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Manganese concentrations in soil and settled dust in an area with historic ferroalloy production

Brian T. Pavilonis¹, Paul J. Liroy¹, Stefano Guazzetti², Benjamin C. Bostick³, Filippo Donna⁴, Marco Peli⁴, Neil J. Zimmerman⁵, Patrick Bertrand⁶, Erika Lucas⁶, Donald R. Smith⁶, Panos G. Georgopoulos¹, Zhongyuan Mi¹, Steven G. Royce¹, and Roberto G. Lucchini^{4,6,7}

¹Environmental and Occupational Health Sciences Institute. Rutgers University. Piscataway, NJ

²Local Health Unit, Reggio Emilia, Italy

³Lamont-Doherty Earth Observatory. Columbia University. New York City, NY

⁴Institute of Occupational Health. University of Brescia. Brescia, Italy

⁵School of Health Sciences. Purdue University. West Lafayette, IN

⁶Microbiology and Environmental Toxicology. University of California. Santa Cruz, CA

⁷Icahn School of Medicine at Mount Sinai. New York City, NY

Abstract

Ferroalloy production can release a number of metals into the environment, of which manganese (Mn) is of major concern. Other elements include lead, iron, zinc, copper, chromium, and cadmium. Manganese exposure derived from settled dust and suspended aerosols can cause a variety of adverse neurological effects to chronically exposed individuals. To better estimate the current levels of exposure, this study quantified metal levels in dust collected inside homes (n=85), outside homes (n=81), in attics (n=6), and in surface soil (n=252) in an area with historic ferroalloy production. Metals contained in indoor and outdoor dust samples were quantified using inductively coupled plasma optical emission spectroscopy while attic and soil measurements were made with a XRF instrument. Mean Mn concentrations in soil (4600 µg/g) and indoor dust (870 µg/g) collected within 0.5 km of a plant exceeded levels previously found in suburban and urban areas, but did decrease outside 1.0 km to the upper end of background concentrations. Mn concentrations in attic dust were approximately 120 times larger than other indoor dust levels, consistent with historical emissions that yielded high airborne concentrations in the region. Considering the potential health effects that are associated with chronic manganese inhalation and ingestion exposure, remediation of soil near the plants and frequent, on-going hygiene indoors may decrease residential exposure and the likelihood of adverse health effects.

Introduction

Ferroalloys have been used for over a century in the manufacture of steel. Production at these facilities can release large amounts of trace metals into the atmosphere which has the potential to settle in outlying residential areas.^{1,2} Even after production at these plants has ceased, populations living in close proximity can be exposed to contaminated settled dust

and soil through multiple pathways including inhalation of re-suspended particles and incidental ingestion.^{3–5}

Although essential for human health, frequent exposure to high concentrations of manganese (Mn) can often cause a variety of adverse health effects in occupationally and/or environmentally exposed populations.^{6–18} In occupational settings, where workers are exposed to large sustained concentrations of Mn, individuals can develop manganism, which is characterized by impaired motor function, extra-pyramidal movements, propensity to fall backwards, and erratic behavior.^{7,8,12,17,19,20} Although similar to Parkinsonism, the classical manganism is a separate and distinct, Parkinson-like disease. Less pronounced neurological effects have also been observed in occupational settings at lower exposure levels. Workers at a ferromanganese and silicomanganese plants had significantly altered mood disturbances including tension, anger, and confusion, as well decreased motor function relative to workers with no occupational manganese exposure.¹⁴ Individuals employed at an alkaline battery factory, exposed occupationally to Mn, also exhibited reduced visual reaction time, hand-eye coordination, and hand steadiness compared to a control group.¹⁶

Recently, researchers have begun to document similar health effects in populations with chronic environmental Mn exposure. Lifetime exposure to low levels of manganese is shown to increase the frequency of Parkinsonism in exposed populations. Lucchini et al.⁹ determined the prevalence of Parkinsonian cases in communities downwind from three former ferromanganese plants located in Valcamonica, Italy. Significantly higher standardized prevalence rates of Parkinsonism (492/100,000; 95% CI: 442.80–541.20) were found in communities with historic Mn exposure compared to communities with lower exposure levels in the same Province of Brescia, Italy (321/100,000; 95% CI 308.80–333.20). The prevalence rates of Parkinsonism were positively associated with the levels of manganese in deposited dust sampled in outdoor public locations.⁹ Adolescents (11–14 years) and elderly recruited from the same areas showed significant deficits in motor coordination, hand dexterity, and odor identification compared to individual residing in reference areas.¹⁰ The impairment of olfactory and motor functions was associated with the concentration of manganese in environmental media and biomarkers of exposure.^{21,22}

Young children are at an increased risk of settled dust exposure due to their propensity for hand-to-mouth contact as well as increased time spent on the floor where settled dust loading can be high.¹⁵ Mn levels found in hair samples collected from children (1–10 years) living in close proximity to a ferromanganese plant were an order of magnitude larger than children from a reference area.² Studies have found a significant correlation between elevated levels of Mn in hair samples and IQ deficits in children living within a 2-km radius from an active ferromanganese alloy plant¹³ and a hazardous waste site.¹⁸

The objective of this study was to characterize manganese and other trace metals in soil and dust samples in Valcamonica, Italy which has a history of ferroalloy production. Three different ferroalloy manufacturing plants operated for almost a century in the region. In 2001 operations at all the plants ceased and no alloy production has occurred in the area since that time. Here, we examine the impact of these operations on contamination levels in

soil, and the extent to which household dusts, a significant potential pathway of exposure, are currently contaminated by these historical Mn sources.

