UNIVERSITY OF CINCINNATI

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I, Matthew Terrell, hereby submit this original work as part of the requirements for the degree of:
Master of Science in Industrial Hygiene (Environmental Health)

It is entitled:
PM2.5 and Metal Exposures in Children Living Near a Ferromanganese Refinery

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Committee Chair: Tiina Reponen, PhD

Erin Nicole Haynes, DrPH

Patrick Ryan, PhD
PM$_{2.5}$ and Metal Exposures in Children

Living Near a Ferromanganese Refinery

A thesis submitted to the
Division of Research and Advanced Studies of the University of Cincinnati
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By

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ABSTRACT
Occupational studies have shown that excess exposure to manganese (Mn) can cause neurotoxic effects though little is known regarding health effects of ambient Mn exposure in children. A ferromanganese refinery in Marietta, OH reports the greatest amount of Mn fugitive air emissions in the nation. The aim of this study was to compare ambient levels of Mn in Marietta with those in a control city (Cambridge, OH) and to compare personal air monitoring results with the results obtained at stationary outdoor sites in Marietta. This study is part of a larger epidemiological study on the neurotoxic effects of Mn exposure in children, the Communities Actively Researching Exposure Study (CARES).

Stationary outdoor air samples were collected at two locations: Marietta College and Robinson Hill Rd, 5 and 2 miles from the refinery, respectively. The sampling was conducted for 8 months at Marietta College (n=83) and during three weeks at the Robinson Hill station (n=8). In Cambridge, 43 miles north of Marietta, stationary sampling was conducted for one week per season (n=10). Stationary samples were collected on Teflon filters for approximately 48 hours using Harvard-type PM2.5 impactors (MS&T Area Sampler; Air Diagnostics, Inc.). Personal air samples were collected on 20 participants, ages 7-9, living in non-smoking households enrolled in CARES. The personal sampling was conducted for 48 hours using PM2.5 samplers (Personal Modular Impactor; SKC Inc). Time weighted average (TWA) distance was computed to determine how far the personal sample was from the Mn refinery, based on reported activities. All air samples were analyzed for PM2.5 mass gravimetrically and for Mn, Al, Cr and Pb using inductively coupled plasma mass spectrometer. Al was selected as a crustal indicator element. Cr and Pb were selected because these elements are emitted from the refinery and other facilities in Marietta.

The PM2.5 mass measured at the three stationary sites varied from 0.07 to 27.5 μg/m³ and was not significantly different between the three sites. In contrast, Mn concentrations increased when the distance to the refinery decreased. The geometric mean concentrations (GM) for Cambridge, Marietta College and Robinson Hill were 2.0, 6.7, and 46.1 ng/m³, respectively (ANOVA: p < 0.001). A similar trend was seen for Al and Cr, but the differences were not statistically significant.

Personal samples had higher GM for PM2.5 and for the four metals than respective stationary samples. The largest differences between personal and outdoor stationary results were found with the crustal indicator Al, which was 4.2 times higher in personal than in stationary samples (p=0.03) and with the PM2.5 mass (2.9 times higher; p=0.01). Log-transformed TWA distance was significantly associated with log-transformed personal Mn (p=0.04) and personal Pb (p=0.01) and explained approximately 21% and 29% of the variability in personal exposure to Mn and Pb, respectively. The results indicate that children's PM2.5 exposure in Marietta is uniform throughout the city. Mn exposure is associated with the child's residential and school distance to the refinery.
ACKNOWLEDGEMENTS
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LIST OF ABBREVIATIONS
CARES Communities Actively Researching Exposure Study
Al Aluminum
Cr Chromium
EPA Environmental Protection Agency
GM Geometric Mean
GSD Geometric Standard Deviation
L/min Liters per minute
µg Microgram
µg/m$^3$ Micrograms per cubic meter
Mn Manganese
NAAQS EPA’s regulatory National Ambient Air Quality Standard
ng Nanogram
ng/m Nanograms per cubic meter
Pb Lead
PM$_{2.5}$ Particulate matter with a median cut diameter of 2.5 microns
PM$_{10}$ Particulate matter with a median cut diameter of 10 microns
Rfc EPA reference concentration at which no health effects should occur
BACKGROUND

**PM$_{2.5}$** - Increase in the concentration of airborne particles has been positively associated with increase in respiratory and cardiovascular illness (Norris et al., 1999; Goldberg et al., 2001; Dockery et al., 1993). These health effects have been more clearly associated with PM$_{2.5}$ (particulate matter with a median cut diameter of 2.5 microns) than with larger particles (Schwartz et al., 1996; Pope et al., 2009). The likelihood of exposure is increased with small particles, as they remain suspended in the air for relatively long periods of time, compared to larger particles. Additionally, the surface area to mass ratio increases with a decrease in particle size. So for each unit mass of PM$_{2.5}$ will be able to interact more with the respiratory tract, potentially causing greater harm. Finally, PM$_{2.5}$ will penetrate more deeply into the lungs than larger particles, which will likely deposit into the upper respiratory tract.

Community exposure to airborne particles from outdoor sources is typically measured using outdoor stationary samples, centrally placed in population centers. This may not accurately represent personal exposure because US citizens spend a majority of their time indoors (Klepis et. al, 2001; Robinson and Nelson, 1995). Indoor PM is a mixture of outdoor ambient particles and particles with indoor sources (Wallace, 1996). Personal exposures are often higher than both indoor and outdoor measurements, due to the “personal cloud” effect of particle resuspension from human activity and proximity to pollution sources (Wallace 2000), such as vehicles and industrial facilities. This “personal cloud” effect was demonstrated by a study conducted in Indianapolis, where particulate matter and manganese (Mn) were measured for 240 adult subjects using personal sampling, indoor, and outdoor sampling (Pellizzari et. al, 2001). Personal
sample results were higher than outdoor and fixed monitoring results for PM$_{2.5}$, but not for Mn. Low correlations were found between personal and outdoor PM$_{2.5}$ concentrations. High correlations between indoor and personal concentrations were found for PM$_{2.5}$ (r=0.923) and Mn (r=0.636) and attributed to the resuspension of dust during the subjects’ activities.

**Properties of Mn** - Manganese (Mn) is a trace mineral in humans required for biochemical reactions affecting brain function, bone and cartilage, and enzymatic activity (Freeland-Graves, 1988), but is neurotoxic at elevated concentrations. At high levels of exposure, Mn can cause a wide range of central nervous system (CNS) disorders, including mental confusion, decrease in motor function, and manganism. The neurodegenerative effects of manganism cause Parkinson’s-like symptoms that can progress even after exposure has ceased. In occupational studies, visual reaction time, hand-eye coordination, and hand steadiness were significantly impaired with high exposures to Mn (Roels et al, 1996). Children may be at risk at much lower concentrations than those found in occupational studies, because developing brains of children may be more susceptible to Mn disorders than the adult brain. Very little data exist for Mn exposure in children. Increased environmental Mn exposure in Canada was found to be associated with decrease in cognitive function (Mergler et al, 1999) and postural stability (Hudnell, 1999) at concentrations near the EPA’s reference concentration (Rfc) of 50 ng/m$^3$, a level thought to be safe for chronic inhalation exposure (EPA IRIS, 2009). Given the unique susceptibility of children to toxicant exposure, lower exposures than those found in the Hudnell study may present an
increased risk in children. Pilot data from the CARES study suggest children chronically exposed to low levels of Mn have subclinical impairment of postural balance (Standridge et al, 2008).

