

# Health Consultation

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WASHINGTON COUNTY AIR QUALITY

MARIETTA, OHIO

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U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES

Public Health Service

Agency for Toxic Substances and Disease Registry

Division of Health Assessment and Consultation

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## **Health Consultation: A Note of Explanation**

An ATSDR health consultation is a verbal or written response from ATSDR to a specific request for information about health risks related to a specific site, a chemical release, or the presence of hazardous material. In order to prevent or mitigate exposures, a consultation may lead to specific actions, such as restricting use of or replacing water supplies; intensifying environmental sampling; restricting site access; or removing the contaminated material.

In addition, consultations may recommend additional public health actions, such as conducting health surveillance activities to evaluate exposure or trends in adverse health outcomes; conducting biological indicators of exposure studies to assess exposure; and providing health education for health care providers and community members. This concludes the health consultation process for this site, unless additional information is obtained by ATSDR which, in the Agency's opinion, indicates a need to revise or append the conclusions previously issued.

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Prepared By:

U.S. Department of Health and Human Services  
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## Background and Statement of Issues

On May 22, 2000, the Agency for Toxic Substances and Disease Registry (ATSDR) was petitioned by United States Senator Mike DeWine (Ohio) to evaluate the health impacts from air pollution on residents of Marietta, Washington County, Ohio (ATSDR, 2000).

Although the Ohio River valley is a highly industrialized area, residents in the area are most concerned about exposure to emissions from an industrial complex just outside the Marietta city limits. This complex is the former site of a single facility, Union Carbide, which is currently occupied by four companies including: Eramet Marietta, Inc. (EMI), Eveready Battery, Solvay Advanced Polymers, and Chevron-Phillips Chemical Company. American Municipal Power (AMP) Ohio, originally built to provide power to Union Carbide, is located across the street from the complex. This complex of facilities was identified for our investigation by conversations with residents and local health officials.

The City of Marietta is located 4 miles northeast of the facility (see Appendix A). In 2000, the United States Census Bureau reported that the population of Marietta was approximately 14,500 people. The land use in the city limits is mostly residential and commercial, and heavy industry is located to the south of the city along the Ohio and Muskingham Rivers. The land surrounding the city is mostly rural residential properties, or agricultural. The predominant wind direction in the area is out of the southwest. A residential area is located to the north of the former Union Carbide complex.

Residents are concerned about the contributions of each facility to their general air quality, but feel that EMI is the greatest contributor of air pollutants in the area (ATSDR, 2002). Residents have reported a variety of symptoms they believe are related to emissions from these facilities, including: headaches, burning eyes, nausea, difficulty breathing, fatigue, muscle aches, tremors, sinus problems, bloody noses, a metallic taste in their mouths, a bitter metallic taste in their throats, an ammonia smell, and sore throats (ATSDR, 2002).

In a Health Consultation document dated February 26, 2004, ATSDR noted that although outdoor concentrations of manganese and arsenic (and to a lesser degree chromium and cadmium) exceeded health based guidelines, data were limited for assessing the potential health impacts of facility emissions from the former Union Carbide complex. To enable the agency to better address health concerns, ATSDR recommended: 1) modeling of emissions from the facilities which make up the facility complex; 2) determine from the modeling what additional data are necessary to help evaluate health impacts in the area; 3) request additional sampling in areas where modeling predicts the highest concentrations of emissions from these facilities; and 4) evaluate the data from this sampling to identify air pollutants and their concentrations in maximum impact areas.

This document summarizes the results of the air modeling activities and evaluates additional air monitoring that was recommended in the February 2004 Health Consultation. The recommendations are listed in the following sections in *italics*.



## **I. Modeling**

ATSDR made the following recommendation in its 2004 Health Consultation:

*ATSDR or USEPA should model emissions from EMI, Eveready, Solvay, Chevron, and AMP Ohio to determine what contaminants could be present in ambient air, and the locations where they are likely to most significantly impact human health. This information will aid in determining the most appropriate locations for additional air sampling.*

### **A. Modeling design**

ATSDR contracted with the Environmental Response Team (ERT), Response Engineering and Analytical Contract (REAC), of the United States Environmental Protection Agency (USEPA) to conduct the modeling of the five facilities now operating at the former Union Carbide complex. Modeling is a computer-generated estimation of air concentrations that are calculated with the use of measured weather information (wind direction, windspeed, temperature, pressure, etc.), terrain data (hill and valley elevations), and facility emissions data.

Due to the very complex terrain in the area, windspeeds and wind directions measured near the facility may not represent those in other parts of the community. This is because the hills and valleys can cause abrupt shifts in windspeeds and wind directions. A simple plume model cannot adequately account for the effects of complex terrain how weather conditions affect the *dispersion* (spreading) and *deposition* (fall out) of air contaminants. To control these variables, the USEPA ERT contractors used the CALPUFF model, which is a more complex model that is capable of successfully estimating air concentrations in an environment with complex terrain (REAC, 2004). CALPUFF is a Lagrangian puff model. The model is programmed to simulate continuous puffs of pollutants being emitted from a source into the ambient wind flow, and does not assume continuous emissions from a facility the way that plume models do. As the wind flow changes from hour to hour, the path each puff takes changes to the new wind flow direction. Puff diffusion is Gaussian and concentrations are based on the contributions of each puff as it passes over or near a receptor point (USEPA, 1998).

