Published in final edited form as:

Environ Monit Assess. ; 193(7): 419. doi:10.1007/s10661-021-09206-8.

AERMOD modeling of ambient manganese for residents living near a ferromanganese refinery in Marietta, OH, USA

Adrienne Stolfi

Department of Pediatrics, Wright State University, Dayton, OH, USA

Florence Fulk, Tiina Reponen, Timothy J. Hilbert

Department of Environmental and Public Health Sciences, College of Medicine, University of Cincinnati, Cincinnati, OH, USA

David Brown,

Department of Biology & Environmental Science, Marietta College, Marietta, OH, USA

Erin N. Haynes

Department of Epidemiology, College of Public Health, University of Kentucky, Lexington, KY, USA

Abstract

Elevated exposure to ambient manganese (Mn) is associated with adverse health outcomes. In Marietta, Ohio, the primary source of ambient Mn exposure is from the longest operating ferromanganese refinery in North America. In this study, the US EPA air dispersion model, AERMOD, was used to estimate ambient air Mn levels near the refinery for the years 2008–2013. Modeled air Mn concentrations for 2009–2010 were compared to concentrations obtained from a stationary air sampler. Census block population data were used to estimate population sizes exposed to an annual average air Mn $> 50 \text{ ng/m}^3$, the US EPA guideline for chronic exposure, for each year. Associations between modeled air Mn, measured soil Mn, and measured indoor dust Mn in the modeled area were also examined. Median modeled air Mn concentrations ranged from 6.3 to 43 ng/m^3 across the years. From 12,000–56,000 individuals, including over 2000 children aged 0–14 years, were exposed to respirable annual average ambient air Mn levels exceeding 50 ng/m^3 in five of the six years. For 2009–2010, the median modeled air Mn concentration

[✉] adrienne.stolfi@wright.edu .

Author contribution Adrienne Stolfi: contributed to conception and design, acquisition of data, analysis and interpretation of data, drafting of article, revision of article for intellectual content, and final approval of version submitted for publication. Florence Fulk: contributed to conception and design, acquisition of data, interpretation of data, revision of article for intellectual content, and final approval of version submitted for publication. Tiina Reponen: contributed to conception and design, interpretation of data, revision of article for intellectual content, and final approval of version submitted for publication. Timothy J. Hilbert: contributed to interpretation of data, revision of article for intellectual content, and final approval of version submitted for publication. David Brown: contributed to acquisition of data, and final approval of version submitted for publication. Erin N. Haynes: contributed to conception and design, acquisition of data, interpretation of data, drafting of article, revision of article for intellectual content, and final approval of version submitted for publication.

Supplementary information The online version contains supplementary material available at <https://doi.org/10.1007/s10661-021-09206-8>.

Ethics approval The study was approved by the Institutional Review Board of the University of Cincinnati.

Conflict of interest The authors declare no competing interests.

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at the stationary site was 20 ng/m³, compared to 18 ng/m³ measured with the stationary air sampler. All model performance measures for monthly modeled concentrations compared to measured concentrations were within acceptable limits. The study shows that AERMOD modeling of ambient air Mn is a viable method for estimating exposure from refinery emissions and that the Marietta area population was at times exposed to Mn levels that exceeded US EPA guidelines.

Keywords

AERMOD; Manganese; Emissions; Dispersion

Introduction

Manganese (Mn) is an essential nutrient required for normal brain development and functioning but can be toxic in excess. Mn occurs naturally in the environment, in air, surface water and ground-water, rocks, soil, crops, and other vegetation. In the USA, the average ambient air concentration is 20 ng/m³, ranging from 10 ng/m³ in rural or remote areas to 40 ng/m³ in urban environments (ATSDR, 2012). Ambient air Mn concentrations can range much higher than background levels in areas with anthropogenic sources. In the USA, the Environmental Protection Agency (EPA) has set a reference concentration (RfC) of 50 ng/m³ for chronic exposure to Mn in the respirable fraction, while the Agency for Toxic Substances and Disease Registry (ATSDR) established 300 ng/m³ as the chronic duration inhalation minimal risk level (MRL) (USEPA, 2002; ATSDR, 2012). The World Health Organization (WHO) recommended a guideline of average annual ambient air exposure of 150 ng/m³ (WHO, 2000). Primary sources of excess Mn in the environment include industrial emissions, mining activities, pesticides, fungicides, and the gasoline additive methylcyclopentadienyl manganese tricarbonyl. Globally, ferromanganese alloy plants have been associated with some of the highest average annual air Mn concentrations in communities near the plants (Otero-Pregigueiro & Fernández-Olmo, 2018). Ledoux et al. (2006) found a 12-h average total particle mass air Mn concentration of 7560 ng/m³ near a ferromanganese plant in France, and Boudissa et al. (2006) reported a 2-h concentration of respirable Mn of 3500 ng/m³ near a ferromanganese plant in Canada. Across five stationary sampling sites near a ferromanganese refinery in Marietta OH, the site of the present study, Colledge et al. (2015) reported monthly average total suspended particulate Mn concentrations of 110–390 ng/m³ from 2003 through October 2013.

A number of methods have been used to monitor airborne exposure to environmental pollutants from specific industrial sources in or near communities. Personal exposures can be quantified with personal air samplers worn by individuals that measure continuous exposures over specified periods of time. This is considered the most accurate method but is expensive and not suitable for large populations (Han et al., 2017). A more feasible method is to employ stationary air samplers placed at different locations in a community, but these lack spatial and temporal resolution and may not adequately capture individual variability (Ozkaynak et al., 2013). Distances from homes to the exposure site are often used as surrogate measures of exposure. The limitations of this method are that wind speeds and directions, terrain, and land use are not taken into account.