Marietta, OH - Marietta, OH offers a unique opportunity to study exposure to Mn in children because it is home to the only manganese refinery, Eramet Marietta, Inc, in the US and Canada. The refinery has been emitting Mn into the air and water for over 50 years. Manganese emissions from Eramet Marietta, Inc average over 468,000 pounds per year since tracking began in 1988, making it one of the highest point source in the nation (EPA TRI, 2009). Community members have reported symptoms consistent with Mn exposure and expressed concern about the industrial emissions for over twenty years. Reported symptoms include: bloody noses, headaches, burning eyes, metallic tastes, tremors, muscle aches, fatigue, nausea, sore throats, and difficulty breathing.

Crustal and Source Elements - Aluminum is the most abundant metal and the third most abundant element in the earth’s crust, comprising about 8.8% by weight. As trace elements (< 0.1%) in the earth’s crust, Mn and Pb are good markers to evaluate the effect of human generated pollution within the PM$_{2.5}$ composition. While Mn is the major pollutant emitted from Eramet Marietta, 390 pounds of Pb were reported in the EPA’s Toxic Release Inventory for 2007 from the Mn refinery’s neighbor, a power plant. Pb releases are also expected from automotive combustion and resuspension of lead-containing particles. Cr can be found in the earth’s crust at about 0.02% and is also generated through several pollution mechanisms. Chromium is emitted in the atmosphere during the combustion of coal and natural gas, wearing down of chromium-
containing asbestos brake linings, and in exhaust emission from automobile catalytic converters. Over 15,000 pounds of chromium was released into the air in 2007 from the Mn refinery and over 900 pounds from a power plant northwest of Marietta (EPI TRI, 2009).

**Communities Actively Researching Exposure Study (CARES)** - The purpose of this study is to investigate children’s exposures to PM$_{2.5}$ and metals for the larger CARES epidemiologic cohort study. The primary objective of the CARES study is to understand the long-term effects of air pollution, specifically Mn on children’s health. In achieving that long-term objective, baseline personal exposure samples were collected, along with stationary outdoor samples to assess airborne Mn exposure in Marietta children.

**HYPOTHESIS AND SPECIFIC AIMS**

Hypothesis$_1$ – Personal air monitoring results for PM$_{2.5}$ and Manganese will be significantly higher than stationary outdoor area air sampling results. To test Hypothesis$_1$, the following specific aims were conducted:

Specific Aim 1: Assess personal air exposure to Mn on children ages 7-9 years old.
Specific Aim 2: Assess outdoor stationary airborne Mn levels at Marietta College.

Hypothesis$_2$ – There is a negative association between distance from the ferromanganese refinery and Mn concentration in personal and outdoor stationary samples. To test Hypothesis$_2$, the following specific aims were conducted:

Specific Aim 3: Assess outdoor stationary airborne Mn levels at two additional sampling sites located at different distances from the refinery.
Specific Aim 4: Calculate each child’s TWA (Time Weighted Average) distance from the Mn refinery, based on locations reported by parents on the Time-Activity log, and investigate association between TWA distance and Mn levels.

METHODS

Recruitment - By the completion of the CARES study 400 children of age 7-9 will have been recruited; 200 from Marietta and 200 from a control city, Cambridge, OH. Cambridge was selected as a control city because of it is an Appalachian foothill city with similarity in size and population demographics. To be eligible to participate, the mother of the child must have lived in Marietta during her pregnancy. Children were recruited in various ways, including sending recruitment letters home through schools, radio ads, and fliers.

Parents of the child were asked a series of questions to determine the child’s eligibility for participation in the study. Children of smokers were not eligible to participate in the personal air sampling portion of the study. The first 26 eligible children were selected to participate in the personal air monitoring portion from the overall Marietta CARES study population. The parent and child were offered nominal compensation for their time and travel.

The characteristics of the children can be found in Table 1. Only 20 of the 26 children sampled are included because the other samples were invalid due to wet filters or pump failure. The high rate of invalid samples is expected, due to the active nature of young children and the long sampling period.
Table 1: Characteristics of the children from the Marietta Study Population

<table>
<thead>
<tr>
<th>Variables (n=20)</th>
<th>N</th>
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<tbody>
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<td>35%</td>
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<td>40%</td>
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<td>10</td>
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<td>5%</td>
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<tr>
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<td>40%</td>
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<td>Female</td>
<td>12</td>
<td>60%</td>
</tr>
<tr>
<td>Race</td>
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</tr>
<tr>
<td>Caucasian</td>
<td>19</td>
<td>95%</td>
</tr>
<tr>
<td>Non-Caucasian*</td>
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<td>5%</td>
</tr>
</tbody>
</table>

*Parents are Native American and Caucasian

Stationary outdoor air samples were collected at three stations, which were located on roofs unobstructed by trees or buildings, while avoiding locations where diesel trucks idle to avoid interference from Mn contaminants in the fuel. One of the three sampling stations was continuously operated for 8 months (from October, 2008 to June 2009) on the roof of a building on the Marietta College campus. The Marietta College sampling station was 5 miles from the Manganese Refinery. A total of 83 valid samples were collected at the Marietta College location during the 8 month sampling period. Ten samples were voided, due to wet filters, torn filters, or pump failure.

Stationary samples were also collected at the Robinson Hill Road station in Marietta to evaluate the effect of distance from the Mn refinery. The Robinson Hill Road sampling station, on the walkout roof of a 2 story home, was 2 miles from the Mn refinery. A total of 10 samples (8 valid) were collected at this station in a three week period in February, 2009. The sampling locations for the two stationary samplers in Marietta are shown in Figure 1.
For comparison purposes, stationary samples were collected in Cambridge, OH for 1 week in each fall (November 2008), winter (January 2009), and spring (May 2009). The sampling station of Cambridge, on the roof of a one story elementary school, was 43 miles from the Mn refinery. A total of 10 samples were collected at the Cambridge sampling station and all samples were valid.