Facility-specific emissions information was acquired from USEPA for modeling purposes. This information was acquired by USEPA under the Clean Air Act Section 114 administrative authority. Weather data were obtained from several sources, including a weather station owned and operated by AMP Ohio on property adjacent to the Complex, and from weather stations in Parkersburg and Wheeling, West Virginia (REAC 2004).

Each of the facilities handles specific materials that are unique to their processes and the products they create, so each facility was considered separately. Their processes were often modeled as separate ‘sources’. A source characterization was performed at each facility to identify the processes that could contribute to air emissions of specific compounds. Some facilities had many processes that could contribute to the total emission of a compound, and some only had a single process where a compound was used.



Based on major processes for each of the facilities in the former Union Carbide Complex, nine compounds and metals were modeled from the five facilities. These include the following:

**Table 1. List of modeled substances emitted from area sources.**

Facility	Organic Compounds Modeled	Metals Modeled
<i>Eramet</i>	Ammonia (NH <sub>3</sub> )	Chromium (Cr), Manganese (Mn)
<i>Chevron/Phillips</i>	Styrene, Toluene	None modeled
<i>Eveready</i>	None modeled	Manganese (Mn)
<i>Gorsuch/ AMP Ohio</i>	Hydrochloric Acid (HCl), Sulfuric Acid (H <sub>2</sub> SO <sub>4</sub> )	None modeled
<i>Solvay</i>	Chlorobenzene, Chloromethane	None modeled


## B. Modeling results

Sources of emissions from facilities were modeled as either “point” sources, “area” sources, or “volume” sources. A point source is a stack, pipe, or other discrete source from which pollutants are emitted. An area source is defined as a source of air pollution that is released over a relatively small area but which cannot be classified as a point source (USEPA, 2006), such as a landfill. Volume sources are sources that emit equally in all directions (three dimensionally). Maps produced from modeling runs can be found in Appendix B for selected compounds.

To determine whether the modeled level of emissions could pose a health threat, ATSDR screened the concentrations of compounds against health based comparison values (CVs), and reviewed scientific literature that document health effects caused by exposure to these compounds. In this evaluation, the modeled air data were compared to ATSDR minimal risk levels (MRLs) for chronic or intermediate exposures (those occurring longer than 365 days or from between 14-365 days) and USEPA Reference Concentrations (RfCs) and inhalation unit risk factors where MRLs were not available. MRLs and RfCs are estimates of daily human exposure to a hazardous substance that are below concentrations that have caused adverse health effects in exposure studies. If modeled concentrations of compounds were below health based guidance values, they were not considered to be a health threat; if the modeled concentrations were higher than the health based guidelines, monitoring to confirm ambient concentrations was recommended.

In order to understand the various units of concentrations discussed in this section properly, the units of concentration are as follows. All are a mass weight of the particle per volume (in this case a cubic meter of air).



Guide to mass per volume concentrations			
	Unit	Unit notation	Comments
<b>Largest</b>  	Milligram per cubic meter	mg/m <sup>3</sup>	1 gram/1000 = 1 milligram (mg)
	Microgram per cubic meter	µg/m <sup>3</sup>	1 milligram/1000 = 1 microgram (µg)
	Nanogram per cubic meter	ng/m <sup>3</sup>	1 microgram/1000 = 1 nanogram (ng)
	Picogram per cubic meter	pg/m <sup>3</sup>	1 nanogram/1000 = 1 picogram (pg) 1 microgram/1,000,000 = 1 picogram 1 milligram/1,000,000,000 = 1 picogram
<b>Smallest</b>			

### Ammonia

Ammonia emissions from the Eramet facility came from three sources;

1. P020 Manganese Metal Process (also call the “ElMang” process), which ceased operations in October 2000. The model input for this point source was from an annual average derived from 1998, 1999, and 2000 data for the ElMang process.
2. the Unox Equalization Basin, modeled as an area source and
3. the North Impoundment, also modeled as an area source.

Annual emission rates for the area sources were averaged from 1998-2002 to represent a chronic exposure scenario.

The model estimated maximum annual concentrations of ammonia between 100 micrograms per cubic meter (µg/m<sup>3</sup>) and 3,500 µg/m<sup>3</sup>. Concentrations above 100 µg/m<sup>3</sup> were estimated to be over and immediately adjacent to the North Impoundment and directly around the ElMang process, both on the facility property. Concentrations less than 100 µg/m<sup>3</sup> extend uniformly out from the fenceline a very short distance, while levels up to 10 µg/m<sup>3</sup> extend approximately 1000 meters from the fenceline (REAC 2004).

The model estimated that maximum annual offsite ammonia concentrations less than 100 µg/m<sup>3</sup> extend uniformly out from the fenceline a very short distance, while levels up to 10 µg/m<sup>3</sup> extend approximately 1000 meters from the fenceline. The ATSDR chronic minimum risk level (MRL) is 210 µg/m<sup>3</sup>. Since the levels of ammonia extending out from the Eramet property are below the MRL, it does not pose a health threat and was not selected for further evaluation.

It is important to note that these numbers may fluctuate above the odor threshold at times. Sensitivity to ammonia varies a great deal; some people can smell it as low as approximately 25 µg/m<sup>3</sup>, while others can't smell it until it reaches concentrations about 1000 times higher (about 40 mg/m<sup>3</sup>) (ATSDR, 2004a; Michaels, 1999). Since most offsite values were modeled to be within the range of 1-10 µg/m<sup>3</sup>, it is more likely that odors would be detected very close to the North Impoundment, and with the exception of intermittent releases, would not carry far from the source.