Methods

Study Site

This study was conducted in the Valcamonica region of Northern Italy (Figure 1). Valcamonica is a pre-Alpine glacial valley that runs for about 80 km in the northeast-southwest direction. The valley has an average width of about 3 km and steep sidewalls that contain atmospheric contamination. Wind speed and direction fluctuate diurnally throughout the year in response to thermal expansion and contraction of trapped air. During the day the wind blows up the valley at an average speed of 1.3 m/s, while at night the wind blows down the valley at an average speed of 1.3 m/s. Generally, at the ferroalloy plants, there were no daily shutdowns and production continued 24 hours a day. Therefore, depending on the time of day, daily atmospheric emissions from the plants oscillated along the valley floor.

The three ferromanganese plants are about 12 km from each other and are located in the towns of Sellero (population 1500) - operated from 1950 to 1985; Breno (population 5000) - operated from 1902 to 2001; and Darfo (population 13,200) - operated from 1930 to 1995. The town of Breno, home to the largest plant, had approximately 200 workers in its last decades of operation. Darfo employed about 100 workers, whereas Sellero had the smallest facility.

Sample collection

The study was approved by the Ethical Committee of Brescia (Ref. n.7/2012 on November 27, 2012). Indoor (n=85) and outdoor dust (n=81) samples were collected at 87 homes located in the Valcamonica valley. Sampling was carried out as part of a larger children, workers, elderly, and Parkinsonian patients' health study; subject recruitment strategies have been previously published¹⁰. Briefly, households were enrolled through the public school system according to a community-based participatory approach publicized by the local media and conferences. Households with children (age 11–14) were included in the study if the participating child was born in the study area and lived there since birth and their mother lived in the area during pregnancy. Children were excluded if they were diagnosed with a pathological condition potentially affecting neuro-development, took any medications for neuropsychological conditions, had clinically diagnosed motor deficits of hand and fingers, clinically diagnosed cognitive impairment and behavioral manifestations, or visual impairments not adequately corrected.

Surface area measurements were recorded for all locations in which dust was collected. Indoor samples were collected at a minimum of three different locations throughout the home, except the floor, that were observed to have accumulated settled dust (e.g. indoors on tops of tall furniture, cabinets, pipes, shelves, and door frames). Indoor dust samples were collected with either a cyclone vacuum cleaner that collected dust into a plastic sample jar or

a clean sampling brush. Outdoor dust was collected with a clean brush from window ledges, railings, and wooden beams that were protected from rain by the overhangs of house.

Household dust samples (excluding attic dust) were shipped to the trace metal analytical facility at the University of California, Santa Cruz for analyses. Non-dust materials were picked out of the samples by hand using cleaned stainless steel forceps to the greatest extent possible while at the same time retaining sufficient representative dust for processing. The extraction method used in this study has been previously described by Borgese et al. (2013).²³ Briefly, approximately 100 mg dust was leached in 1 mL trace metal grade 7.5 N HNO₃ at 80°C for 4 hours, diluted to 7 mL with Milli-Q water and centrifuged at 3000 × g for 20 minutes for analysis by inductively coupled plasma optical emission spectroscopy (ICP/OES) (Perkin-Elmer Optima 4300 DV Series). The analytical detection limits for Mn, Al (aluminum), Cd (cadmium), Cr (chromium), Cu (copper), Fe (iron), Pb (lead), and Zn (Zinc) were 1.3, 26, 1.6, 2.7, 2.6, 22, 35, and 5.5 ng/mL, respectively. The procedural reproducibility was ~ 5% RSD or better for all elements measured based on triplicate processing of house dust samples and certified reference material (CRM) BCR – 483 (European Commission, Joint Research Centre, Institute for Reference Materials and Measurements). The analytical accuracy ranged from ~95 – 110% of expected (i.e., indicative) values, based on analyses of CRM BCR-483.