Complete sampling protocol and the air sampling datasheet can be found in Appendix 3. Stationary samples were collected using Harvard-type PM$_{2.5}$ impactors (MS&T Area Sampler; Air Diagnostics, Inc, Harrison, ME) with a high volume sampling pump, calibrated to 10 liters per minute (LPM) ± 0.5 LPM. The sampler was equipped with a sampler ring, a Whatman support pad to prevent filter blow out, and a 37 mm pre-weighed Teflon membrane filter (2μm pore size; SKC Inc., Eighty-Four, PA) to collect airborne particles smaller than 2.5 μm. The sampling times were 48 hours ±2 hours. Three 48-hour samples were collected each week so that six out of seven days were sampled each week.
**Personal air samples** were collected using a Personal Modular Impactor, PMI coarse (SKC Inc.). The PMI coarse sampler is a two stage impactor, capable of sampling for PM$_{2.5}$, PM$_{2.5-10}$, or both. The PMI coarse sampler was selected to minimize the bounce of large particles on the PM$_{2.5}$ filter by using an oiled impaction plate on the PM$_{2.5-10}$ stage instead of a collection filter. Initially, repeated attempts were made to use a one-stage impactor, PMI$_{2.5}$ (SKC Inc.). This, however, resulted in large, non-PM$_{2.5}$ debris on the filters.

![Figure 1: Map of Marietta and surrounding area, showing primary residence of subjects, elementary schools, sampling locations, and the manganese refinery](image-url)
Complete personal air sampling protocol and the sampling datasheet can be found in Appendix 4. Air pumps and battery packs were placed in a backpack, with a short Tygon® tube to connect the PMI sampler to the air sampling pump. The pumps were calibrated to 3 LPM ±0.1 LPM. The PMI sampler was equipped with the same type of Teflon filters used for outdoor sampling. The air sampling technician demonstrated how to wear the backpack and the sampler and how to store the backpack near the child when it could not be worn (school, car, bed). The sampling time was 48 hours ± 2 hours and remained in or near the child’s breathing zone for the duration of the sampling time. All personal samples were collected during April-May, 2009.

After completion of the sampling, an investigator asked a series of questions to the parent to determine if the child was exposed to any Mn sources, other than ambient outdoor levels during the sampling period (see post-sampling questionnaire in Appendix 1). This included questions on exposure to cigarette smoke, use of heating and cooking devices, candle use, and time sampling setup was not with subject or was outside of the Marietta area. Throughout the 48 hour period, parents of participants filled out an activity log (Appendix 2) to indicate what the child was doing during the sampling period and when the sampling device was not with the child. For a subset of participants, a GPS and cellular signal tracking device was placed in the backpack of participants to identify whether they left the Marietta region and document the accuracy of self-reporting of their locations during the sampling. The GPS device was difficult to use because the device had no indicator light to show if it was on. Determination of whether the unit was on required logging on to the tracking device website. The GPS device was rarely used because it was not user-friendly.
Teflon filters for personal and stationary outdoor samples were analyzed for particle mass gravimetrically and for the metal fraction of PM$_{2.5}$ of Aluminum, Chromium, Lead, and Manganese using a Thermo X Series II inductively coupled plasma mass spectrometer (ICP-MS) by a commercial laboratory (Research Triangle Institute, NC). Mn was the primary metal of interest. Cr was analyzed because it is emitted from the Mn refinery and has several other potential sources. Pb was selected because of its relationship to traffic pollution and the high level of pollution originating mainly from the power plant next to the refinery. Al was selected to represent crustal elements. Results were reported in μg/m$^3$ (PM$_{2.5}$ mass) and ng/m$^3$ (metals). In keeping with good Industrial Hygiene practices, 10% of the samples were laboratory and field blanks to protect the validity of the sample results. Results were blank corrected for Al and Cr. There was no weight gain or metal contamination found on any blanks other than Al and Cr. The detection limits were 4.1 μg/sample for PM$_{2.5}$ mass, 12.5 ng/sample for Al, 12.5 ng/sample for Cr, 5 ng/sample for Pb, and 2.5 ng/sample for Mn. When results were less than the detectable limit, half of the Limit of Detection (LOD) was substituted as the amount found on the filter when calculating airborne concentration.
**TWA (Time Weighted Average) Distance** was calculated to determine where the child and the air sampling apparatus were located in relation to the Mn refinery. TWA distance to the Marietta College outdoor stationary sampling site was also calculated. The TWA distance is mainly affected by the child’s residential and school distance to the refinery, but also can include other locations reported on the “Time Activity Log.” By knowing the TWA distance from the refinery and the Marietta College stationary sample location, we can determine if there was a correlation between the child’s distance from the plant and Mn concentration. The TWA distance was calculated as follows:

\[
\text{TWA distance} = \frac{(\text{home dist.} \times \text{home time}) + (\text{school dist.} \times \text{school time}) + (\text{other known dist.} \times \text{time})}{\text{total sampling time} - \text{unknown location time}}
\]

**Data analysis** was performed using statistical software packages of Microsoft® Excel and SAS. All air sampling data were found to be log-normally distributed, so the Geometric Mean (GM) was used as the “average” for each contaminant. Geometric Standard Deviation (GSD) was used to determine the statistical dispersion of air sampling results and plot error bars. ANOVA was used to determine if there was a significant difference between the GM’s of Robinson Hill Road, Marietta College, and Cambridge outdoor stationary samples for PM$_{2.5}$ and metals. Three means were compared, so any statistically significant difference between the means were subjected to Scheffé’s method to determine if the variation between the means was from Robinson Hill vs. Marietta, Robinson Hill vs. Cambridge, Marietta vs. Cambridge, or more than one source of variation. A T-test (2 sample, equal variance not assumed) was used for each
contaminant to test the hypothesis that personal sample results were higher than area sample results. Linear regression was used to determine if there was an association with log transformed TWA distance and log transformed contaminant concentration. Where there was a statistically significant association, the $R^2$ value was calculated to determine how much contaminant variability can be explained distance from the refinery.

RESULTS

**Outdoor Stationary Sample** results are summarized in Figure 2. The GM of each airborne contaminant is plotted on the log scale for Robinson Hill Road (n=8), Marietta College (n=83), and Cambridge (n=10). The concentration, GM, error bars, EPA Reference Concentration, and EPA NAAQS (National Ambient Air Quality Standard) are all in nanograms per cubic meter (ng/m$^3$). The NAAQS is displayed in the figure as a dotted line above the respective airborne contaminant. There are two NAAQS limits for PM$_{2.5}$ concentration at outdoor stationary sample locations. As an annual average, the EPA requires the community maintain average PM$_{2.5}$ levels below 15,000 ng/m$^3$. For a 24-hour period the results are not to exceed 35,000 ng/m$^3$ (EPA NAAQS 2008). The NAAQS for Pb is 150 ng/m$^3$, averaged over a 3 month period. The EPA reference concentration, or RfC, is an estimate of a continuous inhalation exposure concentration to people and sensitive subgroups that is likely to be without risk of deleterious effects during a lifetime. Displayed as a solid line above the contaminants, the RfC for Cr and Mn are 100 and 50 ng/m$^3$, respectively.