### Chlorobenzene

Chlorobenzene emissions used in the model came from one process with four “point” sources at



the Solvay facility. The process was the P003 Polysulfone Polymer Production Unit, which has four point source stacks that comprise the P010 Radel Polymers Production Unit. Each stack was modeled separately and the emission estimates were combined to estimate annual total chlorobenzene emissions. The emissions data came from an annual averages measured between 1998 and 2002.

The model estimated maximum concentrations of chlorobenzene between  $0.10 \mu\text{g}/\text{m}^3$  and  $15 \mu\text{g}/\text{m}^3$ . The modeled values did not exceed the chronic minimum risk level (MRL) of  $90 \mu\text{g}/\text{m}^3$ . Thus, ATSDR does not consider even the maximum modeled concentrations of chlorobenzene to be a health concern.

### Chloromethane

Annual chloromethane emissions from Solvay were modeled based on measured stack data from two processes averaged between 1998 through 2002 (REAC, 2004). These processes included the P003 Polysulfone Polymer Production Unit and the P010 Radel Polymers Production Unit (which includes four stack units). Emissions from the P010 process were assumed to be equally distributed among the four stacks. The emissions data came from an annual average concentration from these processes measured between 1998 and 2002.

The model estimated maximum annual concentrations of chloromethane between 10 and  $40 \mu\text{g}/\text{m}^3$ . ATSDR's chronic inhalation MRL is  $103.5 \mu\text{g}/\text{m}^3$  (ATSDR, 1998a). Modeled peak concentrations are below ATSDR guidance values, and are not considered to be a health concern.

### Chromium

Chromium emissions from Eramet were modeled based on measured data collected from four processes. These include: 1) the P025 "EM" Briquetting System; 2) the P026 Manganese Milling System; 3) the CF017BAG6 #1 Ball Mill Baghouse; and 4) the El Chrome Mill Wet Cyclone. Briquetting encompasses both of the P025 and P026 processes, thus a bulk emission rate was provided as a combination of the two (REAC, 2004).

The model estimated maximum concentrations from facility emissions of chromium that were extremely low, between 20 and 1500 picograms per cubic meter ( $\text{pg}/\text{m}^3$ ). Chromium was not *speciated* during lab analyses, that is, the chemical form of chromium was not identified. More than likely, the chromium detected was comprised of a mixture of trivalent and hexavalent chromium. To be conservative, ATSDR compared the measured data against the more toxic hexavalent chromium comparison values. The ATSDR intermediate minimum risk level (MRL) is  $5,000 \text{ pg}/\text{m}^3$  for chromic acid and other dissolved hexavalent chromium aerosols and mists. The intermediate MRL for hexavalent chromium particle compounds is  $1,000,000 \text{ pg}/\text{m}^3$ . The modeled values are far below ATSDR MRLs (ATSDR, 2000). Thus, ATSDR does not consider even the maximum modeled concentrations of chromium to be a health concern.



### Hydrochloric Acid

Hydrochloric acid (HCl) emissions from Gorsuch were modeled based on measured stack data in yearly HCl emission rates in tons/year for 1998 through 2002 (REAC, 2004).

The model estimated maximum annual concentrations of HCl that were extremely low, between 40 and 180 picograms per cubic meter ( $\text{pg}/\text{m}^3$ ). The USEPA Reference Concentrations (RfC) for HCl is 20 million  $\text{pg}/\text{m}^3$  (IRIS, 2006). Modeled peak concentrations are well below 20 million  $\text{pg}/\text{m}^3$ , and are not considered to be a health concern. ATSDR does not have MRLs for hydrochloric acid.

### Manganese

#### **Eveready**

Eveready manganese emissions used in the model came from 2 major processes and 12 subprocesses at the facility. These include (REAC, 2004):

- P001: Raw Ore Storage A1, A2, A3; Calciner Feed Bin B1, B2, B3, and B4; Calcined Ore South, East, and West; and
- P003: Crush Collector; Mill Collector; Bagging Collector; and Stripping Press Collector.

The emissions data came from an annual average concentration from this process measured between 1998 and 2002.

The modeled concentrations of manganese were extremely low, between 0.4 and 1.2 picograms per cubic meter ( $\text{pg}/\text{m}^3$ ). The MRL for inhaled manganese is 40,000  $\text{pg}/\text{m}^3$ . Since the modeled values are far below this guidance value, even the maximum modeled manganese concentrations from the Eveready facility do not represent a health concern (ATSDR, 2000; IRIS, 2006). The low levels of manganese emitted from the Eveready facility are not likely to migrate beyond the Union Carbide Complex Property due to the low emission rate and large particle size of manganese from these processes (see the Eveready manganese dispersion map in Appendix B). The particle sizes from these processes were characterized by USEPA when manganese was “fingerprinted” through stack tests to identify their shape and size in 2005. The particles from Eveready were generally greater than 10 micrometers in diameter, thus they are too large and heavy to disperse far from their emission source. That was not the case with manganese particles from Eramet (they were generally much smaller).

#### **Eramet**

Manganese emissions from Eramet were modeled based on measured as annual averaged concentrations collected from twelve point sources. These include (REAC, 2004):

- SP020BAG1 (Manganese Metal Processing- Packing Dust Collector)
- SP020BAG2 (Manganese Metal Processing- Ball Mill Dust Collector)



- P025 (EM Briquetting System)
- P026 (Manganese Milling System- Ball Mill)
- P901SCR (Furnace #1 Silicomanganese Melting- Wet Scrubber)
- P901BAG (Furnace #1 Silicomanganese Melting- Taphole Baghouse)
- P908 (Furnace #12 (Ferromanganese))
- P909 (Furnace #18 (Ferromanganese))
- P909 (Furnace #18 – Four draft stacks (these are what are visible from Route 7))

The emissions data came from an annual average concentration from this process measured between 1998 and 2002.