Metal concentrations in soil were quantified at the sampling site with a portable X-ray fluorescence (XRF) instrument (Thermo Scientific Niton, model XL3t), set on soil mode. The correlation between XRF and ICP/OES was not measured in this study. A previous study found good agreement between the two methods for the metals we measured, with the ICP/OES generally having results 5 to 30% less than the XRF.²⁴ Measurements were taken outside a subset of homes (n=48) where dust samples were collected and in a strategic grid throughout the Valcamonica area (n=204). Two to four readings per-site were taken and averaged to obtain a concentration for each sampling location. The instrument was internally calibrated prior to each usage. Additionally, a series of soil standards reference materials, produced by the U.S. National Institute of Standards and Technology (NIST), were measured prior to each sampling session with the XRF: SiO₂ (Mn=0), NIST 2709a (Mn=529 µg/g) and NCS 73308 (Mn=1010 µg/g). These measurements had to fall within 2 standard deviations (SD) of the NIST reference value; if the reading fell outside that range but within 3 SD, another reading was needed and if acceptable, data collection could start; if not, a system recheck was needed.

Additionally, a pilot sampling of attic dust was completed and analyzed for metals for a small number of homes (n=6) in the Breno region. Cu, Fe, Mn, Pb, and Zn in attic dust were quantified at the sampling site with a portable X-ray fluorescence (XRF) instrument (Thermo Scientific Niton, model XL3t).

Latitude and longitude were recorded for all environmental measurement locations (GlobalSat Bluetooth GPS Receiver BT - 338). The distance from each sampling site was then calculated for each one of the three ferromanganese plants based on GPS coordinates. Due to the limited transport from each site and the presence of near background Mn levels

between them, the plant with the closest distance to the sample was considered as the source of trace metal deposition for that location,

To evaluate factors that may affect metal concentrations in settled dust traffic data, smoking habits inside the house, as well as socioeconomic status were collected at the time of sampling. Traffic outside the household was rated on a four point scale (absent, low, medium, high) based on traffic density and socioeconomic status (SES) was rated on a three point scale (high, medium, low). Parental education and occupational level were used to calculate SES. Education was divided in three levels: low (elementary and junior high school), medium (senior high school) and high (degree and post-degree). Occupations were grouped in three categories: low (skilled/unskilled worker, hospital ancillaries, etc.) middle (clerical workers, teachers, educators, nurses, shop assistant, etc.) and high (engineer, entrepreneur, tradesman, craftsman, etc.). The combination of education and occupation levels was used to obtain three levels of the SES index. Smoking status was classified as either yes or no if either the mother or father identified themselves as a current smoker.

Sampling seasons were assigned based on the sample date: winter was defined as December, January, and February; spring was March, April, and May; summer was June, July, and August; and autumn was September, October, and November.

Statistical Analysis

Statistical analyses were performed using R version 3.0.2. Descriptive statistics were determined, including mean, standard deviation, geometric mean, and empirical quartiles. Metal data distribution was, as expected, highly skewed. Following the Box-Cox approach to data transformation we used a logarithmic transformation of the observed concentrations of metals for the multivariate analyses.²⁵ Spearman's correlation coefficients (ρ) were calculated on untransformed metal concentrations and linear distance to the nearest ferromanganese plant. Distance to the nearest plant was then categorized (0.5 km; 0.5 – <1.0; 1.0 – <1.5; 1.5) and Tukey-Kramer multiple comparison tests were used to determine significant ($p < 0.05$) difference between log-transformed metal levels at various distances

Generalized Additive Models (GAM) were used to examine the relationships between Mn concentration in dust (both indoors and outdoors) and soil and the distance from the nearest ferromanganese plant (Breno, Darfo, and Sellero), correcting the estimates for socioeconomic status, traffic, smoking, latitude, longitude, elevation, and season.²⁶ If information on traffic density or SES was not known, the missing variable was imputed with the mode. GAM models are similar to linear (or generalized linear) models but allow to relax the assumption of linearity between the response variable and (some of) the covariates, using a smooth function of continuous covariates as a linear predictor. Within the GAM framework we studied the functional form of the relationship between Mn concentrations in dust and soil and distance to the nearest plant, using a stratified GAM to detect if the shape of Mn to distance relationship was different for each area, i.e. allowing the smoothing part of the GAM to be different for each plant neighborhood. The solid lines represent the penalized spline fit, where the smoothing parameter has been chosen by generalized cross

validation.²⁶ We obtained the most parsimonious model using a stepwise approach, according to the Akaike's Information Criterion (AIC) guidance.

Results

Demographic information of the homes surveyed is shown in Table 1. Most indoor and outdoor dust samples were collected from homes located in Sellero (55%), with very few from Darfo (2%). The majority of participants had medium socioeconomic status (56%), lived in a residence with low street traffic (52%), and did not smoke inside the home (99%).