The mass concentration of PM$_{2.5}$ ranged from 0.07 to 27.54 µg/m$^3$. The GM for PM$_{2.5}$ at all three sampling locations did not exceed the EPA National Ambient Air Quality
Standard (NAAQS) annual average of 15 µg/m³ (EPA NAAQS, 2009). Among the individual 48-hour samples, 15 µg/m³ was exceeded 2 times at the Robinson Hill road location, 11 times at the Marietta College location, and 1 time at the Cambridge location. With a highest result of 22.4 µg/m³ for Robinson Hill Road, 27.5 µg/m³ for Marietta College, and 15.5 µg/m³ for Cambridge, the 24-hour average limit of 35 µg/m³ (EPA NAAQS, 2009) for PM₂.₅ was never exceeded at any of the three sampling locations. ANOVA was used to determine there was no statistical difference (p=0.81) between the GM’s of Robinson Hill Road, Marietta College, and Cambridge outdoor stationary samples for PM₂.₅. There was no clear difference in the PM₂.₅ concentration between the sites (p > 0.05).

Individual Aluminum sample results varied from 0.208 ng/m³ to 35.6 ng/m³. No EPA NAAQS or Rfc could be found for Al. The highest results for Al were 35.6 ng/m³ at Robinson Hill Road, 60.7 ng/m³ at Marietta College, and 28.9 ng/m³ at Cambridge. Robinson Hill Road, Marietta College and Cambridge are approximately 2, 5, and 43 miles from the refinery, respectively. The GM for the three sampling locations decreased as distance from the Mn refinery increased, but the difference was not statistically significant (p=0.84). The GM of Al concentrations obtained in this study ranged from 10.2 to 13.1 ng/m³. There was no clear difference in Al concentration between the three sites (p > 0.05).
Figure 2: Average airborne concentration of PM$_{2.5}$ and metals at the outdoor stationary sites of Robinson Hill Road, Marietta College, and Cambridge. Outdoor stationary sites are approximately 2.5, and 43 miles, respectively from the Mn refinery. Average concentrations are the geometric means for each contaminant. Error bars show the geometric standard deviations.

*Indicates the difference between Robinson Hill Road and the other 2 Outdoor Stationary Sampling locations are statistically significant.

Individual Chromium sample results varied from 0.193 ng/m$^3$ to 4.8 ng/m$^3$. Neither the GM nor any individual result for Cr at any of the three sampling locations exceeded the EPA Rfc of 100 ng/m$^3$ (EPA NAAQS, 2009). The highest results for Cr were 4.5 ng/m$^3$ for Robinson Hill Road, 4.8 ng/m$^3$ for Marietta College, and 0.6 ng/m$^3$ for Cambridge. The GM of Cr concentration measured at the three sampling locations decreased as distance from the refinery increased, but the difference was not statistically significant ($p > 0.05$).
Individual Lead results varied from 0.083 ng/m³ to 23.4 ng/m³. Neither the GM nor any individual result for Pb at any of the three sampling locations exceeded the EPA NAAQS of 150 ng/m³ (EPA NAAQS, 2009). The highest results for Pb were 13.6 ng/m³ for Robinson Hill Road, 23.4 ng/m³ for Marietta College, and 9.8 ng/m³ for Cambridge. The GM of Pb results obtained in this study ranged from 2.7 to 3.4 ng/m³. There was no clear difference in Pb concentration between the three sites (p > 0.05).

Individual Manganese results varied from 0.395 ng/m³ to 561.9 ng/m³. The GM for Mn at the three sampling locations did not exceed the EPA Rfc of 50 ng/m³ (EPA IRIS, 2009). The highest results for Mn were 561.9 ng/m³ for Robinson Hill Road, 72.9 ng/m³ for Marietta College, and 10.9 ng/m³ for Cambridge. The Rfc for Mn was exceeded in half of the samples (4 times) at the Robinson Hill road location, 1 time at the Marietta College location, and no times at the Cambridge location. GM results ranged from 1.98 at Cambridge to 46.11 ng/m³ at the Robinson Hill Road location. The GM of Mn concentrations measured at the three sampling locations decreased as distance from the Mn refinery increased, and the difference was statistically significant (ANOVA: p<0.001). A post hoc test showed that concentration at Robinson Hill, which was closest location to the refinery, was statistically different from those at Marietta College and Cambridge.

**Personal Sample** results are summarized in Figure 3. In contrast to Figure 2, Figure 3 includes the results of only the 17 stationary outdoor samples collected at Marietta College during April and May for direct comparison to the personal samples (n=20) collected during that time period. Personal sample results were higher than stationary
outdoor samples for PM$_{2.5}$ and all metals. The highest personal result for PM$_{2.5}$ was 42.2 μg/m$^3$, which would have exceeded the daily NAAQS if it were an area sample. The GM for personal PM$_{2.5}$ exposure was 15.8 μg/m$^3$, which would have exceeded the annual NAAQS if this group of samples were outdoor stationary samples. One Mn personal sample result (51.8 μg/m$^3$) exceeded the EPA Rfc.

![Personal vs. Outdoor Stationary](image)

**Figure 3:** Average Personal (n=20) vs. Outdoor Stationary (n=17) concentrations of PM$_{2.5}$ and metals and at the Marietta College outdoor stationary sample location. The outdoor stationary samples from the 2 months of personal sampling (April and May) are used in this figure. Average concentrations are the geometric means. Error bars show the geometric standard deviations.

*indicates the differences in personal and outdoor stationary levels are statistically significant using a 2-sided T-test

Potential Mn sources for each child have been documented and summarized in Table 2. Despite attempts to exclude children of smokers, one subject was reported to live in a household with a smoker; however, no smoking near the child was reported during the
air sampling period. That child’s Mn exposure of 6.8 ng/m\(^3\) was less than the geometric mean (GM) of 7.3 ng/m\(^3\) for the 20 children.

Table 2: Summary of potential manganese sources in the child’s home during sampling (n=20 children)