The modeled maximum concentrations of manganese exceeded  $6.0 \mu\text{g}/\text{m}^3$  onsite, and the highest modeled concentrations offsite were approximately  $1\text{--}2 \mu\text{g}/\text{m}^3$  (see the Eramet manganese dispersion map in Appendix B). The emissions were predicted to be greatest due north of the facility. As stated above, the ATSDR MRL for inhaled manganese is  $0.04 \mu\text{g}/\text{m}^3$ . The modeled values exceed this guidance value by as much as 50 times on properties immediately surrounding the facility, thus additional ambient measurements of manganese emissions from the Eramet facility are needed to better characterize human exposures.

### Styrene

Styrene emissions from Chevron Phillips were modeled based on 31 styrene volume sources and one styrene point source. These include:

- P6 Process Vent H-2200 and H2210 (point source)
- P103A, P103B, P301, P1109, P1115, P1120, P1130, P1140, P2107, P2113, P2114, P2115, P2116, P2147, P2148: Styrene/Rubber Syrup
- P107A, P107B, and P204: Styrene Residue
- P201 and P2104: Styrene Distillate
- P204: Styrene Residue
- P501, P502, P530, and P531: Styrene Process
- P602: Recovered Styrene
- P607 C000 Tops/C3000 Feed
- P901 and P906: C000 Feed
- P1105: Zinc Stearate/Styrene
- P1114 and P3058: Irganox/Styrene

The emissions data came from an annual average concentration from these processes measured between 1998 and 2002.

Since the majority of these are volume sources, emissions of styrene did not travel far from their sources. Volume sources emit pollutants passively at low rates, so there is no “exit velocity” like point sources.



The model estimated annual maximum concentrations of styrene between 1 and 75  $\mu\text{g}/\text{m}^3$ . As mentioned previously, styrene is not likely to frequently travel offsite due to being emitted from volume sources. ATSDR's chronic inhalation MRL for styrene is 250  $\mu\text{g}/\text{m}^3$  (ATSDR, 1999b). Since modeled peak concentrations are below the ATSDR MRL, they are not considered to be a health concern.

### Sulfuric Acid

Sulfuric acid ( $\text{H}_2\text{SO}_4$ ) emissions from Gorsuch were modeled based on measured stack data in yearly  $\text{H}_2\text{SO}_4$  emission rates in tons/year for 1998 through 2002 (REAC, 2004).

The model estimated annual maximum concentrations of  $\text{H}_2\text{SO}_4$  that were extremely low, between 40 and 180 picograms per cubic meter ( $\text{pg}/\text{m}^3$ ). There are no guidance values for sulfuric acid, however no studies were found that associated adverse health effects with human exposures lower than 70 million  $\text{pg}/\text{m}^3$  in a recent analysis of available scientific research (ATSDR, 1998b). Modeled peak concentrations are well below 70 million  $\text{pg}/\text{m}^3$ , and are not considered a health concern in this analysis.

### Toluene

Toluene emissions from Chevron Phillips were modeled based on 15 styrene volume sources and one toluene point source. These include:

- P6 Process Vent H-2200 and H2210 (point source)
- P201: Styrene Distillate
- P605: Recovered Toluene
- P607 C000 Tops/C3000 Feed
- P901 and P906: C000 Feed
- P1105: Zinc Stearate/Styrene
- P2801 C300 Bottoms
- P3007: Ional/Toluene
- P3012 and P3013: Toluene/Cat-O
- P3018 and P3019: Toluene Cat-B
- P3030 and P3031: Oil Violet/Toluene
- P3058: Irganox/Toluene

The emissions data came from an annual average concentration from these processes measured between 1998 and 2002.

As with styrene emissions, the majority of toluene emission points are volume sources, thus rate of toluene releases were low and emissions did not travel far from their sources. The model estimated maximum concentrations of toluene between 0.01 and 4  $\mu\text{g}/\text{m}^3$ . ATSDR's chronic inhalation MRL for toluene is 300  $\mu\text{g}/\text{m}^3$  (ATSDR, 2000). The modeled peak concentrations are below ATSDR guidance values, and are not considered to be a health concern.



## **II. Monitoring**

In the 2004 Health Consultation, ATSDR made the following recommendation regarding sampling outdoor air in the Marietta Community:

- *After modeling is completed, ATSDR, Ohio EPA, and USEPA should determine what additional ambient air data are necessary to adequately investigate the impact of facility emissions on the health of residents.*
- *When contaminants of concern have been identified, additional, long term sampling should be performed (for 1 year or more); and*
- *ATSDR should evaluate the data from additional air monitoring and air modeling to better assess air pollutant exposure levels and the potential for health consequences in area residents.*

As with the modeling data, ATSDR used health-based guidelines and a review of scientific studies to identify compounds of concern to evaluate in the Health Implications section of this document. In our evaluation, the ambient air metals data were compared to ATSDR chronic environmental media evaluation guides (EMEGs) and cancer risk evaluation guides (CREGs), and USEPA Reference Concentrations (RfCs) and inhalation unit risk factors. EMEGs are calculated from ATSDR minimal risk levels (MRLs) for chronic or intermediate exposures (those occurring longer than 365 days or from between 14-365 days). CREGs are estimated contaminant concentrations expected to result in a cancer risk of no more than one excess cancer in a million persons exposed over a lifetime, and are calculated from EPA's cancer slope factors (SFs) using default values for exposure rates.