Air dispersion modeling is a method frequently used in air quality assessments for regulatory purposes but less so in epidemiologic studies. Air dispersion models predict concentrations of pollutants in the environment using information about emission sources, topography, meteorological data, distances, and other factors. Compared to direct exposure assessment methods, air dispersion models have several advantages, including the ability to separate contributions of different chemicals, reconstruct historical exposures, and predict future exposures (Zou et al., 2009). For epidemiologic studies where direct measurement of Mn exposure levels from industrial sources is prohibitive, air dispersion modeling can be a viable option.

In addition to Mn in the air, surface soil and indoor dust contain settled Mn particles and represent additional sources of exposure. Children are at greater risk than adults due to spending greater amounts of time close to the floor as well as having increased hand-to-mouth contact (Moya et al., 2004). In uncontaminated environments, soil Mn levels range from 40 to 900 µg/g, but much higher levels have been measured in areas near industrial Mn sources (Boudissa et al., 2006; Aelion et al., 2009; ATSDR, 2012; Pavilonis et al., 2015). Elevated levels of Mn have also been found in indoor dust near industrial Mn sources. Pavilonis et al. (2015) found that in homes within 0.5 km of a ferromanganese plant in Italy, house dust Mn levels were 2.4 times higher than in homes 1.0 km from the plant. In Brazil, classroom dust loadings were negatively associated with distance from a ferromanganese alloy plant and positively associated with Mn levels in outdoor dust (Menezes-Filho et al., 2016). Further, a number of studies have found significant associations between Mn in soil or indoor dust and blood, hair, or other biomarkers in children (Butler et al., 2019; Fulk et al., 2017; Lucchini et al., 2017; Zota et al., 2016).

The purpose of this study was to estimate the ambient Mn concentrations to identify populations exposed to levels above the RfC and examine the association between modeled ambient air Mn, Mn measured in air from January 2009 to October 2010, and Mn measured in soil and indoor dust from 2008 to 2013. The study site is Marietta, Ohio, and neighboring towns, which are exposed to airborne Mn from Eramet Marietta, Inc. (EMI), a ferromanganese refinery in operation for over 60 years. The refinery is the largest and longest running emitter of Mn in the USA (USEPA, 2015). Air Mn concentrations over the 6-year period of 2008–2013 were modeled using the American Meteorological Society/Environmental Protection Agency Regulatory Model (AERMOD), a steady-state Gaussian plume air dispersion model recommended by the US EPA for modeling emissions from industrial sources (USEPA, 2004). Data for stationary air, soil, and indoor dust measurements were obtained from the Marietta Communities Actively Researching Exposure Study (CARES), a community-based participatory research partnership that investigated the impact of increased environmental exposure to Mn on neurological outcomes in children.

Materials and methods

Modeled study area and population estimates

The modeled study area is from CARES, which recruited children from October 2008 through February 2013 from Marietta, Ohio, and the surrounding area (Haynes et al., 2011)

(Fig. 1). The purpose of CARES is to address the community-identified research question, “Does Mn affect cognitive development of children?” (Haynes et al., 2015). In order to characterize potential routes of exposure, an environmental sampling team was trained to collect soil and indoor dust from residences of study participants following US Department of Housing and Urban Development (HUD) protocols (HUD, 1995; Fulk et al., 2017). In Marietta, samples were collected from 241 of 258 participating residences. The sites furthest from the Mn refinery in all directions were used to establish the geographic boundary for modeling exposure.

For estimating the population size exposed to Mn in the study area, census block data including census block code, 2010 total population size, population size for children aged 0–14 years, and block centroid latitude and longitude from the 2010 US Census were downloaded from the US Census Bureau website (US Census Bureau, n.d.-a). All census blocks in Washington Co., Ohio, and Wood Co., West Virginia, were extracted from the data file and merged with a census block boundaries shapefile obtained from the Esri Data and Maps website (Environmental Systems Research Institute [Esri], n.d.). ArcGIS Pro Desktop software from Esri was used to create a map of the counties with census blocks, population sizes, the modeled study area, and location of the Mn refinery. For 105 of the 116 census blocks in the counties, the census block centroid was within the modeled study area; these 105 blocks were included in the study.

Modeling of ambient air Mn concentrations in Marietta and surrounding areas

Ambient air concentrations of Mn were modeled using AERMOD, which is designed for modeling pollutant concentrations up to 50 km from a source. AERMOD incorporates planetary boundary layer turbulence structure and scaling concepts, meteorological conditions, elevated sources and emissions, and simple or complex terrains (USEPA, 2004). Model inputs include wind data, hourly surface weather data, upper air data, land cover data, elevation data, emissions sources and quantities, and receptor locations. The AERMOD model has three components: a meteorological preprocessor (AERMET), a terrain preprocessor (AERMAP), and the dispersion model. All modeling was conducted using AERMOD View version 9.7.0 from Lakes Environmental Software, Waterloo, Ontario.

For preprocessing of meteorological data, Automated Surface Observing System 1- and 5-min wind data files for 2008–2013 for the Parkersburg/Wilson station at Mid-Ohio Valley Regional Airport, the closest weather station, were downloaded from the National Climatic Data Center, Automated Surface Observing System website (National Centers for Environmental Information, n.d.-a). Integrated Surface Hourly weather observations data files were downloaded for the Parkersburg/Wilson station from the National Climatic Data Center, Quick Links website (National Centers for Environmental Information, n.d.-b). The files were processed through AERMOD to calculate average hourly wind speeds and directions, visibility, and air temperatures between ground level and 10 m. Upper air data files for the Wilmington, OH, US Upper Air Station, which is the closest station to the study area, were downloaded from the NOAA/ESRL Radiosonde Database website (National Oceanic and Atmospheric Administration, n.d.).