<table>
<thead>
<tr>
<th>Variables</th>
<th>N</th>
<th>Percent</th>
</tr>
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<tbody>
<tr>
<td>Smokers in the household</td>
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<td></td>
</tr>
<tr>
<td>No</td>
<td>19</td>
<td>95%</td>
</tr>
<tr>
<td>Yes</td>
<td>1</td>
<td>5%</td>
</tr>
<tr>
<td>Gas stove used in home</td>
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<td></td>
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<tr>
<td>0 uses</td>
<td>11</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>0 uses</td>
<td>12</td>
<td>60%</td>
</tr>
<tr>
<td>1 use</td>
<td>2</td>
<td>10%</td>
</tr>
<tr>
<td>2 or more uses</td>
<td>6</td>
<td>30%</td>
</tr>
<tr>
<td>Gas heat used in home</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 hours</td>
<td>16</td>
<td>80%</td>
</tr>
<tr>
<td>More than 4 hours</td>
<td>4</td>
<td>20%</td>
</tr>
<tr>
<td>Fireplace used in home</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 hours</td>
<td>19</td>
<td>95%</td>
</tr>
<tr>
<td>2 hours</td>
<td>1</td>
<td>5%</td>
</tr>
<tr>
<td>Near smokers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 hours</td>
<td>20</td>
<td>100%</td>
</tr>
<tr>
<td>Candles or incense used in home</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 hours</td>
<td>15</td>
<td>75%</td>
</tr>
<tr>
<td>1 or more hours</td>
<td>5</td>
<td>25%</td>
</tr>
<tr>
<td>Time spent outside Marietta area</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 hours</td>
<td>15</td>
<td>75%</td>
</tr>
<tr>
<td>1-2 hours</td>
<td>2</td>
<td>10%</td>
</tr>
<tr>
<td>More than 3 hours</td>
<td>3</td>
<td>15%</td>
</tr>
<tr>
<td>Time sampling setup was not with child</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 hours</td>
<td>14</td>
<td>70%</td>
</tr>
<tr>
<td>1-2 hours</td>
<td>3</td>
<td>15%</td>
</tr>
<tr>
<td>3-4 hours</td>
<td>3</td>
<td>15%</td>
</tr>
</tbody>
</table>
It is possible that combustion sources during the personal sampling may have an effect on Mn exposure. Parents of the child with the highest personal Mn result of 51.8 ng/m³ reported heavy use (16 hours or more) of gas heat, moderate use (3-4 times) of a gas stove, and moderate use (1-2 hours) of incense. Parents of the child with the third highest Mn concentration reported moderate use (3-4 times) of a gas stove. These same two samples were also among the ones that had the closest TWA distances from the Mn refinery (under 4 miles). Thus, the elevated Mn is likely to be at least partially caused by the proximity to the Mn refinery.

**TWA (Time Weighted Average) Distance.** It was important to know the location of the child in relation to the Mn refinery and the stationary sample location throughout the sampling period to determine if there was a correlation between the child’s distance from the plant (TWA distance) and Mn concentration. TWA distance results summarized in Table 3 and individually shown in Figure 4 were computed for each of the 20 children.

A majority of the child’s time was spent at home and school, 72% and 18%, respectively. Transportation and unknown time were excluded from the TWA calculations because exact location was not available. The average transportation and unknown distance that was excluded from the calculations was only 3.9 out of 48 hours.

<table>
<thead>
<tr>
<th>Location</th>
<th>Average time in hours spent at location (range)</th>
<th>Percent of Time at Location</th>
<th>Average distance in miles from Mn refinery (range)</th>
<th>Average distance in miles from Marietta College outdoor stationary sampler (range)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Home</td>
<td>34.5 (24.5-46.5)</td>
<td>72.42%</td>
<td>6.7 (2.9-13.1)</td>
<td>6.3 (0.4-18)</td>
</tr>
<tr>
<td>School</td>
<td>8.4 (0-16)</td>
<td>17.57%</td>
<td>8.8 (2.5-13.6)</td>
<td>6.1 (0.7-13.5)</td>
</tr>
<tr>
<td>Other</td>
<td>1.2 (0-4)</td>
<td>2.52%</td>
<td>5.6 (3.7-7.8)</td>
<td>5.9 (0.1-13.6)</td>
</tr>
<tr>
<td>Transportation and unknown</td>
<td>3.9 (0.25-10)</td>
<td>9.24%</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>ALL LOCATIONS</td>
<td>48.0</td>
<td>100%</td>
<td>6.4 TWA</td>
<td>5.6 TWA</td>
</tr>
</tbody>
</table>
While there were obvious increases in Cr, Pb, and Mn with decreased distance from the Mn refinery for stationary samples shown in Figure 2, there was lower correlation between personal sample results and TWA distance from the Mn refinery as shown in Figure 4. The linear regression models indicate a slight negative association between the airborne contaminant and TWA distance from the refinery. With $R^2$ values of 0.054 or less, personal PM$_{2.5}$, Al, and Cr had little to no association with TWA distance. Personal Pb and Mn results, with $R^2$ values of 0.29 and 0.21 respectively, had a stronger association with TWA distance (Pb $p=0.01$ and Mn $p=0.04$).

**Figure 4:** PM$_{2.5}$ and Metals as a function of Time Weighted Average (TWA) distance from Mn refinery for each subject ($n=20$).
DISCUSSION

Outdoor Stationary Samples – The EPA RfC and NAAQS for the metals are based on the total Cr, Mn, and Pb concentrations. However, because we collected airborne particles in the PM$_{2.5}$ fraction, our results likely underestimate the total Cr, Mn and Pb concentrations. In Toronto, 80-100% of the Mn mass was found to be from the PM$_{2.5}$ fraction (Pellizzari et. al, 1999) and in Indianapolis, 56%-80% of the Mn mass was found to be in the PM$_{2.5}$ fraction (Pellizzari et. al, 2001). Given those numbers, the total concentrations of airborne metals could be as much as 44% higher than what we measured in the PM$_{2.5}$ fraction. Due to the larger Mn mass not being sampled, our results are not directly comparable to EPA RfC or NAAQS given for metals.

Among the studied contaminants, only Mn was found to differ statistically significantly between the three stationary locations. Mn was on average 3.3 times higher at Marietta College than Cambridge and even higher yet at Robinson Hill Road, the closest location to the refinery. The GM for Mn at Robinson Hill Road was 23 times higher than Cambridge and 6.9 times higher than Marietta College. Despite the spatial range of nearly 50 miles between the sampling sites in the current study, there was no significant difference in the concentration of PM$_{2.5}$, Al, Cr, and Pb between the three sites.

The results obtained in this study were compared with results obtained with the same sampling method in Cincinnati, OH, which is located 165 miles west from Marietta. PM$_{2.5}$ concentrations and concentrations of several metals were measured at 11 stations in greater Cincinnati area throughout one year (Martuzevicius et al., 2004). In Cincinnati, most of the PM$_{2.5}$ mass originates from traffic and coal power plants (Hu et al., 2006). The average daily PM$_{2.5}$ concentrations in Cincinnati ranged from 10.8 to 28.6 $\mu$g/m$^3$ and
exhibited low spatial variation (Martuzevicius et al., 2004). This is consistent with the results of the current study, where GM results ranged from 8.7 to 10.7 μg/m³.

The Al results were lower than those of Cincinnati, where average daily Al concentrations ranged from 23.7 ng/m³ to 158 ng/m³ and exhibited higher spatial variation than in the current study (Martuzevicius et al., 2004). The higher Al levels in Cincinnati may be attributed to several factors, including possible Al point sources, local differences in Al concentrations in the soil, and more reentrainment of Al from the ground due to the higher population.

The Pb results were lower than those of Cincinnati, where average daily Pb concentrations ranged from 1.79 ng/m³ to 28.4 ng/m³ and exhibited higher spatial variation than in the current study (Martuzevicius et al., 2004). The higher Pb levels in Cincinnati may be attributed to several factors, including Pb point sources such as power plants, more reentrainment of Pb from the ground due to the higher population. Furthermore, significantly more Tetraethyl lead may be present from many years of use in unleaded gasoline.