ATSDR also evaluated occupational and epidemiologic studies of human exposures, and sometimes discusses the lowest observed adverse effect level (LOAEL) and no observed adverse effect level (NOAEL). The LOAEL is the lowest exposure in a study that resulted in a measurable health effect. A NOAEL is the highest exposure in a study that *did not* result in a measurable health effect. Often, ATSDR and EPA health based guidelines are based on LOAELs and NOAELs.

### **Environmental Data**

A Health Consultation, dated February 2004, reviewed data through 2002 at the Washington County Career Center. In that document, we concluded that concentrations of volatile organic compounds measured in the area do not exceed health-based guidelines (ATSDR, 2004b). Data collected from 2000 to 2002 indicated levels of arsenic, cadmium, chromium, and manganese exceeded the ATSDR and USEPA health-based comparison values. This document will evaluate data collected from 2003 through 2005 at the Washington County Career Center and from December of 2004 through 2005 at the Blue Knob Road site.

The Ohio Environmental Protection Agency (Ohio EPA) has collected Total Suspended



Particulate (TSP) data from the Washington County Career Center (WCCC) monitor since November 2000 (Ohio EPA, 2005a,b). This monitor is located approximately 4.5 miles to the north/northeast of the former Union Carbide complex on the roof of the Washington County Career Center, in a suburban area. A second monitor began operations in December 2004 at the Blue Knob Road (BKR) site, west-northwest and less than 1 mile from the complex. At these locations, a total suspended particulate (TSP) filter sample was collected every 6 days, and a composite of the samples collected during a month was analyzed as a monthly average. The filters were analyzed for the following metals: arsenic, beryllium, cadmium, chromium, lead, manganese, nickel, and zinc. See Appendix C, Tables 1 and 2, for detailed annual data for both locations.

### Discussion

Levels of arsenic, cadmium, chromium, and manganese exceeded the ATSDR and USEPA health based comparison values (CVs) at both monitoring locations during the sampling period. Beryllium concentrations did not exceed health based guidelines in any air samples. CVs are not available for lead or zinc concentrations in ambient air. However, there were no exceedances of the USEPA National Ambient Air Quality Standard for lead of an average of  $1.5 \mu\text{g}/\text{m}^3$  per quarter (USEPA, 2006). The chromium composition of the samples was not *speciated*, or broken down and measured in its different forms, during lab analysis. However, as a protective measure, ATSDR compared levels of chromium in Marietta to USEPA and ATSDR hexavalent chromium CVs. Chromium was only intermittently detected in samples collected at both locations, however each detect was above the ATSDR and USEPA health based guidelines.

**Table 2. Metals above CVs: arsenic, cadmium, chromium, and manganese.**

Table 2. Review of annual average concentrations: Metals above CVs, 2003-2005 ( $\mu\text{g}/\text{m}^3$ )*				
Metal	Average concentration Washington County Career Center location*	Average concentration Blue Knob Road location*	Comparison Value ( $\mu\text{g}/\text{m}^3$ )	Agency Guideline†
Arsenic	0.0012	0.0014	0.00020 (Ca)	ATSDR CREG
			0.00020 (Ca)	USEPA
Cadmium	0.0010	0.00065	0.00060 (Ca)	ATSDR CREG
			0.00060 (Ca)	USEPA
Chromium	0.0044	0.0037	1.0 (N), 0.00008 (Ca)	ATSDR MRL/CREG
			0.1 (N), 0.00008 (Ca)	USEPA
Manganese	0.098	0.35	0.040 (N)	ATSDR MRL
			0.051 (N)	USEPA RfC

\* $\mu\text{g}/\text{m}^3$  = micrograms of metal per cubic meter of air; all values represent geometric averages

† (Ca) notates cancer endpoints, and (N) notates non-cancer endpoints; the most conservative health based guidelines are represented in this table;

NOTE: ATSDR and USEPA health based comparison values are based on hypothetical risk analysis. Cancer risk comparison value denotes an estimated  $10^{-6}$  cancer risk (risk of one excess cancer case per million exposed individuals).



The detected levels of arsenic, cadmium, and chromium were generally less than naturally occurring levels of metals in outdoor air (“background levels”). In the United States, particulate background levels range as follows: arsenic, 0.001-0.003  $\mu\text{g}/\text{m}^3$  in rural areas and 0.02-0.1  $\mu\text{g}/\text{m}^3$  in urban areas; cadmium, generally less than 0.005  $\mu\text{g}/\text{m}^3$ ; chromium, less than 0.01  $\mu\text{g}/\text{m}^3$  in rural areas to 0.01-0.03  $\mu\text{g}/\text{m}^3$  in urban areas; and manganese, 0.005  $\mu\text{g}/\text{m}^3$  in rural areas and 0.03  $\mu\text{g}/\text{m}^3$  in urban areas in the United States (ATSDR, 2004).

As observed in the 2004 Health Consultation evaluating data from the Career Center only, arsenic and manganese consistently exceeded CVs during the sampling period for this evaluation (2003-2005). Chromium was rarely detected but when detected, exceeded these criteria as well. Cadmium exceeded this level nine months of the 36-month period. Thus, arsenic, cadmium, chromium, and manganese were selected as contaminants of concern for further evaluation.