Descriptive statistics including mean, geometric mean, standard deviation, percentiles, and range for soil, indoor dust, and outdoor dust are shown in Table 2. Fe and Al were found in the greatest abundance of any of the metals quantified while Cr, Cd, and Pb concentrations were the lowest. Mean indoor dust concentrations of Mn (410 µg/g) were an order of magnitude smaller compared to soil (2500 µg/g) and outdoor dust (1300 µg/g) concentrations. Conversely, Cu, Pb, and Zn were lower in soil compared to indoor and outdoor dust. The mean ratio of indoor dust concentrations to soil concentrations were 0.37 for Mn, 4.9 for Cu, 0.26 for Fe, 2.7 for Pb, and 4.8 for Zn. Mn concentrations in soil were varied with a coefficient of variation (CV) of 192% and a range spanning two orders of magnitude (190–47000 µg/g). The variability of Mn in indoor and outdoor dust samples was less pronounced with a CV of 83% and 108%, respectively.

The distance from the ferroalloy plant was the single largest determinant of Mn concentrations in soil ($\rho = -0.27$, $p < 0.001$) and indoor dust ($\rho = -0.26$, $p = 0.018$) (Table 3). A significant negative correlation was observed between distance to nearest ferromanganese plant and Pb ($\rho = -0.22$, $p < 0.001$) and Zn ($\rho = -0.23$, $p < 0.001$) soil concentrations. No significant correlations were found in outdoor dust concentrations and plant distance, with Mn ($\rho = -0.17$, $p = 0.122$) having a marginal correlation. Far fewer indoor ($n = 7$) and outdoor ($n = 6$) dust samples were collected than soil samples ($n = 88$) in areas < 0.5 km from the plants. The lack of obvious relationships between Pb and Zn dust concentrations and distance to the plant may reflect limited sampling, particularly near the plants, where contamination could be highest but also most variable.

Distance was stratified into four categories for further analysis (Table 4). Geometric mean Mn levels in soil were significantly higher at a distance of < 1.0 compared to measurements taken at ≥ 1.0 . Likewise, a significant increase was observed in indoor Mn dust measurements taken with ≤ 0.5 km compared to levels at ≥ 1.0 . Levels of Pb and Zn were significantly increased in soil samples collected within 0.5 km of the plants compared to samples collected beyond 1.0 km. No significant trend was observed in outdoor dust, with Mn, Pb, and Zn levels all comparably at various distances.

The effect of three different ferromanganese plants (Breno, Sellero and Darfo) on Mn concentrations in soil was examined for the using GAMs. Distance from the nearest ferromanganese plant (m), plant (categorical), season (winter, spring, summer, autumn), geographic localization (latitude and longitude degrees), and altitude (m) were analyzed as possible explanatory variables. In the final model only the distance from the nearest plant

and the geographic localization were found to be significant predictors of soil Mn concentrations. Higher Mn levels (as well as higher Mn variability) were observed in the vicinity of plants and the shape of the functional relationship between Mn and distance from the nearest plant seem to vary by plant (Figure 2). The fall and the rise of Mn with distance from the Breno plant could be due to its proximity to other sources. Breno is in the middle of the valley and as the distance from the Breno plant increases there could be an additive effect of the Sellero and Darfo plants. Of the three plants Mn levels in Darfo were the lowest closest to the plant, while levels in Breno were the highest. Mean Mn concentrations and standard deviation in soil within 0.5 km of the Breno plant were $8000 \pm 10000 \mu\text{g/g}$ compared to 2600 ± 4300 at the other sites. Levels outside 2.0 km were comparable in Breno and Sellero.

Indoor and outdoor dust explanatory variables that were evaluated using GAM analyses included traffic, distance to the ferroalloy plant, SES, geographic localization, elevation, and season. One participant indicated that they smoked inside the home, therefore smoking was dropped from analysis. Additionally, only two indoor measurements were recorded near the Darfo facility, these measurements were not included in the analysis. Only distance from the nearest plant and the geographic localization were found to be significant predictors of indoor and outdoor Mn concentrations in the final model. As with the soil concentrations, indoor Mn dust levels in Breno were elevated closest to the plant but leveled off at approximately 1 to 1.5 km (Figure 3).

Attic dust accumulates undisturbed slowly over time, and thus represents an integrated measure of exposure. Metal levels were measured in the attic dust samples in a small subset of homes ($n=6$), in the Breno region (Table 5). None of the homes sampled were within 0.5 km of a plant, yet Mn concentrations were high and variable, with a mean of $46000 \mu\text{g/g}$ and a standard deviation of $45000 \mu\text{g/g}$. Dust collected in one attic had Mn concentrations as high as $130000 \mu\text{g/g}$. With the exception of Cu, metal concentrations in attic dust were 3.6 to 115 times higher than those measured in indoor dust from Breno. Concentrations in the attic were also elevated compared to outdoor dust samples with a 2.3 to 32 times increase.