National Land Cover Data (NLCD) files for 2006 and 2011 were obtained from the Multi-Resolution Land Characteristics Consortium (<https://www.mrlc.gov/data>). The NLCD 2006 data file was used for the 2008–2010 AERMOD modeling, and the NLCD 2011 data file was used for 2011–2013. The files were processed to obtain the average surface characteristics albedo, surface roughness length, and Bowen ratio for input into AERMET. For 2008–2010, the surface characteristics were albedo = 0.16, surface roughness = 0.22 m, and Bowen ratio = 0.64. For 2011–2013, the values were albedo = 0.16, surface roughness = 0.22 m, and Bowen ratio = 0.65. A digital terrain elevation data file was directly accessed from within the AERMOD View terrain preprocessor from [webGIS.com](http://www.webgis.com), a geographical information systems resource website (<http://www.webgis.com/>). The data file, created by the US Geological Survey, is a National Elevation Dataset (NED) consisting of ground surface elevation data at a resolution of 1/3 arc second (~10 m). The terrain elevations were used for all emissions sources and receptors in the AERMOD models.

Annual Mn emissions data reported by the refinery for the years 2008–2013 were obtained from the US EPA through a Freedom of Information Act (FOIA) request (EPA-HQ-2019–004,104, FOIA online, n.d.). The FOIA data included point source and fugitive annual Mn emissions in pounds (lb), stack locations, heights, diameters, and exit temperatures, fugitive heights, lengths, widths, and rotation angles, emission rates, and days operating per year. Mn emissions were reported as elemental Mn (Chemical Abstracts Service Registry Number 7439–96–5). The primary point sources of emissions were stack emissions from three submerged electric arc furnaces, the metal oxygen refining process, and the crushing, sizing, and packing system. Fugitive sources were roadways, storage piles, and furnace casting operations.

Receptors for AERMOD modeling included all soil/indoor dust sampling sites, census block centroids, and a single stationary air sampler site located in Marietta. All addresses were geocoded, and distances from the Mn refinery in kilometers were determined with ArcGIS Pro Desktop.

For each year, AERMOD modeling was conducted with a modeling domain of 32 km from the emissions source. The default regulatory options were used, with a rural setting and output concentrations set to ng/m^3 . Annual and monthly averaging time options were selected for concentration outputs. Building downwash was modeled using the Building Profile Input Program (BPIP) within AERMOD. Four buildings were modeled that were in close proximity to the vertical stacks and housed the furnaces that were the primary source of emissions.

The US EPA FOIA data included information on total hours in operation for each source operating in a given year. Sources are assumed to be operating 24 h per day, 365 days per year, for a total of 8760 h. For modeling, emissions in grams/second were evenly distributed across all hours and days per year. For sources that were in operation for fewer than 8760 h, no information was available as to the specific days and times the sources were operating. In these cases, AERMOD variable emission options were used to distribute the reduced operating hours evenly over the 365-day period. The only exception was for emission sources from a furnace that only operated for the first 64 days of 2010. The total

emissions amount for that furnace's stacks was modeled as occurring over the first 64 days of the year, with zero emissions occurring after 64 days.

Stationary Mn air sampling

For all of 2009 and the first 10 months of 2010, the CARES study team measured air Mn with a stationary air sampler positioned on the roof of the Rickey Science Center at Marietta College, 7.8 km northeast of the Mn refinery (Haynes et al., 2012). A detailed description of the sampling equipment and methodology is available from Haynes et al. (2012). Briefly, stationary samples were collected with Harvard-type PM_{2.5} impactors with a high volume sampling pump calibrated to 10 ± 0.5 L per minute. Samples were collected on 37 mm pre-weighed Teflon membrane filters with 2- μ m pore size to collect airborne particles with diameters of 2.5 μ m or less. Samples were collected three times per week over 48-h time periods for the duration of the monitoring period. Ten percent (10%) of the samples were laboratory blanks, and 10% were field blanks for quality control of the sample results. The stationary samples were analyzed for Mn (ng/m³) with an inductively coupled plasma mass spectrometer at a commercial laboratory at Research Triangle Institute in NC. The analysis method had a detection limit of 2.5 ng/sample. Average monthly values of measured Mn were determined from the 48-h samples for comparisons to modeled Mn for January 2009 to October 2010.

Collection and analysis of residential soil and indoor dust samples

Over the 6-year study period, CARES team members collected soil and indoor dust samples from 241 participant homes. Samples were collected following US Department of Housing and Urban Development (HUD) protocols and guidelines (HUD, 1995). Details of the sampling methodology for soil and dust have been described in detail in Fulk et al. (2017). At each site, surface soil samples were collected from six separate locations in the yard free of rocks and other materials. Half-inch soil samples were collected with a stainless steel spatula and transferred to a sealable plastic bag. The six samples from a site were all transferred to the same plastic bag, double-bagged, and labeled for analysis as a composite sample.