### ***Health Implications***

Current data indicate that ambient concentrations of arsenic, cadmium, chromium, and manganese have often exceeded ATSDR and USEPA health-based comparison values (CVs) used for evaluating chronic exposures. Therefore, the four compounds have been identified as contaminants of concern. It should be noted that CVs are intended to be conservative, and are often orders of magnitude lower than levels where health effects have been observed. Therefore, when screening values have been exceeded, it is often necessary to review scientific exposure studies to further evaluate measured concentrations of contaminants in air. Arsenic, cadmium, and chromium were not detected at levels remarkably different from expected background concentrations. Arsenic, cadmium, and chromium only exceeded ATSDR or USEPA’s most conservative cancer CV, but did not exceed noncancer guidelines. The cancer CV is a number at which cancer *risk* (not actual diagnosis) could be increased in one in one million people if they were exposed to a contaminant every day for 24 hours a day for a lifetime (70 years). Typically, USEPA guidance for risk assessment determines the “target risk dose” for cancer to be between  $10^{-4}$  and  $10^{-6}$  risk, or between risk of 1 additional case of cancer per 10,000 people and risk of 1 additional case of cancer per 1,000,000 people. Any risk greater than this is considered an unacceptable increase in cancer risk.

The data indicate that concentrations of pollutants, and thus exposures, vary significantly the further away from the sources of manganese residents live. Additional community exposure data would help identify any other areas of concern, and would provide a basis from which to recruit volunteers for a community health study. A health study will only be considered by ATSDR if data indicate it is warranted. An air investigation is being conducted throughout the Marietta area to determine whether or not a health study is an appropriate course of action.

### ***Arsenic***

As mentioned previously, arsenic can range from 0.001-0.003  $\mu\text{g}/\text{m}^3$  in rural areas to 0.02-0.1  $\mu\text{g}/\text{m}^3$  in urban areas. In comparison, the highest monthly concentration of arsenic detected in the



Marietta area by the existing monitoring system is  $0.003 \mu\text{g}/\text{m}^3$ , detected at the Washington County Career Center in May and September 2005. Concentrations of arsenic in Marietta are within the ranges of normal background concentrations of arsenic in the United States. Both “typical” rural concentrations of arsenic in ambient air and the highest concentrations detected in Marietta exceed the conservative ATSDR cancer CV of  $0.0002 \mu\text{g}/\text{m}^3$ . The lowest adverse effect level (LOAEL, or the lowest concentration of arsenic in air that has resulted in health effects), in existing scientific research was quantified by Ihrig et al. in 1998. The case-control study conducted near a Texas arsenic pesticide factory observed a statistically significant increase in the risk of stillbirth in the residents exposed to the highest concentrations of arsenic from the factory. This concentration was  $0.7 \mu\text{g}/\text{m}^3$ , whereas residents exposed to  $0.06 \mu\text{g}/\text{m}^3$  arsenic did not experience these health effects. These concentrations are well below all other LOAELs documented in the epidemiologic literature for inhalation arsenic exposure. The maximum value of arsenic detected in the three year collection period in the Marietta area is approximately 250 times lower than this lowest LOAEL of  $0.7 \mu\text{g}/\text{m}^3$  (ATSDR, 2005). As noted above, average concentrations of arsenic are  $0.0013 \mu\text{g}/\text{m}^3$  at the Career Center and  $0.002 \mu\text{g}/\text{m}^3$  at Blue Knob Road. Based on available data, arsenic exposure in ambient air does not pose a public health hazard to residents in the Marietta area.

### Cadmium

Cadmium levels in ambient air are typically below  $0.005 \mu\text{g}/\text{m}^3$ . The lowest concentration of cadmium in air that has been documented to adversely impact human health (LOAEL) is  $23 \mu\text{g}/\text{m}^3$ , which resulted in a 9.2% increased incidence of *proteinuria* (excess protein in the urine as a result of kidney damage) (Jarup, et al., 1988). Also, in an occupational study, an increase in lung cancer was noted in workers with a work lifetime of exposure (45 years) of an average of  $100 \mu\text{g}/\text{m}^3$ . (Stayner, 1992). The highest concentration of cadmium detected in the Marietta area by the existing monitoring system is  $0.014 \mu\text{g}/\text{m}^3$ , detected at the Washington County Career Center in June of 2003. This value is approximately 1600 times lower than the LOAEL. Thus, the available data do not suggest a public health hazard to residents in the Marietta area from cadmium exposure.

### Chromium

In ambient air, chromium is typically measured at less than  $0.01 \mu\text{g}/\text{m}^3$  in rural areas to  $0.01$ - $0.03 \mu\text{g}/\text{m}^3$  in urban areas. It should be noted that chromium composition in the community's air is unknown (was not *speciated*, or broken down and measured in its different forms, during lab analysis), and as a protective measure, ATSDR compared levels in Marietta to USEPA and ATSDR hexavalent chromium CVs. Hexavalent chromium is the most toxic form of chromium. The LOAEL for human health effects is  $2 \mu\text{g}/\text{m}^3$  of hexavalent chromium. This exposure resulted in minor decreases in lung function and nasal effects (ATSDR, 2000a). The highest concentration of chromium detected in Marietta was  $0.0057 \mu\text{g}/\text{m}^3$ , detected at the Washington County Career Center in November of 2001. This value is lower than average background concentrations in the United States and is approximately 350 times lower than the lowest exposure observed to cause adverse health effects in existing scientific studies. In addition, it is highly likely that a much greater percentage of this total chromium concentration is trivalent