Discussion

The objective of this analysis was to characterize Mn concentrations in soil and dust in areas with historic ferroalloy production facilities. Although the ferromanganese production at these facilities ceased more than a decade ago, individuals living in this area would still become exposed to Mn through the re-suspension of contaminated soil and dust.^{3,4} Additionally, children may be at higher risk of exposure through inadvertent or intentional ingestion of soil and dust¹⁵. In fact, several playgrounds, soccer fields, and other outdoor recreational areas are located around the old plant sites. Mean soil concentrations within 0.5 km of all ferroalloy plants were $4600 \pm 7400 \mu\text{g/g}$ which is one to two orders above the average range of Mn found in typical uncontaminated soil ($40\text{--}900 \mu\text{g/g}$).²⁷ A previous study conducted in Valcamonica found Mn was readily extractable from soil, suggesting that the Mn was bioavailable and therefore a potential health risk²³. Soil concentration decreased over relatively short distances, with concentrations approaching background

within 1.0 km. We attributed the drop-off in Mn levels to the rapid fallout of emissions of larger particles in the aerosol and light prevailing winds.

Mn concentrations in close proximity to the Breno plant were higher in soil than the other two plants. The Breno facility was the largest of the three plants and was the last to cease operations. Outside a soccer field, where community members regularly congregate in Breno, concentrations were as high as 47000 µg/g (Figure 4). Concentrations of Mn in soil within 0.5 km (8000±10000 µg/g) of the Breno plant were similar to those adjacent to a closed ferromanganese plant outside of Montreal, Canada (6232±5100 µg/g). At 800m from the Montreal site, atmospheric concentrations of respirable Mn (0.13 ±0.03 µg/m³) were approximately 3 times higher than the US Environmental Protection Agency (EPA) reference concentration (0.05 µg/m³). The authors inferred that settled dust was becoming re-suspended and possibly impacting the air surrounding the community a decade after the plant was closed.¹ Re-suspension of metals contained in contaminated soil has been found to impact air quality and may serve as an important exposure pathway in Valcamonica.^{4,28–30} This is a concern as Mn is more efficiently adsorbed by the body via inhalation compared to other routes of exposure³¹.

Mn levels found in indoor dust were also increased in residences located near the closed ferroalloy facilities, likely the result of track-in or penetration from outdoors. Average concentrations for homes within 0.5 km of a plant (870 µg/g) were 2.4 times greater than levels found in homes located 1.0 km from a plant (370 µg/g). The highest indoor level (2100 µg/g) was observed at a home located next to (0.13 km) the plant in Sellero. This value is similar to levels detected in Mn contaminated soil found near the plant. Indoor Mn levels within 0.5 km of a plant were 3 to 11 times higher in the Valcamonica region compared to concentrations found in previous urban and suburban studies.^{32–34} Rasmussen et al.³³ sampled 48 homes in Ottawa, Canada and found mean manganese concentrations of 269 µg/g and a maximum concentration of 423 µg/g. Mean concentrations found in Sydney, Australia (n=82) were 76 with a maximum concentration of 624 µg/g.³²

Distance to the nearest plant and geographic localization predicted 43% of the variability in indoor Mn concentrations. However, other factors that could affect settled dust concentrations inside the home include cigarette smoke³⁵, motor vehicle traffic³⁶, low socioeconomic status³², and home cleanliness.^{34,37} Except for one family, all participants identified as not smoking inside the home. In a generalized additive model, which included distance to a ferromanganese plant and geographic localization, SES and traffic were highly non-significant. Although it appears that distance to the plant and geographic localization were the largest contributor to indoor Mn levels, other unmeasured variables such as hygiene, indoor air exchange rates, and heating may have attenuated the effect.

Since attics are rarely cleaned they have served as a historical record of past air pollution deposition³⁸. Mn concentrations in the attic were approximately 120 times higher than mean indoor dust samples collected in the Breno region. The high attic dust Mn concentrations likely reflect the high levels of Mn enrichment in aerosols produced while plants were still operational. Given that it is also likely that the aerosol concentrations were higher during the period of active emissions, it is also likely that respirable Mn levels were

higher a decade ago than they are today. Despite this progress, indoor Mn concentrations are still elevated compared to urban and suburban areas, which shows the persistent effect of metal contamination in the environment.

Italian regulatory agencies do not have any contamination guidelines for manganese. The US EPA has derived a reference dose of 0.14 mg/kg-day for chronic ingestion of Mn.³⁹ Assuming a worst case exposure scenario, living within 0.5 km of a plant in Breno, a 10 kg child would be over-exposed to Mn ingesting 175 mg of contaminated soil per day. This is neglecting Mn intake from inhalation of re-suspended dust, possible well water contamination, and ingestion of indoor dust which, depending on the residential location, may be on the same order of magnitude as soil levels. Notably, motor and odor deficits have been observed in the children living in households located in this area with Mn levels in soil above 1000 µg/g.¹⁰ Given the distribution of Mn concentrations observed in soils, motor and olfactory deficits are probably highly heterogeneous and localized in the vicinity of the plant. Remediation is a potential means of decreasing Mn exposure. These data suggest that remediation should be focused within 1.5 km of plants, particularly in the Breno area where contamination is highest, and include a means of decreasing the re-suspension of soil particles.