The average daily Mn concentrations measured at 11 stations in Cincinnati throughout one year ranged from 1.56 to 9.01 ng/m³ and exhibited high spatial variation (Martuzevicius et al., 2004). The Mn results of the current study were higher at Marietta and Robinson Hill stations but comparable in Cambridge. Furthermore, in contrast to PM₂.₅, Cr, Mn, and Pb, the spatial variation of Mn in the current study was higher than in Cincinnati, likely due to the ferromanganese refinery.
**Personal Samples** – The “personal cloud effect” was evident in the sample results. Personal sample results were more than double the outdoor stationary results from Marietta College for PM$_{2.5}$, Cr, and Al. The difference between personal and outdoor stationary results for these three airborne contaminants was also statistically significant. Traffic and pollution related elements Pb and Mn were higher in personal samples than in stationary outdoor samples, but the difference was not statistically significant. Our results for PM$_{2.5}$ show agreement with the Indianapolis study, where personal sample results were higher than outdoor and fixed monitoring results for PM$_{2.5}$ (Pellizzari et. al, 2001).

Unlike our PM$_{2.5}$ data which shows a statistically significant difference between personal and outdoor stationary, a study in Los Angeles (Delfino et. al, 2008) found a moderate correlation between the two ($r=0.60$). This may be due to the overall high pollution level in Los Angeles, which masks the “personal cloud” effect. Other possibilities include constant re-entrainment of particulate mass in cities compared to relative calm of rural Marietta. Perhaps the most significant factor is that our subjects were 7-9 years old and are more likely to play on or near the ground compared to asthmatic 9-18 year old subjects in Los Angeles.

Our data show combustion sources, including a gas stove, may have an effect on personal Mn exposure. Although Mn was not measured, a study done in Vancouver, a city where ambient outdoor particulate mass is also low, found that pregnant adult women using gas stoves at home have 35% higher exposure to particulate mass, measured as PM$_{2.2}$, than those without gas stoves (Nethery et. al, 2008).
**TWA Distance** – Over 72% of the child’s time was spent at home, showing agreement with previous studies (Klepeis et al., 2001; Robinson and Nelson, 1995). The child’s time spent at school was less than one would expect, but that is because some samples included weekend days. A few samples were collected when school was not in session. Transportation and unknown time were excluded from the TWA calculations because exact location was not available.

The average distance from the refinery was less for homes than for schools, indicating that homes were closer to the refinery, on average, than schools. The stationary sampler at the Marietta College was centrally located in Marietta’s population and business center, so the average distance from the Marietta College sampling site was similar for home and school.

TWA distance was associated with Pb and Mn results. Neither Pb nor Mn showed significant difference between personal and outdoor stationary concentrations. As a result, several outdoor stationary sampling locations at varying distances from the ferromanganese refinery may be an adequate surrogate for personal sampling of Pb and Mn when the child’s TWA distance from the refinery is known, which is primarily a function of school and home distance.

**CONCLUSIONS**

Concentrations of PM$_{2.5}$ mass and metals were consistently higher for personal samples than for stationary outdoor samples. The “personal cloud” effect was most pronounced for PM$_{2.5}$ and Al, due to the numerous sources of PM$_{2.5}$ mass and its crustal abundance. Pb and Mn appear to be less likely to be resuspended by the child’s activities and more
likely to be from industrial or traffic sources. Therefore, the concentrations of these metals were found to strongly depend on the residential and school distance to the refinery.

While negative associations existed between the distance from the refinery and the concentrations of Mn and Pb measured with the personal and stationary outdoor samplers, more stationary outdoor sampling locations are needed for more conclusive results. Furthermore, only 20 valid personal samples were able to be collected, so additional personal samples are needed to strengthen the personal TWA distance relationships. Several outdoor stationary sampling locations at varying distances from the ferromanganese refinery may be an adequate surrogate for personal sampling of Pb and Mn when the child’s TWA distance from the refinery is known. The CARES cohort study is scheduled to continue at least four more years, so more robust characterization of Marietta air pollution will continue.

**IRB APPROVAL NOTE**
IRB approval was granted in January 2009 (IRB #08-03-06-01; P.I.: Dr. Haynes)
REFERENCES


Post-Sampling Parental Questionnaire

In the past 48 hours, how many hours was your child in the house when gas heat was used?
- None
- Up to 4 hours
- 4-8 hours
- 8-16 hours
- 16 or more hours

In the past 48 hours, about how many hours was your child near (in the same room or car) as someone who was smoking?
- 0
- 1-2
- 3-4
- 4 or more

In the past 48 hours, how many times did you or someone in your household use a gas stove for cooking?
- None
- 1
- 2
- 3-4
- 4 or more

In the past 48 hours, about how many hours was your child near (in the same room) a lit candle or incense?
- 0
- 1-2
- 3-4
- 4 or more

Does anyone who lives in your household currently smoke?
- No
- Yes

In the past 48 hours, how many times did you or someone in your household use an electric stove for cooking?
- None
- 1
- 2
- 3-4
- 4 or more

In the past 48 hours, about how many hours was your child more than 20 miles from home?
- 0
- 1-2
- 3-4
- 4 or more

In the past 48 hours, about how many hours was the pump not with the child?
- 0
- 1-2
- 3-4
- 4 or more
Appendix 2: Daily Activity Log

# Daily Activity Log

<table>
<thead>
<tr>
<th>LOCATION</th>
<th>DAY 1</th>
<th>DAY 2</th>
<th>DAY 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOME</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bedroom</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Windows Closed)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bedroom with Open Windows</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rest of House (Windows Closed)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rest of House with Open Windows</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OUTDOORS</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Playing within a block of home</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Playing Elsewhere</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Walking To/From School</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Other (Specify in Comments)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VEHICLE</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bus To/From School</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Car in Town</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SCHOOL</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>School</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Parent: Please fill out the Daily Activity Log below, including location and duration of your child’s activities. If the child needs to remove the backpack, please record why, for how long and where the backpack was placed during this time.

Comments and Observations: ____________________________________________________________
________________________________________________________________________________
________________________________________________________________________________
Appendix 3: Protocol and Sample Datasheet for Outdoor Stationary Samples

Communities Actively Researching Exposure Study

Last Updated: 09/30/08

PROTOCOL FOR HARVARD PM2.5 OUTDOOR SAMPLER

I. ASSEMBLY OF IMPACTOR

1) Use a clean surface to lay out the components except the filter and drain disk that are pre-loaded in the Andersen filter cassettes (see separate instruction on loading the filters at the end of this document). Clean all inside surfaces of the impactor and flow adaptor with a KimWipe tissue as needed.

2) If needed, apply a thin layer of silicone spray or tube type lubricant to the impactor O-rings. Do not over spray. When attaching sections with O-rings, align the pieces well and twist/slide them together smoothly to avoid displacing or damaging the O-rings.