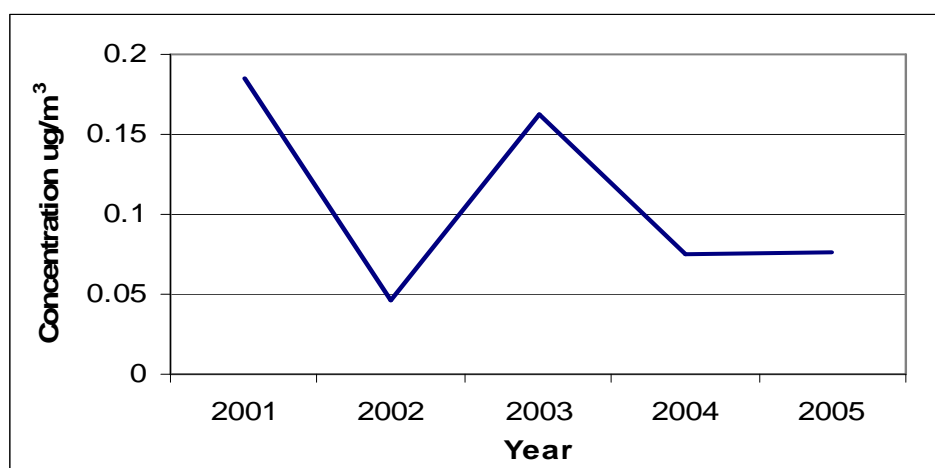


chromium (less toxic) than is hexavalent chromium (more toxic). USEPA (1990) estimated that approximately 35% of chromium emitted into the air from manmade sources is in the hexavalent form. Thus, the available data do not suggest a public health hazard to residents in the Marietta area from chromium exposure.

### Manganese

Manganese concentrations usually range from  $0.005 \mu\text{g}/\text{m}^3$  in rural areas to  $0.03 \mu\text{g}/\text{m}^3$  in urban areas in the United States (ATSDR, 2000). At the Washington County Career Center (WCCC) from 2001 through 2005, annual average concentrations have ranged from 0.05 to  $0.19 \mu\text{g}/\text{m}^3$  (geometric mean). For more detailed data, please see Table 1 in Appendix C.

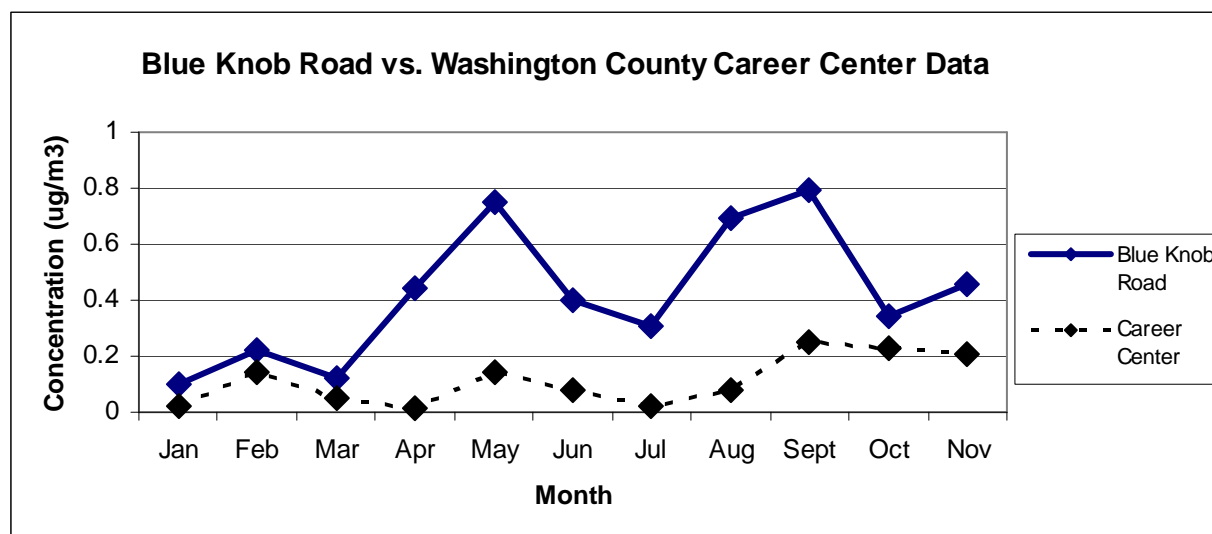
**Figure 1. Average annual concentrations of manganese at the Washington County Career Center, 2001-2005.**



At the Blue Knob Road (BKR) site, the annual average concentration (geometric mean) in 2005 was  $0.35 \mu\text{g}/\text{m}^3$ , compared to  $0.076 \mu\text{g}/\text{m}^3$  at the WCCC. On average, monthly concentrations at the BKR site were approximately three times greater than those at the WCCC. Generally, the trends in concentration from month to month show temporal similarities and suggest that sources at the former Union Carbide complex contribute to the ambient manganese detected at both sampling sites, although modeling indicates most manganese traveling offsite is emitted from Eramet. For more detailed data, please see Tables 1 and 2 in Appendix C.



**Figure 2. Average monthly manganese concentrations at two sampling sites near the former Union Carbide complex, 2005 data.**



Exposure to manganese via inhalation seems to cause primarily neurological effects in humans at chronic, low levels. Occupational studies have found deficits in motor skills (such as finger tapping, reaction time, hand-eye coordination, etc.) with chronic exposures to levels as low as  $27 \mu\text{g}/\text{m}^3$  (ATSDR, 2000b; Iregren, 1990; Lucchini et al., 1995; Lucchini et al., 1999; Mergler et al., 1994; Roels et al., 1987).