On the same day as the soil sample collection, indoor dust samples were collected from the floors of three areas of the residence: the front entrance of the home, the kitchen, and the child's bedroom or other room where the child spent the most awake time. Dust samples were collected using a wet wipe method in 1-square-foot sample areas marked off with tape boundaries or a plexiglass template. Sample areas were cleared of foreign objects and dusted using a two-pass approach. The first step was to pass a wet wipe from right to left in an S-shaped pattern across the marked off surface; the wet wipe was then folded in half and a second pass was made in an S-shaped pattern from top to bottom, using the side of the wipe opposite of the side used in the first pass. The wet wipe was then folded, placed in a centrifuge tube, and labeled with a sample identification number, room location, surface type (vinyl, bare wood, carpet, painted, concrete, or other), and surface condition (good, fair, poor). A total of 696 dust wipe samples were collected from the 241 homes. The majority were from vinyl or bare wood surfaces (80%), 11% were from carpeted surfaces, and 9.0%

were from other surface types. Where surface conditions were specified, 79% were good, 20% fair, and 1.0% poor.

Soil and indoor dust samples were analyzed for Mn at Research Triangle Institute (Research Triangle Park, NC) using a method modified from USEPA Method 3050B Acid Digestion of Sediments, Sludge's, and Soils (USEPA, 1996). A description of the analysis process is provided in Fulk et al. (2017) and briefly summarized here. For each composite soil sample, 1 g was removed and placed in an extraction tube. For indoor dust samples, each wipe collected from a residence was placed in a separate extraction tube. Five milliliter of equal parts water and nitric acid (HNO_3) and 2 ml of hydrochloric acid (HCl) were added to each extraction tube. Samples were placed in a 48-well SCP Science DigiPREP digestion block for 1 h at 95 °C to allow a 15–20-min reflux of the sample. Samples were then removed and cooled to room temperature. After cooling, 2.5 ml of concentrated HNO_3 was added, and samples were returned to the digestion block for 2 h at 95 °C. Once again, samples were removed and cooled to room temperature, after which 1 ml of deionized water and 1.5 ml of hydrogen peroxide (H_2O_2) were added. The samples were returned to the digestion block for a final 2 h at 95 °C. Samples were diluted to a final volume of 50 ml with deionized water after removal and cooling to room temperature, then capped, shaken, and centrifuged at 1700 rpm for 20 min. For dust wipe samples, all samples from a single residence were combined prior to final dilution to create a single sample from a residence. All samples were analyzed with a Thermo X-Series II Inductively Coupled Plasma Mass Spectrometer (ICP-MS) (Thermo Fisher Scientific, Inc., Waltham, MA). The limit of detection (LOD) for Mn in dust was 5.0 μg , and for soil Mn the LOD was 25 $\mu\text{g/g}$. For statistical analysis of dust Mn levels, the number of grams of Mn was divided by the number of sample wipes, each 1 square foot in size, to obtain dust loadings of Mn in $\mu\text{g/ft}^2$. Values were then converted to $\mu\text{g/m}^2$ for all analyses.

Data analysis

Average annual ambient air Mn concentrations in ng/m^3 for the 105 census block centroids were summarized with mean (standard deviation, SD), median (interquartile range, IQR), and minimum and maximum values. For each centroid, the association between the natural log-transformed Mn concentration and distance from the Mn refinery was determined within each year with Pearson correlation coefficients and 95% confidence intervals (CI). Within each year, the proportion of census blocks and the estimated total population sizes with Mn concentrations that exceeded 50 ng/m^3 were determined. The 2010 US Census populations were used for exposure estimates, although the populations varied slightly over the 6-year period. Over the 2008–2013 time period, the estimated populations ranged from 61,333 to 61,705 in Washington Co. and from 86,502 to 87,147 in Wood Co (US Census Bureau, n.d.-b).

The ambient air Mn concentrations measured at the Rickey Science Center for 2009 through October 2010 were compared to average monthly concentrations determined with AERMOD. Three statistical measures of model performance were calculated: fractional bias (FB), normalized mean square error (NMSE), and the fraction of modeled concentrations within a factor of 2 of the observed concentrations (FAC2) (Hanna & Chang, 2012; Herring

& Huq, 2018). A Pearson correlation coefficient for the log-transformed values was also determined.

Fractional bias (FB) is a measure of the difference between modeled (C_M) and measured (observed, C_O) concentrations calculated as

$$FB = \frac{(\overline{C_O} - \overline{C_M})}{0.5(\overline{C_O} + \overline{C_M})}$$

While FB is a measure of systematic error only, the NMSE reflects both systematic and random errors. The NMSE is calculated as

$$NMSE = \frac{(\overline{C_O - C_M})^2}{(\overline{C_O})(\overline{C_M})}$$

The FB ranges from -2.0 to $+2.0$; the closer to 0, the less the model is biased. Absolute values of 0.30 or less are considered within the bounds of acceptable performance for air dispersion models using a rural setting. Acceptable values for NMSE and FAC2 are < 3.0 and > 0.5 , respectively (Herring & Huq, 2018).

To determine whether soil concentrations and dust loadings were associated with modeled air Mn concentrations and whether different averaged time periods for ambient air Mn affected the associations, modeled air Mn concentrations were averaged for 1, 6, and 12 months prior to the soil and dust sample collections. Air, soil, and dust Mn levels were summarized with descriptive statistics and then natural log transformed for correlation analyses. Pearson correlation coefficients were determined for soil and dust Mn with the air Mn concentrations, and with distance from the Mn refinery for the different years. Correlations between soil and dust Mn were determined for all years combined, and for the years 2009–2012 separately. The correlations for the separate years were determined in order to explore whether correlations were higher for years with higher Mn emissions. Correlations were not determined for 2008 and 2013 due to the small sample sizes ($n = 4$ for both years).

All descriptive and inferential statistics were conducted with SAS version 9.4 statistical software (SAS Institute, Cary, NC). Continuous variables were tested for normality with Shapiro–Wilk tests, and natural log transformed if the data were not normally distributed. For all Pearson correlation coefficients, 95% confidence intervals were calculated using the Fisher z transformation method. The t statistic was used to determine whether correlation coefficients were significantly different from 0. $P < 0.05$ were considered statistically significant.