Conclusions

Although production of ferromanganese ceased more than a decade ago, Mn still persists in the environment in the Valcamonica region. Residents in this area are exposed to increased levels of Mn in soil and indoor settled dust compared to urban and suburban populations. Mn concentrations were significantly elevated in soil and indoor settled dust samples collected within 0.5 km radius but decreased to around background levels at 1.0 km from the plant. In an effort to characterize historical exposure, dust samples were collected in the attic of a small number of homes. Mn concentrations were approximately 120 times higher than mean indoor dust samples, which is likely the result of high levels of Mn enrichment in aerosols produced while plants were still operational. Results from this study suggest that Mn contamination in soil and indoor dust in this area are still problematic and may warrant remediation to reduce exposure.

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Figure 1.
Ferroalloy plant location in the Valcamonica region

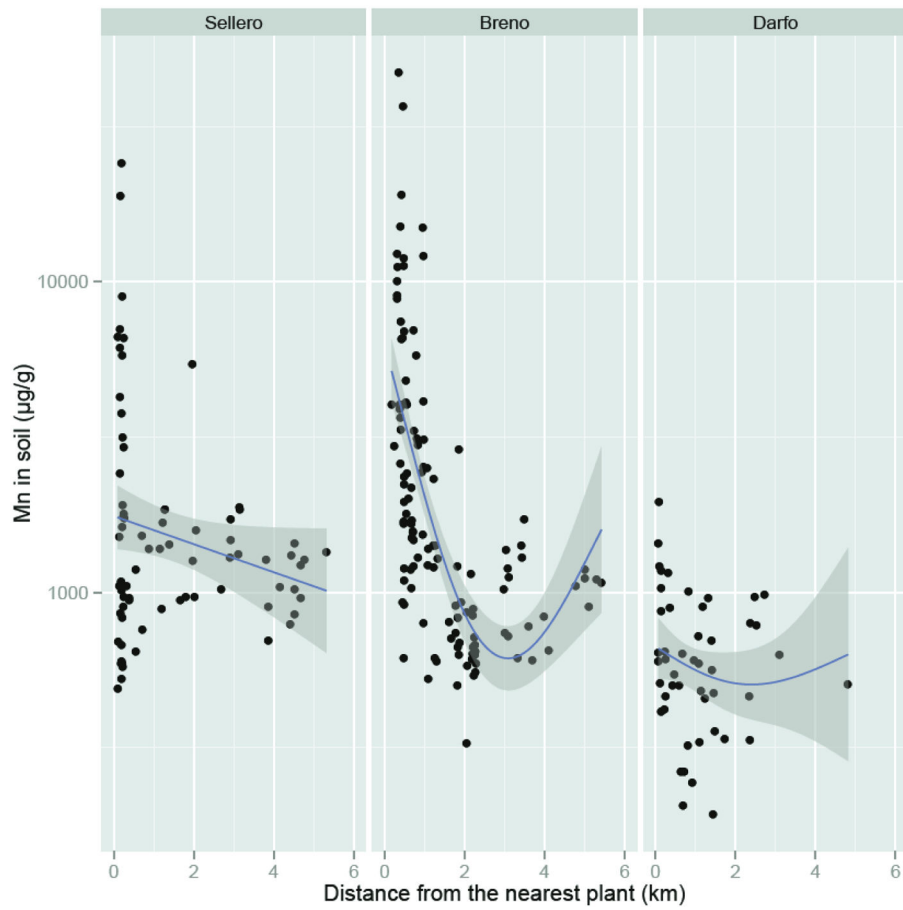


Figure 2. Soil Mn decay and a function of the distance from the nearest plant, stratified by plant (town)

