8 (19)	4.0 (21)	2.6 (19)	3.9 (22)	1.9 (12)
Calculated Mass	15.7	20.0	19.1	14.3	17.4	15.2

*Units of ng m^{-3}

Organic matter includes gasoline vehicles, biomass burning and secondary organic aerosol.

Table 3. Average CMB Source Contribution Estimates in μg m^{-3} (% of mass) for the DEARS Residential Outdoor Samples.

EMA	1	3	4	5	6	7
EMA Type	**Industrial**	**Diesel**	**Traffic/Industrial**	**Industrial**	**Highway**	**Regional**
Season 1 (Summer 2004)						
Motor Vehicles	6.3 (35)	6.5 (38)	4.6 (27)	-	4.8 (34)	3.8 (23)
Steel Manufacturing*	237 (1.3)	85 (0.50)	20 (0.12)	-	41 (0.29)	60 (0.37)
Mixed Industrial*	52 (0.29)	19 (0.11)	13 (0.08)	-	8.8 (0.06)	9.1 (0.06)
Season 2 (Winter 2005)						
Motor Vehicles	4.5 (30)	4.8 (24)	2.9 (20)	-	4.6 (21)	2.7 (22)
Steel Manufacturing*	255 (1.7)	181 (0.93)	37 (0.25)	-	147 (0.69)	52 (0.43)
Mixed Industrial*	34 (0.23)	29 (0.15)	11 (0.07)	-	26 (0.12)	14 (0.11)
Season 3 (Summer 2005)						
Motor Vehicles	6.4 (32)	6.6 (34)	4.8 (24)	6.2 (30)	5.9 (33)	5.2 (30)
Steel Manufacturing*	243 (1.2)	193 (1.0)	43 (0.21)	375 (1.8)	70 (0.39)	60 (0.35)
Mixed Industrial*	33 (0.16)	20 (0.10)	19 (0.10)	32 (0.18)	11 (0.06)	13 (0.07)
Season 4 (Winter 2006)						
Motor Vehicles	4.5 (29)	5.0 (32)	3.7 (25)	5.2 (28)	3.7 (26)	3.3 (29)
Steel Manufacturing*	330 (2.1)	297 (1.9)	102 (0.70)	923 (5.0)	172 (1.2)	16 (0.14)
Mixed Industrial*	32 (0.20)	25 (0.16)	22 (0.15)	84 (0.45)	22 (0.15)	7.1 (0.06)

*Concentration in ng m^{-3}

Table 4. *P*-values for the Non-parametric One-way Wilcoxon Score Test Comparing Variability of Sources in DEARS Allen Park and Residential Outdoor Samples.

	All EMAS[*]	EMA1	EMA3	EMA4	EMA5[#]	EMA6	EMA7
Road Dust	**< 0.01**	**< 0.01**	**0.01**	0.91	**< 0.01**	0.27	0.88
Secondary Sulfate	0.12	0.86	0.57	0.96	0.49	0.17	0.49
Secondary Nitrate	0.66	0.18	0.41	0.43	0.43	0.68	0.61
Motor Vehicles	**< 0.01**	0.98	0.77	**< 0.01**	0.81	**< 0.01**	**< 0.01**
Steel Manufacturing	**< 0.01**	**< 0.01**	0.82	**< 0.01**	**< 0.01**	**0.02**	**< 0.01**
Mixed Industrial	**< 0.01**	**< 0.01**	**0.19**	0.14	**< 0.01**	**0.02**	**< 0.01**
Organic Matter	**< 0.01**	**0.99**	**< 0.01**	0.98	**0.03**	0.49	**< 0.01**

p-values in bold are significant at $\alpha < 0.05$
[*] Not compared to Allen Park
[#] Season 3 and 4 Only

Supplement

Table S1. Number of Homes and Measurements for the DEARS Residential Outdoor and Allen Park Samples. Exposure Measurement Area (EMA). Only Valid Samples are Shown.

	Season 1 (Summer 2004)		Season 2 (Winter 2005)		Season 3 (Summer 2005)		Season 4 (Winter 2006)	
	Homes N	Samples N	Homes N	Samples N	Homes N	Samples N	Homes N	Samples N
EMA1 (Industrial)	8	38	6	20	9	38	9	43
EMA3 (Diesel)	8	38	10	46	5	23	5	25
EMA4 (Traffic/Industrial)	8	30	5	21	8	40	8	37
EMA5 (Industrial)	-	-	-	-	8	39	8	36
EMA6 (Highway)	9	36	7	27	10	46	10	49
EMA7 (Regional)	6	26	7	28	1	26	1	35
Ambient (Allen Park)	N/A	28	N/A	35	N/A	32	N/A	35

Table S2. CMB Source Profiles (in weight % of fine particle mass).