Results and discussion

Mn refinery emissions across 2008–2013

The Mn emissions varied widely over the study period, primarily due to changes in the number and hours of operation of the furnaces as well as upgrades to emissions-limiting systems. Stack locations, heights, diameters, and exit temperatures, fugitive heights, lengths, widths, and rotation angles, emission rates, and days operating per year for all emissions sources by year are provided in Online Resource 1. Emissions were highest in 2008, with 237,012 lb, and lowest in 2010, with 41,531 lb (Table 1). Beginning in March 2009, the Mn refinery curtailed operation of two of its three furnaces due to a significant reduction in demand for steel products, which in turn reduced demand for Mn alloys (Corathers, 2011). Production was resumed at full capacity in 2010, but in March one furnace was shut down due to damage caused by a buildup of pressure that blew material off its top (Corathers, 2012). The proportion of stack emissions, which would tend to travel farther than fugitive emissions, also varied across the years. The lowest percent was in 2013, with 53% of total emissions comprised of stack emissions, and the highest percentage was in 2010, with 82% of total emissions comprised of stack emissions.

Ambient air Mn concentrations modeled with AERMOD

Contour maps of the concentration gradients for modeled average air Mn in ng/m^3 and locations of the census block centroids and the Mn refinery are shown in Fig. 2a–f. Air Mn concentrations decreased with distance from the Mn refinery but not uniformly because of the effects of wind speed and direction on dispersion. In general, the direction of the winds from the Mn refinery was toward the northeast, with speeds of 0.50–11.10 m/s. The percent of calm periods (wind speeds < 0.50 m/s), which AERMOD cannot use in dispersion calculations, ranged from 3.82 to 7.13% across the years. Wind roses for each modeled year are provided in Online Resource 2.

For all census blocks combined, the median (IQR) annual average air Mn concentrations (ng/m^3) varied from 6.3 (8.1) in 2010 to 43 (38) in 2008 (Table 2). The median (IQR) distance from the Mn refinery for census block centroids was 11.2 (5.5) km, range 2.9–29.2 km. Log-transformed modeled air Mn concentrations were negatively correlated with distance from the Mn refinery, with correlation coefficients ranging from -0.65 (95% CI $-0.75, -0.53$) to -0.84 ($-0.89, -0.77$). The R^2 values for the log-transformed average annual air Mn concentrations indicated that 43 to 71% of the variability in modeled air Mn could be explained by the distance from the centroids to the Mn refinery (Fig. 3a–f).

Table 3 shows the percent of centroids with annual average air Mn concentrations exceeding US EPA ($50 \text{ ng}/\text{m}^3$) and WHO ($150 \text{ ng}/\text{m}^3$) guidelines. In 2008, 41% of the census blocks, representing an estimated total population of 56,201, including 9370 children aged 0–14 years, had annual average airborne Mn concentrations $> 50 \text{ ng}/\text{m}^3$. The percent was lower in 2009 and 2010 but was then again relatively high in 2011 (27%, estimated population 36,911) before decreasing in 2012 and 2013 from 2011. Only a few census blocks had annual average concentrations above $150 \text{ ng}/\text{m}^3$, with the highest 5.7% of the census blocks (estimated population of 8,715) in 2008 (Table 3). In 2008 and 2011, the two census block

centroids closest to the Mn refinery had air Mn concentrations that exceeded the ATSDR MRL of $>300 \text{ ng/m}^3$.

Based on the models, from 12,000 to 56,000 individuals were exposed to respirable ambient air Mn levels exceeding 50 ng/m^3 in five of the six years modeled, potentially posing a health risk to those living in the area. The exception was 2010, the year with unusually low reported emissions. In four of the modeled years, more than 2000 individuals were exposed to $>150 \text{ ng/m}^3$ (Table 3). Further, an estimated 10,000 individuals in the six census blocks immediately surrounding the Mn refinery would have been exposed to $>50 \text{ ng/m}^3$ for the entire time period with the exception of 2010, if they lived in the area from 2008–2013. Exposures prior to 2008 were likely to have been much higher, based on emissions data for the Mn refinery available at the Toxics Release Inventory Program web site (USEPA, n.d.-b). The refinery has been operating for over 60 years, with annual Mn emissions that were higher than the emissions for the years modeled in the present study. For example, the fugitive and stack emissions of Mn compounds for the years 2000–2005 averaged 467,550 lb, while for 2008–2013 the average was 127,700 lb.

Studies in adults and children have found significant negative associations between environmental air Mn levels and adverse health outcomes, although the studies are not directly comparable because they differ in the particle sizes measured or modeled. Lucchini et al. (2014) measured 24-h personal air Mn in PM_{10} in 254 adults aged 65–75 years living near ferromanganese plants. The median (range) air Mn was 21 (30–103) ng/m^3 . Air Mn was negatively associated with odor discrimination and identification, tests of motor coordination, and tests of clear-thinking ability and spatial planning. Kim et al. (2011) and Bowler et al. (2012) compared neurological outcomes in adult residents of Marietta with adults in Mount Vernon, Ohio, a town with no industrial Mn exposure. Median (range) modeled air Mn levels for the Marietta group were 160 (40–960) ng/m^3 , but the authors did not specify particle size. Marietta residents scored significantly poorer on motor and bradykinesia scales, tests of postural sway, finger-tapping, and generalized anxiety. In a study of children aged 7–11 years living in the Molango mining district in Mexico, Torres-Augustin et al. (2013) found that the children scored significantly lower on the Children's Auditory Verbal Learning Test for almost all subscales compared to children of the same age living outside of the exposure area. The median (range) outdoor air Mn in $\text{PM}_{2.5}$ was 80 (20–240) ng/m^3 in the exposed group compared to 20 (3–90) ng/m^3 in the unexposed group.