3) Do not touch the filter at any time with anything except clean filter forceps if you must. If a filter is contaminated by touch or any other way, or if it is damaged, replace it with another filter. Keep all used and voided filters in their numbered Petri dishes.
4) Select a pre-weighed Teflon 37 mm filter (note the sample ID) with attached support ring and drain disk that has been pre-loaded in the Andersen cassette. Be sure it is not a field blank. Place a sample ID number label on the impactor. It is important that the same ID stays with each filter because these are pre-weighed.

5) With the impactor base down, place the loaded cassette over a 0.060 inch thick (1/16) inch silicone washer (red o-ring) in the base, the collection surface of the filter side up, drain disk side down.
6) Carefully clamp the cover of the impactor on top of the base section. Do not allow the filter cassette to shift off the center of the impactor base.

7) Open the upper part of the sampler and check the impactor plate. Change with cleaned and oiled impactor plate once a week. If it is not time to replace the impaction plate with a clean one, wipe any dirt from previous sampling off the top of the sintered stainless steel frit with Kimwipes. Put a small drop of the pharmacy type mineral oil in the center of the plate. If it is not all absorbed in 30 seconds, wipe any remaining oil off. Do not use silicone grease.
8) Connect the impactor nozzle stage above the cover of the base, using a freshly oiled impactor plate after the nozzle. Make sure that the impactor plate is installed with the sintered disk facing upward, toward the tapered inlet of the impactor nozzle.

9) Install a slotted inlet over the impactor nozzle if it is not already in place.
10) If the sampler is moved: To protect the sampler during transport from the field lab to the sampling site, cover the inlet of the impactor stage with a ziplock bag and elastic, or a large plastic red cap. This allows safe transport. It is preferable to transport loaded impactors standing upright to minimize the chance of oil coming out of the impactor plates.

II START-UP SAMPLING

For flow controlled sampling pump or sonic flow limited sampling system:

1) The sampling pumps must be warmed up for at least 5 minutes before starting sampling or testing pump flows. *A protective inline filter must be kept on the sampling pump tubing at all times.*

2) Flows for all pumps must be within allowed limits, as measured with the rotameter. *The allowed limit is plus or minus 5% of the desired flow of 10 l/min. Thus, the flow can range from 9.5 to 10.5 l/min. This corresponds to a rotameter reading of 55 (52.5 to 57.5). If the flow is out of range, adjust the pump until the desired flow is achieved. Report any problems immediately, so that repairs can be made.*
3) *Rotameters must be stored at the temperature they will be used at all the time, protected from direct sun and water.* The basic principle is that the rotameter must be at approximately the temperature of the indoor or outdoor air, wherever it will be used, to make a correct flow measurement, it cannot be either too cold or too hot. Rotameters must be allowed to equilibrate at the air temperature they will be used at for about 30 min before measuring flows to minimize error.

4) **REMOVE ZIPLOCK BAGS AND ELASTICS OR REDCAPS FROM INLETS OF ALL SAMPLERS BEFORE ATTACHING PUMP LINES!!** Failure to do this can "pop" filters.

5) Normal Leak tests: Measure the pump flow without the impactor. Record this flow in the "LEAK TEST FLOW" column on the field data log. Then test the flow at the inlet of the impactor using the flow adaptor. Record this flow in the "ON" column on "SAMPLE FLOW" on the log.

6) If the flow value with the impactor differs by more than 4 rotameter divisions from the pump-only flow value, re-check both flows. If the difference persists, remove the impactor and reinstall the filter. If the difference is still more than 4 rotameter divisions, use a different impactor and/or filter holder frame, and further evaluate the clamping force on the cassette and washer thickness when the unit is not in the field.
Communities Actively Researching Exposure Study

Last Updated: 09/30/08

7) Set the timer on the pump system to start at the correct date and time for sample to be collected. **Record the pump's elapsed timer reading to the nearest 0.1 hr** in the "TIMER READING" column of the sample log.

8) Special Leak Test: Situation Rare Possibility of Filter Bypass leak: If the red silicone rubber fixation ring is at the upper end of the manufacturer’s tolerance, (greater than 0.200 inches thick), there is a potential for leakage around the filter to occur that would not be found by the normal leak check procedure. **Elimination of any possible bypass:** Based on our testing at over 100 inches of water suction, any possibility of bypass leakage appears to be eliminated by using one 0.060 washer under the cassette. It is our opinion that either the leakage occurs or it does not, that it is not a sometimes thing. **Evaluation of Your Impactor:** The simplest way that we can conceive to test if your unit has any potential for bypass leakage is to cut a very thin 0.002 inch (2 mill) disk from a thin poly bag and place it between the Teflon filter ring and the drain disk in a cassette and install it in the sampler with a calibration inlet adapter and flow measurement device on your impactor base. With approximately 60 to 80 inches of water column suction placed on the impactor base via the pump hose, there should be no flow registered at the inlet of the calibration adapter. The Teflon filter ring material is 0.016 inches thick. [a thin sandwich bag is 0.002 inches thick (2 mill) the desired thickness to test with a filter in place.]

III END SAMPLING

1) **After 48-hours of sampling** check the flow through the impactor. If the pump is not running at the time of sample pick-up, turn the pump on and record the flow after a 5 minute warm-up. Record the reading on the log, in the "Off Flow" column. **Do not turn power to pumps off if another sample will be loaded during the current visit!**

2) Disconnect the pump line from the impactor, and record the timer in the "TIMER OFF" column on the data logs. Connect covers or caps to the inlets and outlet of the sampler.

3) Calculate the total elapsed time and enter the value in the log.
IV. UNLOADING THE SAMPLER

1) Place the sampler on a clean surface.

2) Open the base of the sampler carefully. The filter cassette sometimes sticks to the top part of the base (cover). Carefully remove the filter cassette and put it into the Petri dish, which has the correct sample ID.

3) Disassemble the rest of the sampler. Remove the impaction plates, which are not to be re-used until cleaned (wiped off) and re-oiled. Inspect all the other parts for dust or dirt, and clean them if necessary with a damp Kimwipe.
V. CLEANING IMPACTOR PLATES

1) Clean impactor plate once a week.
2) Place the plates in a plastic tub with 2 small scoops of powdered detergent such as Alconox used for lab glassware, and cover the plates with hot water, making sure that the detergent is dissolved.
3) Let soak approx. 30 minutes, gently agitating periodically.
4) Rinse the plates thoroughly in warm water then wash them a second time.
5) After the second wash, rinse the plates again, drain and place in a clean tub to rinse.
6) Place the tub in a sink with the faucet running, let the water fill the tub and overflow till there is no oil on the surface of the water.
7) Drain and place the plated sintered side up on a cookie sheet and dry them in an oven at approx. 50 deg. C or at less than 170 deg. F for about three hours.
8) Turn off the oven and let the plates cool.
9) Place the clean plates in a zip-lock bag.
10) Using ultrasonic baths or other means to clean the plates in not recommended.