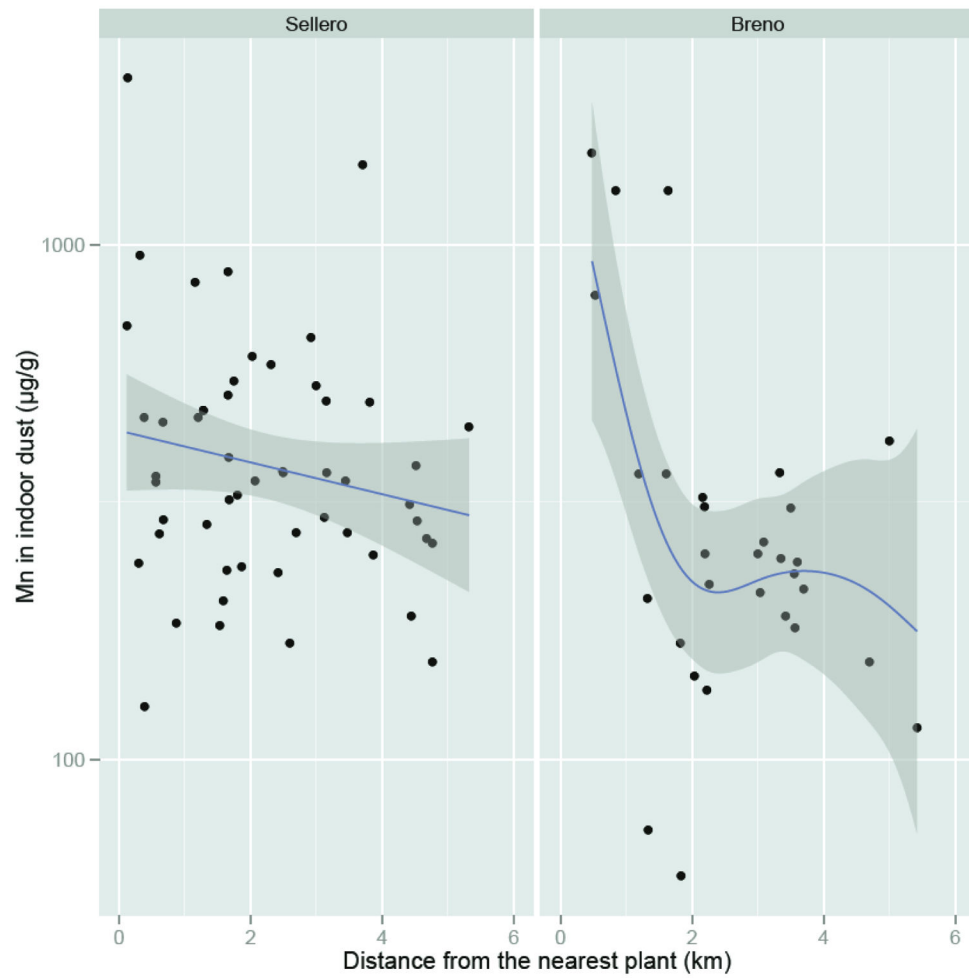


Figure 3.
Relationship between dust Mn and the distance from the nearest plant, stratified by plant (town)

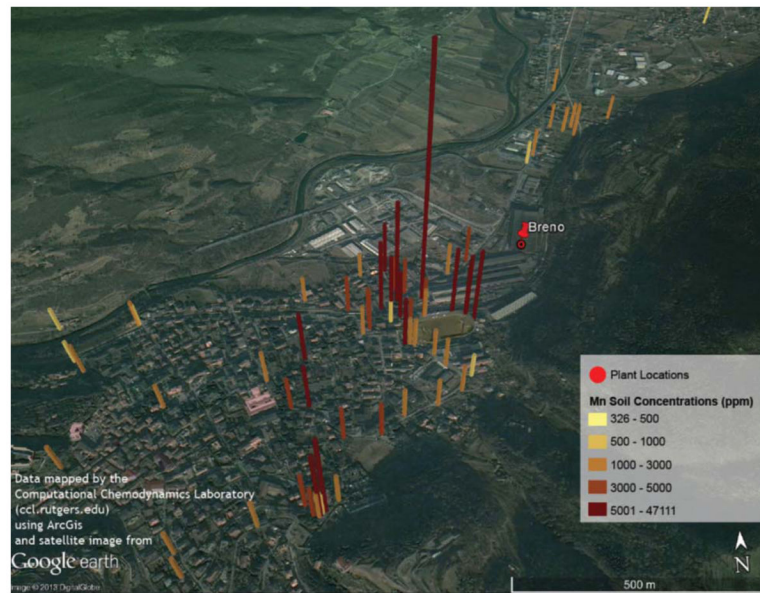


Figure 4.
Mn soil concentrations in the vicinity of the Breno plant

Table 1

Demographic characteristics of homes (n= 87) sampled

Variable	N (%)
Socioeconomic status	
Low	18 (21)
Medium	49 (56)
High	20 (23)
Traffic	
Absent	18 (16)
Low	45 (52)
Medium	21 (24)
High	7 (8)
Smoke inside the home	
Yes	1 (1)
No	86 (99)
Season of sampling	
Autumn	16 (18)
Spring	24 (26)
Summer	40 (46)
Winter	7 (8)
Town	
Breno	30 (34)
Darfo	2 (2)
Sellero	55 (63)

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Table 2

Mean concentration, SD, GM, percentiles, and range of metals in indoor dust, outdoor dust, and soil samples.