Modeled air Mn compared to measured air Mn at a stationary monitoring site

Measurements of ambient air Mn taken from January 2009 through October 2010 at the stationary sampling site were used to evaluate the accuracy of air Mn concentrations modeled with AERMOD. The median ambient air Mn measured across 2009–2010 was 18 ng/m^3 , compared to 20 ng/m^3 for modeled air Mn over the same time period (Table 4). For individual monthly averages, the modeled values were higher than measured values for 13 of 22 months, with no discernable pattern to the under or overestimation across the time period (Fig. 4). For the entire time period as well as 2009 and 2010 analyzed separately, the measures of model performance were all within acceptable limits (Table 4). The modeled ambient air Mn averages across 2009–2010 slightly overestimated the measured air Mn

values, with a FB of -0.10 . For 2009, the FB was also negative, but for 2010, the value was positive, indicating the modeled values slightly underestimated the measured values. The overall deviation in modeled and measured values (NMSE) was 0.20, suggesting that air Mn concentrations modeled with AERMOD can reasonably represent measured air Mn concentrations. All but one of the differences between modeled and measured air Mn were within a factor of 2, resulting in a very high FAC2 of 0.96. The outlier occurred at the lowest measured monthly concentration of air Mn of 7.5 ng/m^3 , with a modeled concentration of 18 ng/m^3 . The closeness of the modeled air Mn concentrations with the air Mn concentrations measured in $\text{PM}_{2.5}$ at the stationary sampler indicates that Mn at that distance (7.8 km) from the refinery is most likely present in the $\text{PM}_{2.5}$ fraction. Stack emissions, which were predominant in this study, would tend to be finer and travel further than fugitive emissions due to greater buoyancy (Carter et al., 2015; WHO, 2000).

The modeled monthly concentrations of air Mn for 2009 are slightly higher than those of Fulk et al. (2016), who performed AERMOD modeling of the Mn refinery emissions for 2009 only and compared modeled air Mn to measured values at the stationary sampling site. In the Fulk et al. study, the median (range) modeled concentration was 13 (5.5–33) ng/m^3 , compared to 19 (7.6–38) ng/m^3 in the present study. One possible reason that could account for the higher modeled values in the present study is that the emissions data for 2009 provided by the U. EPA FOIA were different from the data reported in the Fulk et al. (2016) study. This suggests that the emission inventory data were updated after the Fulk et al. (2016) study. For the five stacks modeled in the Fulk et al. (2016) study, the combined emissions totaled 41,859 lb, while in the present study, the emissions totaled 51,201 lb.

Residential soil and indoor dust Mn samples

For the 241 sites with soil and indoor dust samples, the median soil concentration was 537 $\mu\text{g/g}$, and ranged from 94 to 2604 $\mu\text{g/g}$. Forty of the soil samples (17%) exceeded the range of 40–900 $\mu\text{g/g}$, considered the normal background range (ATSDR, 2012). The median indoor dust loading was 71 $\mu\text{g/m}^2$ (Table 5). The descriptive statistics for modeled ambient air Mn averaged over 1, 6, and 12 months prior to the soil and dust sample collection are also shown in Table 5. The values varied only slightly over the 3 time periods, ranging from a median of 24 ng/m^3 averaged over 1 month to 25 ng/m^3 averaged over a 12-month period. For 2008–2013 combined, the correlation (95% CI) between log transformed soil and dust Mn was 0.24 (0.12, 0.36). For individual years, the correlations were $r = 0.29$ (0.07, 0.49) for 2009 ($n = 72$), $r = 0.02$ (-0.27 , 0.30) for 2010 ($n = 47$), $r = 0.22$ (-0.02 , 0.43) for 2011 ($n = 72$), and $r = 0.29$ (-0.02 , 0.54) for 2012 ($n = 42$). For the individual years, only the correlation for 2009 was statistically significant. Among the four years, the Mn emissions were highest for 2011 (126, 821 lb), followed by 2012 (83,924 lb), 2009 (68,845 lb), and 2010 (41,531 lb), suggesting that higher correlations were not related to higher Mn emissions. For 2008 ($n = 4$) and 2013 ($n = 4$) correlations were not assessed due to the small sample sizes.

Table 6 shows the correlations for soil and indoor dust Mn levels with distance from the Mn refinery and modeled ambient air Mn levels averaged over 1, 6, and 12 months prior to soil and dust sample collection. Soil Mn concentration was not associated with distance from the

Mn refinery for any of the years. Indoor dust Mn was negatively associated with distance from the Mn refinery in 2011 but was not associated for any other years. For soil Mn, the only statistically significant association with modeled ambient air Mn was the correlation with air Mn averaged over the 12 months prior to the soil sample collection in 2009. Indoor dust was significantly associated with air Mn averaged over 6 and 12 months prior to the sample collection in 2011. No other correlations between soil or indoor dust with modeled average ambient air Mn were observed (Table 6).