	Road Dust[+]	Secondary Sulfate[#]	Secondary Nitrate[#]	Motor Vehicles[+]	Mixed Industrial*	Steel Manufacturing*	Organic Matter
OC	13.5 ± 1.35	0 ± 0.0001	0 ± 0.0001	17.1 ± 1.85	19.4 ± 1.94	3.18 ± 17.5	100 ± 20.0
EC	1.06 ± 0.106	0 ± 0.0001	0 ± 0.0001	9.25 ± 1.63	5.45 ± 5.45	0 ± 0.0001	0 ± 0.0001
Si	12.4 ± 1.24	0 ± 0.0001	0 ± 0.0001	0.201 ± 0.068	1.12 ± 0.984	0.282 ± 0.559	0 ± 0.0001
S	0.260 ± 0.026	24.3 ± 2.43	0 ± 0.0001	0.188 ± 0.025	0 ± 0.0001	3.50 ± 7.79	0 ± 0.0001
Ca	4.44 ± 0.444	0 ± 0.0001	0 ± 0.0001	0.111 ± 0.073	0 ± 0.0001	1.45 ± 1.36	0 ± 0.0001
Mn	0.120 ± 0.012	0 ± 0.0001	0 ± 0.0001	0.002 ± 0.031	0.851 ± 0.703	0.612 ± 0.358	0 ± 0.0001
Fe	6.23 ± 0.623	0 ± 0.0001	0 ± 0.0001	0.043 ± 0.018	0 ± 0.0001	55.1 ± 26.7	0 ± 0.0001
Zn	0.150 ± 0.015	0 ± 0.0001	0 ± 0.0001	0.071 ± 0.013	7.13 ± 5.01	0 ± 0.0001	0 ± 0.0001
Pb	0.110 ± 0.011	0 ± 0.0001	0 ± 0.0001	0.002 ± 0.056	0.265 ± 0.265	0.299 ± 0.299	0 ± 0.0001
NO_3^-	0 ± 0.0001	0 ± 0.0001	75.1 ± 68.8	0 ± 0.0001	0 ± 0.0001	0 ± 0.0001	0 ± 0.0001

[+] Profiles obtained from LADCO report (Brown et al., 2006)
[#] Profiles obtained from EPA SPECIATE Database.
*Profiles obtained by EPA PMF 4.0 using CSN data (2007-2009) from Gateway Medical Center (Granite City, IL).

Table S3. Seasonal Average CMB Source Contribution Estimates in μg m^{-3} (% of mass) for the DEARS Allen Park and Allen Park CSN Samples.

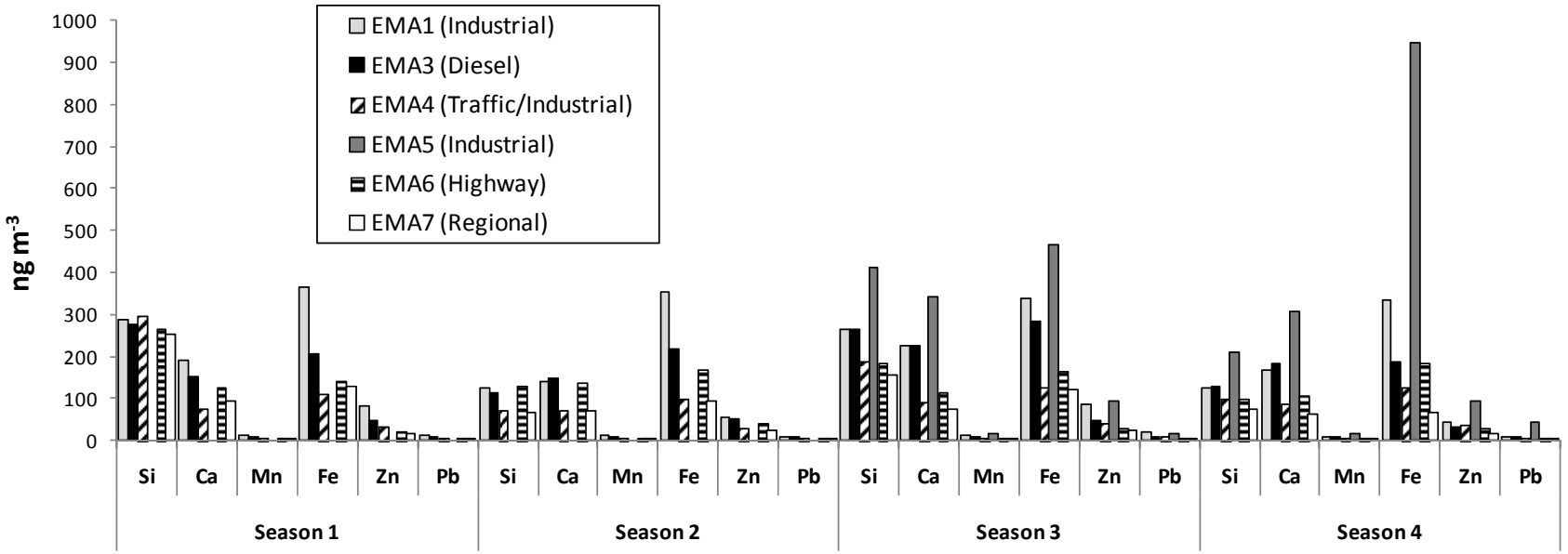
	DEARS Allen Park			Allen Park CSN		
	Average	Summer	Winter	Average	Summer	Winter
Road Dust	0.70 (4.0)	0.87 (4.9)	0.56 (3.2)	0.34 (2.2)	0.40 (2.5)	0.24 (1.5)
Secondary Sulfate	4.6 (26)	6.1 (34)	3.3 (19)	3.9 (26)	5.4 (33)	3.2 (20)
Secondary Nitrate	3.4 (20)	0.96 (5.4)	5.6 (32)	2.9 (19)	0.96 (5.9)	5.1 (32)
Motor Vehicles	5.3 (30)	6.2 (35)	4.5 (26)	6.1 (40)	7.0 (43)	5.4 (34)
Steel Manufacturing*	150 (0.86)	95 (0.54)	197 (1.1)	84 (0.55)	117 (0.72)	79 (0.49)
Mixed Industrial*	22 (0.12)	16 (0.09)	26 (0.15)	12 (0.08)	17 (0.10)	14 (0.09)
Organic Matter	3.9 (22)	3.4 (19)	4.3 (25)	1.9 (12)	1.5 (1.9)	1.9 (12)
Calculated Mass	17.4	17.6	17.3	15.2	16.2	16.0