VI. LOADING AND UNLOADING THE FILTERS

Loading
1) Wipe forceps and Andersen filter cassette (Yellow casket) with Kimwipes and 70% ethanol.
2) Load a Whistman drain disk on the bottom part of the Andersen filter cassette.
3) Load a pre-weighed unused Teflon filter on top of the drain disk.
4) Note that the filter should have been pre-weighed not more than 30 days prior.
5) Place the bottom part of the Andersen filter cassette on top and close tightly.
6) Place the loaded Andersen filter cassette back in the numbered Petri dish.
7) Load the Andersen filter cassette into the sampler.
8) Close the empty Petri dish and store for sample unloading.
Unloading after sampling
9) Wipe forceps with Kimwipes and 70% ethanol.
10) Open the Andersen filter cassette carefully. Do not drop the filter!
11) Take the sampling filter out from the cassette and place it to the numbered Petri dish.
12) Discard the Whatman drain disk.
13) Keep the collected samples in a refrigerator until ready to ship.
14) Ship to RTI every other week (see the schedule).
15) For shipping, pack the Petri dishes holding the filters carefully using bubble wrap. Do not use Styrofoam or pebbles. You could use rubber bands or zip lock bags to hold the Petri dishes together.
16) Include blue ice to keep the samples cool.
17) Ship using overnight service to the following address:

Research Triangle Institute
Attn: Lisa Greene
3040 Cornwallis Road
PO Box 12194
Research Triangle Park, NC 27709
Phone: 919-541-7483
# OUTDOOR SAMPLING DATA LOG

<table>
<thead>
<tr>
<th>Sampling location:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<table>
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<tr>
<th>Sample ID</th>
<th>Date</th>
<th>Time</th>
<th>Leak test flow</th>
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<table>
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<table>
<thead>
<tr>
<th>Notes</th>
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</tbody>
</table>
Appendix 4: Sampling Protocol and Datasheet for Personal Sampling

Preparation, calibration, and sampling procedure for PMI 2.5

1. Unscrew the top (inlet) from the bottom (exhaust) of the SKC PMI 2.5 sampler.
2. Remove the white filter cassette and carefully pry it open on a flat surface using the cassette opener.
3. Without touching the filter, use forceps to place a pre-weighed 37 mm filter on the stainless steel filter support screen.
4. Press the top of the cassette into the bottom and close tightly.
5. Place a pre-oiled impaction disk on top on the cassette with the rough side of the disk facing up.
6. Return the cassette to the sampler and screw the inlet back on the bottom of the sampler.
7. Attach the sample ID sticker on the back side of the PMI 2.5 sampler to match the sample ID number on the plastic container. Place the sample ID sticker on the sample sheet.
8. Align calibration adapter with PMI inlet and press down until a firm seal is established.
9. Using flexible tubing, connect the calibrator outlet (suction port) to the PMI calibration adapter inlet.
10. Using a second length of tubing, connect the PMI exhaust to the inlet of a sample pump.
11. Calibrate the sample pump to a flow rate of 3.0 ± 0.1 L/min.
12. When calibration is completed, remove the calibrator, tubing, and calibration adapter.
13. Write down the exact flow rate in air sampling sheet.
14. Demonstrate to the family how the sampler fits inside the backpack and how it attached onto the child’s shirt. Be sure that the air intake is near the breathing zone.
15. Instruct the family to allow the child to wear the backpack during daytime hours and to leave it near the child during sleeping hours.
16. If the child needs to participate in active play that requires removal of the backpack/monitor, please have the backpack/monitor in a nearby location with supervision.
17. After 48±2 h, measure the airflow rate passing through the personal air sampler using the calibrator adaptor and record it on the sampling sheet.
18. Switch off the pump and record the time.
19. Gently disconnect the tubes from the air sampler without shaking.
20. Store the sampler in a Zip-lock bag without shaking. Keep the sampler in the refrigerator or in a cooler box at all times after sampling.
21. Open the sampler, then remove and discard the impaction media.
22. Remove the sampling filter with the forceps and place it to the plastic container with the matching ID sticker.
23. Store sampling filters in refrigerator until the pre-scheduled shipping date.
24. Send the filters to the RTI and all sampling collection/recording datasheets to the University of Cincinnati.

Cleaning Procedures

1. After 2 sampling periods or upon a noticeable oil buildup on the top of the filter cassette, disassemble the impactor and wash all parts in water with mild detergent/soap.
2. Rinse and air-dry all parts thoroughly in a clean environment.

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PRIOR TO SAMPLING CHECKLIST

- Participants will be screened and recruited through a phone interview process.
- The schedule of air sampling participants will be posted on the CARES shared calendar.
- Charge the batteries for sampling pumps for at least 16 hours.
- Prepare the individual sampling information file for each family including:
  - Consent form for new family and housing conditions form.
  - Map.
  - Sampling Data Sheet.
  - Sampling protocols.
  - Reminder card for picking up the sample pump.
- Check the indoor sampling supplies:
  - Setup for personal sampling (padded backpack, sampler, pump, and charged battery).
  - Air flow calibrator and calibrator adapter.
  - ID labels.
  - Tubes of appropriate diameters, connectors, clamps, and scissors.
- List of houses with addresses and corresponding ID label sheets.

START OF SAMPLING CHECKLIST

- Perform steps 7-16 of “Preparation, calibration, and sampling procedure for PMI 2.5”.
- Provide instructions to the family and place the backpack on the child, with the air inlet in his or her personal breathing zone.
- Affix Subject ID sticker on all pages of sampling sheets.
- Give the “Daily Activity Log” to the family and provide instructions.
- Record start-time and pump reading on “Personal Sampling Data” sheet.

POST SAMPLING CHECKLIST

- When the child comes to clinic visit for the collection of biological samples:
  - Collect the personal air sampler from the child.
  - Check that sample ID stickers are placed on all samples and the respective sampling sheets.
  - Ask parents questions and write answers on the “Post-Sampling Parental Questionnaire”.
  - Provide family with incentive.
  - Have family member sign for receipt of incentive.
- Post-calibrate, turn off pump, fill out “Personal Sampling Data” sheet, and store the sample as described in steps 17-20 of “Preparation, calibration, and sampling procedure for PMI 2.5”.
- Give all samples to Dr. Brown.
- Fax the consent form, sampling sheets and incentive receipts to the Dr. Reponen at University of Cincinnati at 513-589-2263. Scanning and emailing to tina.reponen@uc.edu is also acceptable.
- Return all forms to the child’s file.

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PERSONAL SAMPLING DATA

ADDRESS:

DATE OF SAMPLING STARTS: / /2009  Sampling person initial:
DATE OF SAMPLING ENDS: / /2009  Sampling person initial:

Sample ID Sticker:
Pump Number: Battery Number:

<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td>Sampling Time</td>
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<tr>
<td>Sampling flow rate</td>
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<td>L/Min</td>
</tr>
<tr>
<td>Pump Reading (6 digits)</td>
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Comments: _______________________________________________________
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If you have any questions about air sampling or are having problems with the equipment, please call Matthew Terrell at the University of Cincinnati (317-833-2010)

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