The correlations among modeled air, soil, and indoor dust in this study, although small, were consistent with other studies of environmental Mn exposures (Butler et al., 2019; Fulk et al., 2017; Lucas et al., 2015; Zota et al., 2016). Correlations in these studies were 0.06–0.22 for air and soil Mn, 0.09–0.34 for air and indoor dust Mn, and 0.08–0.37 for soil and indoor dust Mn. Two of the studies (Lucas et al., 2015 and Zota et al., 2016) measured both indoor dust concentrations and indoor dust loadings and found that the correlations with air and soil Mn were higher for the dust concentrations than the dust loadings. There are several possible reasons that correlations among the different environmental measures in the present study were not higher. Modeled air Mn concentrations have inherent uncertainties associated with various model inputs that can affect the resulting estimates. Since air Mn was not measured at the sites of soil and indoor dust sample collection, it is not possible to quantify the degree of error that may be present in the air Mn estimates. In addition, the parent material of soils in the Marietta area is sedimentary rock, which varies in natural Mn concentrations (Carter et al., 2015). Soil Mn concentrations are cumulative and most likely reflect many years of deposition rather than the single year prior to sample collection for which air Mn concentrations were modeled. A number of factors can affect indoor dust Mn levels, including the location that was sampled, heating, ventilation, and air conditioning systems, overall housekeeping, number of occupants, and secondhand smoke. Finally, soil and dust Mn samples were collected at different times of the year, so seasonal variations in indoor dust composition as well as soil Mn deposition may also be a factor (Carter et al., 2015; Lioy et al., 2002).

Conclusion

The results of this study show that air dispersion modeling of Mn concentrations in the vicinity of industrial sources can be a viable option in epidemiologic studies of environmental Mn exposures. For the time period of January 2009 to October 2010, the association between modeled ambient air Mn and stationary air sampler ambient air Mn was well within acceptable limits based on the three criteria measures used. Modeled air Mn levels were negatively correlated with distance from the Mn refinery for all modeled years. Soil and indoor dust Mn were not associated with distance from the Mn refinery with the exception of indoor dust for 2011. None of the time periods assessed for associations between ambient air Mn and soil or indoor dust appeared to be a more accurate measure than any other.

There are limitations to the study that require consideration. First, the accuracy of AERMOD modeling is dependent on the quality of emissions data reported by the facility and used as model inputs. At the Mn refinery, reported annual emissions of Mn in pounds

are estimated based on mass balance equations that incorporate data subject to measurement error. In addition, the operating days and hours for the refinery are provided as total hours per year, so can only be equally distributed across the year in the model. This could have an impact on daily or monthly modeled Mn concentrations, but average annual Mn estimates are less likely to be influenced. Another limitation is that air Mn concentrations measured at the stationary sampling site were only available for January 2009 to October 2010, so comparisons of modeled and measured air Mn could not be made for 2008 and 2011–2013. However, for the almost 2-year period that comparisons could be made, the measures of model accuracy were well within acceptable limits.

For this study, Mn emissions were only modeled for the Mn refinery, so modeled air Mn concentrations may be underestimated because other sources in the study area were not taken into account. However, ATSDR studied health effects of Mn in Marietta in 2009 and concluded that the Mn refinery was the largest emitter, and was responsible for the majority of the Mn emissions in the area (ATSDR, 2009). National Emissions Inventory (NEIS) data available for download for the years 2008 and 2011 showed that in 2008, of eight facilities with Mn emissions in Washington Co., Ohio, 99% of total emissions were from the Mn refinery; in 2011, of ten facilities with Mn emissions, 97% were from the Mn refinery (USEPA, n.d.-a).

A limitation of using modeled ambient air Mn concentrations to estimate individual exposures is that the values may not fully reflect actual personal exposures. Individuals spend varying amounts of time at home, work, school, and other locations, as well as varying amounts of time outdoors, and these variations are not captured with modeling. However, one study (Fulk et al., 2016) compared 48-h air Mn concentrations modeled with AERMOD to personal air Mn in 19 children aged 7–9 years in Marietta. After removal of one outlier, approximately 42% of the variability in personal air Mn was explained by modeled air Mn concentrations ($R^2 = 0.4196$, $P = 0.004$).

Finally, the study shows that during the 6-year study period, residents in Marietta and the surrounding communities were exposed to respirable air Mn levels that often exceeded US EPA guidelines and at which health effects have been observed. The total amount of Mn emitted by the Mn refinery in 2013, the last year of the study, was 87,471 lb; in 2017, the most recent year available for data on Mn emissions from NEIS, the total amount for the Mn refinery was 127,260 lb, suggesting that the excess exposure continues to present a health risk to the community.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgements

The authors acknowledge the contributions of Joelle Strom, Caroline Beidler, Kelly Brunst, Heidi Sucharew, Derek Hennen, Joshua Mickle, and the Marietta Community Actively Researching Exposure Community Advisory Board. This work was completed in partial fulfillment of the Doctor of Philosophy degree in Epidemiology in the Division of Epidemiology, Department of Environmental and Public Health Sciences, College of Medicine, University of Cincinnati, Cincinnati, Ohio.

Funding

This publication was supported by funding from NIEHS (ES02644601A1, ES016531, and P30ES026529).

Availability of data and material

Data sharing agreements can be arranged for data pertaining to the research. Data may be available after review of the data request by the research team's executive team and community advisory board.