*units = ng m^{-3}

Table S4. Average CMB Source Contribution Estimates in μg m^{-3} (% of mass) for the DEARS Residential Outdoor Samples.

EMA	1	3	4	5	6	7
EMA Type	**Industrial**	**Diesel**	**Traffic/Industrial**	**Industrial**	**Highway**	**Regional**
Season 1 (Summer 2004)						
Road Dust	1.6 (8.7)	1.5 (9.0)	1.6 (9.7)	-	1.5 (11)	1.7 (10)
Secondary Sulfate	5.7 (31)	4.8 (29)	5.8 (34)	-	4.1 (29)	6.7 (41)
Secondary Nitrate	1.3 (7.2)	1.2 (7.0)	1.4 (8.3)	-	1.1 (7.4)	1.1 (6.7)
Organic Matter	2.9 (16)	2.8 (16)	3.6 (21)	-	2.7 (19)	3.1 (19)
Season 2 (Winter 2005)						
Road Dust	0.51 (3.4)	0.57 (2.9)	0.53 (3.6)	-	0.76 (3.6)	0.46 (3.8)
Secondary Sulfate	1.8 (12)	3.3 (17)	2.7 (18)	-	4.1 (19)	2.3 (19)
Secondary Nitrate	4.4 (29)	6.9 (35)	5.3 (35)	-	7.5 (35)	3.7 (31)
Organic Matter	3.4 (23)	3.8 (19)	3.4 (23)	-	4.3 (20)	2.9 (24)
Season 3 (Summer 2006)						
Road Dust	1.5 (7.2)	1.5 (7.7)	1.2 (5.8)	2.1 (9.9)	0.89 (5.0)	0.85 (4.9)
Secondary Sulfate	6.9 (34)	6.4 (32)	8.0 (40)	6.5 (31)	6.1 (34)	6.5 (38)
Secondary Nitrate	1.3 (6.5)	1.1 (5.8)	1.4 (6.9)	1.2 (5.7)	1.2 (6.5)	0.97 (5.6)
Organic Matter	4.0 (20)	3.7 (19)	4.7 (23)	4.7 (22)	3.6 (20)	3.7 (21)
Season 4 (Winter 2006)						
Road Dust	0.70 (4.4)	0.98 (6.3)	0.57 (3.9)	1.2 (6.3)	0.63 (4.5)	0.53 (4.6)
Secondary Sulfate	2.9 (18)	2.5 (16)	2.7 (18)	3.0 (16)	2.3 (17)	2.1 (18)
Secondary Nitrate	4.1 (26)	4.1 (26)	4.5 (31)	4.5 (24)	3.8 (27)	3.2 (28)
Organic Matter	3.2 (20)	2.7 (17)	3.0 (20)	3.6 (19)	3.3 (24)	2.2 (19)

Figure S1. Average Species Concentration in ng m^{-3} (% of total metals used in CMB) for the DEARS Residential Outdoor Samples.



Note:
Si and Ca: Markers for road dust
Fe and Mn: Makers for steel manufacturing
Zn and Pb: Markers for mixed industrial