Indoor dust ($\mu\text{g/g}$)						
Metal	N	Mean \pm SD	GM	25 th percentile	75 th percentile	Range
Al	85	4600 \pm 2200	4100	3000	5700	680 – 14000
Cd	85	2.5 \pm 5.0	1.6	1.1	2.4	0 – 40
Cr	85	47 \pm 30	43	33	56	19 – 260
Cu	85	290 \pm 450	200	140	270	38 – 900
Fe	85	5900 \pm 3300	5000	3600	7500	730 – 19000
Mn	85	410 \pm 340	330	230	460	60 – 2100
Pb	85	100 \pm 150	62	41	88	1.8 – 1000
Zn	85	640 \pm 790	510	360	670	130 – 7200

Outdoor dust ($\mu\text{g/g}$)						
Metal	N	Mean \pm SD	GM	25 th percentile	75 th percentile	Range
Al	81	10000 \pm 2500	10000	8400	12000	5100 – 19000
Cd	81	2.3 \pm 2.3	1.9	1.5	2.1	0.8 – 16
Cr	81	71 \pm 58	59	41	80	25 – 410
Cu	81	500 \pm 1500	240	150	280	53 – 12000
Fe	81	21000 \pm 15000	19000	15000	24000	6900 – 140000
Mn	81	1300 \pm 1400	1000	680	1300	410 – 8200
Pb	81	200 \pm 400	120	73	160	32 – 3200
Zn	81	1600 \pm 6000	700	470	800	200 – 53000

Soil ($\mu\text{g/g}$)						
Metal	N	Mean \pm SD	GM	25 th percentile	75 th percentile	Range
Cu	252	61 \pm 52	50	36	71	0 – 610
Fe	252	21000 \pm 8200	20000	16000	27000	4900 – 49000
Mn	252	2500 \pm 4800	1300	700	1900	190 – 47000
Pb	251	68 \pm 90	46	28	64	9.0 – 630
Zn	252	290 \pm 570	180	100	250	42 – 5500

Abbreviation: GM, geometric mean.

Table 3

Spearman's correlations between metal concentration and distance to nearest ferroalloy plant.

Metal	Soil df = 250^a ρ (<i>p</i>)	Indoor dust df = 83 ρ (<i>p</i>)	Outdoor dust df = 79 ρ (<i>p</i>)
Al	<i>b</i>	-0.11 (0.309)	0.04 (0.736)
Cd	<i>b</i>	-0.06 (0.590)	0.05 (0.658)
Cr	<i>b</i>	0.05(0.653)	-0.19 (0.083)
Cu	0.12 (0.056)	-0.02 (0.890)	-0.05 (0.627)
Fe	0.04 (0.490)	-0.01 (0.967)	-0.01 (0.896)
Mn	-0.27 (<0.001)	-0.26 (0.018)	-0.17 (0.122)
Pb	-0.22 (<0.001)	0.01 (0.940)	0.10 (0.368)
Zn	-0.23 (<0.001)	0.03 (0.778)	0.09 (0.407)

^adf =249 for Pb.^bMetals not quantified by XRF instrument.

Table 4

Geometric mean Mn, Pb, and Zn concentration $\mu\text{g/g}$ and (geometric SD) stratified by distance to the nearest ferroalloy plant.

Distance (km)	Soil						Indoor						Outdoor					
	N	Mn	Pb	Zn	N	Mn	Pb	Zn	N	Mn	Pb	Zn	N	Mn	Pb	Zn		
<0.5	88	2200 ^a (3.2)	63 ^a (2.6)	260 ^a (2.8)	7	610 ^a (2.7)	53 ^a (1.5)	470 ^a (2.0)	6	1400 ^a (2.3)	100 ^a (1.9)	670 ^a (1.5)	6	1400 ^a (2.3)	100 ^a (1.9)	670 ^a (1.5)		
0.5 – <1.0	45	1600 ^a (2.7)	46 ^{ab} (2.1)	150 ^b (1.8)	9	420 ^{ab} (1.8)	91 ^a (3.1)	700 ^a (2.6)	8	1400 ^a (2.4)	100 ^a (3.4)	580 ^a (1.9)	8	1400 ^a (2.4)	100 ^a (3.4)	580 ^a (1.9)		
1.0 – <1.5	29	880 ^b (1.9)	37 ^b (1.6)	140 ^b (1.6)	9	310 ^b (2.1)	64 ^a (1.4)	420 ^a (1.5)	8	1200 ^a (1.4)	190 ^a (3.6)	890 ^a (3.0)	8	1200 ^a (1.4)	190 ^a (3.6)	890 ^a (3.0)		
1.5	90	910 ^b (1.5)	36 ^b (1.7)	140 ^b (1.7)	60	300 ^b (1.7)	60 ^a (2.8)	500 ^a (1.7)	59	950 ^a (1.7)	120 ^a (1.8)	690 ^a (2.3)	59	950 ^a (1.7)	120 ^a (1.8)	690 ^a (2.3)		

Same letter indicates no significant difference.

Table 5

Mean concentration ($\mu\text{g/g}$), GM, SD, and range of metals in attic dust samples.

Metal	N	Mean \pm SD	GM	Range
Cu	6	270 \pm 140	230	90 – 420
Fe	6	65000 \pm 23000	62000	39000 – 110000
Mn	6	46000 \pm 45000	29000	7700 – 130000
Pb	6	440 \pm 230	390	180 – 750
Zn	6	2000 \pm 780	1900	980 – 3200

Abbreviation: GM, geometric mean.

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