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Fig. 1.
Location of Washington County, Ohio, and Wood County, West Virginia

Fig. 2. Exposure area, 2010 census block populations, and modeled air Mn for the years 2008 (a) through 2013 (f)

Fig. 3. Modeled ambient air Mn at census block centroids and distance from the Mn refinery for 2008 (a) through 2013 (f)

Fig. 4. Modeled and measured ambient air Mn at the stationary air sampler site for January 2009 to October 2010

Table 1

Reported emissions for the Mn refinery, 2008–2013

Year	Point source emissions (lb)	Fugitive emissions (lb)	Total emissions (lb)
2008	183,890	53,122	237,012
2009	51,201	17,644	68,845
2010	34,094	7437	41,531
2011	84,528	42,293	126,821
2012	45,224	38,700	83,924
2013	46,768	40,703	87,471

Table 2

Descriptive statistics for modeled average annual ambient air Mn (ng/m³) for 105 census blocks within the modeled area

Year	Mean (SD)	Median (IQR)	Range
2008	61 (58)	43 (38)	17–431
2009	28 (23)	23 (16)	4.6–163
2010	10 (11)	6.3 (8.1)	2.6–88
2011	44 (51)	27 (35)	10–377
2012	30 (31)	21 (22)	5.9–248
2013	27 (31)	17 (21)	6.9–241

Table 3

Number of census blocks and estimated population sizes with modeled average annual air Mn greater than 50 ng/m³ and greater than 150 ng/m³ by year

Year	Average annual air Mn > 50 ng/m ³			Average annual air Mn > 150 ng/m ³		
	Number of census blocks, <i>n</i> (%)	Estimated total population	Estimated population aged 0–14 years	Number of census blocks, <i>n</i> (%)	Estimated total population	Estimated population aged 0–14 years
2008	43 (41)	56,210	9370	6 (5.7)	8715	1535
2009	9 (8.6)	13,209	2311	1 (1.0)	984	167
2010	1 (1.0)	959	179	0 (0.0)	0	0
2011	28 (27)	36,911	6219	3 (2.9)	4,655	835
2012	12 (11)	15,868	2743	2 (1.9)	2,374	391
2013	10 (9.5)	12,711	2193	2 (1.9)	2,374	391

The number of census blocks is based on the location of the census block centroids. The percent is the percent of all 105 census blocks in the modeled area. The estimated population is the sum of the populations of the census blocks listed for each year, based on 2010 US Census data

Summary statistics and model fit for ambient air Mn (ng/m³) at the stationary air sampler site for January 2009 to October 2010

Table 4

Time period	<i>n</i>	Mean (SD)	Median (IQR)	Range	FB	NMSE	FAC2
Jan 2009 to Oct 2010							
Measured	22	19 (8.4)	18 (7.6)	7.5–38	−0.10	0.20	0.96
Modeled	22	21 (7.8)	20 (12)	7.6–38			
Jan 2009 to Dec 2009							
Measured	12	16 (6.9)	18 (12)	7.5–28	−0.22	0.23	0.92
Modeled	12	20 (8.9)	19 (10)	7.6–38			
Jan 2010 to Oct 2010							
Measured	10	22 (9.1)	18 (13)	14–38	0.02	0.18	1.00
Modeled	10	22 (6.6)	23 (11)	8.9–30			

FB fractional bias, NMSE normalized mean square error, FAC2 fraction of modeled concentrations within a factor of 2 of the observed concentrations

Table 5
Descriptive statistics for soil Mn, indoor dust Mn, modeled ambient air Mn, and distance from the Mn refinery for 241 modeled sites

Variable	Mean (SD)	Median (IQR)	Range
Soil Mn ($\mu\text{g/g}$)	616 (341)	537 (378)	94–2604
Dust Mn ($\mu\text{g/m}^2$)	122 (198)	71 (86)	7.8–2207
Air Mn previous 1 m (ng/m^3)	33 (31)	24 (30)	0.5–226
Air Mn previous 6 m (ng/m^3)	32 (29)	26 (27)	1.2–261
Air Mn previous 12 m (ng/m^3)	32 (25)	25 (27)	4.4–229
Distance from Mn refinery (km)	12 (5.0)	11 (6.4)	2.5–31

Pearson correlation coefficients for log transformed soil and indoor dust Mn with distance from the Mn refinery and log transformed modeled ambient air Mn by year

	Distance from Mn refinery (km)	Ln air Mn previous 1 m	Ln air Mn previous 6 m	Ln air Mn previous 12 m
Ln soil Mn				
2009 ($n = 72$)	-0.23 (-0.44, 0.003)	0.05 (-0.19, 0.27)	0.09 (-0.14, 0.32)	0.30* (0.07, 0.49)
2010 ($n = 47$)	-0.11 (-0.39, 0.18)	-0.09 (-0.37, 0.20)	0.10 (-0.19, 0.37)	0.17 (-0.12, 0.44)
2011 ($n = 72$)	0.10 (-0.14, 0.32)	0.06 (-0.17, 0.29)	0.02 (-0.21, 0.25)	0.07 (-0.17, 0.30)
2012 ($n = 42$)	-0.15 (-0.43, 0.16)	0.11 (-0.20, 0.40)	0.13 (-0.18, 0.42)	0.02 (-0.29, 0.32)
Ln dust Mn				
2009 ($n = 72$)	-0.12 (-0.34, 0.11)	0.06 (-0.18, 0.28)	0.05 (-0.18, 0.28)	0.15 (-0.09, 0.37)
2010 ($n = 47$)	-0.09 (-0.37, 0.20)	0.19 (-0.10, 0.45)	-0.10 (-0.378, 0.190)	-0.11 (-0.39, 0.18)
2011 ($n = 72$)	-0.24* (-0.50, -0.01)	0.22 (-0.02, 0.43)	0.27* (0.04, 0.47)	0.29* (0.06, 0.49)
2012 ($n = 42$)	-0.10 (-0.39, 0.21)	0.05 (-0.26, 0.35)	0.15 (-0.16, 0.43)	0.08 (-0.23, 0.45)

Values in parentheses are 95% confidence intervals. Correlations were not determined for 2008 ($n = 4$) and 2013 ($n = 4$) due to the small sample sizes

t statistic for testing whether the correlation is significantly different from 0, m month

* $P < 0.05$