The highest annual average concentration (geometric mean) of manganese at the Washington County Career Center was  $0.18 \mu\text{g}/\text{m}^3$  in 2001, and the annual average of manganese at the Blue Knob Road in 2005 was higher than that of the Career Center, at  $0.35 \mu\text{g}/\text{m}^3$ . Both of these exceed the ATSDR MRL for manganese inhalation of  $0.04 \mu\text{g}/\text{m}^3$ , and the USEPA RfC of  $0.05 \mu\text{g}/\text{m}^3$ . The MRL and RfC are both based on an occupational study of workers exposed to manganese in a battery factory and unexposed control subjects (Roels, et al., 1992). These workers were exposed to an average of  $215 \mu\text{g}/\text{m}^3$  and  $948 \mu\text{g}/\text{m}^3$  manganese (total and respirable dust) for approximately 5 years. Neurobehavioral tests (short term memory, visual reaction time, motor skills) were performed on the exposed individuals (workers) and the unexposed control group. The exposed workers scored significantly worse on these tests. ATSDR conducted a “dose-response” analysis on the results of each worker (his/her exposure vs. his/her scores on the tests), and a value of  $74 \mu\text{g}/\text{m}^3$  was chosen as a surrogate for a NOAEL, and was adjusted for continuous exposures instead of occupational exposures. This adjusted number was divided by 500 to account for variability among how people react to exposures, data uncertainties, and to be protective of children (10 for human variability, 10 for uncertainties in available studies to yield the MRL (like reproductive and developmental information), and 5 for children’s susceptibility). USEPA’s process of deriving the RfC is described in more detail on the IRIS database (<http://www.epa.gov/iris>). The study that documented the LOAEL of  $27 \mu\text{g}/\text{m}^3$  is based on an occupational study of presumably healthy adult males working in a ferroalloy



plant that experienced neurological deficits from chronic occupational exposures lasting between 1 and 28 years (Lucchini et al., 1999).

There are very few studies that have evaluated environmental exposures outside of the workplace. However, a series of articles were published in 1999 examining low-level environmental manganese exposures in southwest Quebec. Very limited air sampling data were collected with manganese concentrations in the range of  $0.007 \mu\text{g}/\text{m}^3$  to  $0.035 \mu\text{g}/\text{m}^3$  near a closed ferro and silico-alloy plant.

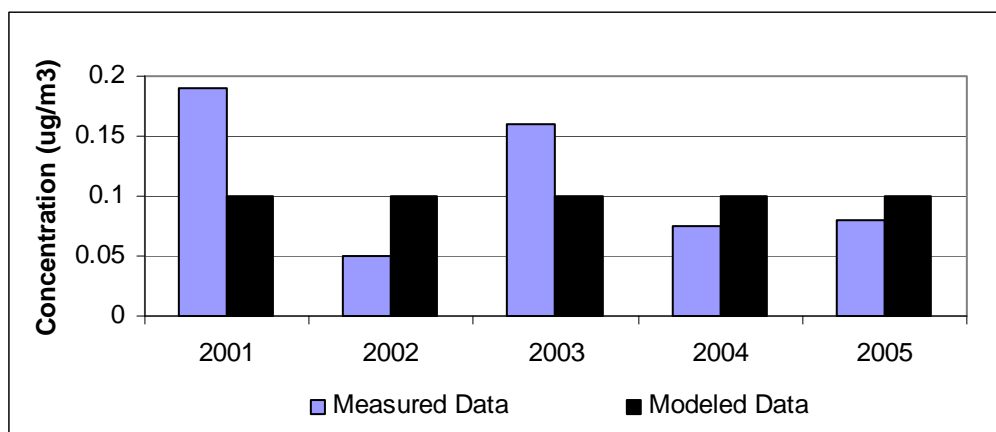
The highest average concentration of manganese at the WCCC is approximately 150 times lower than the lowest concentration of inhaled manganese which has caused measurable neurological health outcomes (the LOAEL of  $27 \mu\text{g}/\text{m}^3$ ) in occupational studies, and the BKR average is approximately 77 times lower than the LOAEL. However, given that communities are comprised of people of varying age and health status, uncertainty exists regarding the impact of measured exposures on the health of Marietta residents, particularly sensitive populations such as children. Most studies of manganese exposures in humans are from occupational settings, which may or may not reflect the duration of time a resident lives in the community. Also, whereas other metals are close to expected background concentrations, ambient manganese concentrations appear to increase in closer proximity to the Union Carbide complex. Therefore, additional sampling to better characterize inhalation exposures in multiple locations is warranted.

### **III. Comparison of modeled and monitored data at the Washington County Career Center**

An outdoor metals monitor has been located at the Washington County Career Center (WCCC) since November of 2000. The Ohio Environmental Protection Agency (Ohio EPA) has been operating the monitor and evaluating the data since that time. The measured data at this location can be compared to our modeled annual average to determine the accuracy of the modeling. For the modeling period discussed above (1998-2002), the modeled manganese concentrations compared fairly well with the measured concentrations at the WCCC (Ohio EPA, 2005a).



**Figure 3. Comparison of Washington County Career Center (WCCC) Annual Averages to Modeled Annual Average at the WCCC.**



*Note: The modeled annual average at this location was 0.1  $\mu\text{g}/\text{m}^3$*

#### ***Modeling summary***

Based on the modeling, manganese is the only compound that is dispersed offsite in quantities that require further evaluation. Thus, ATSDR requested that the Ohio EPA place monitors closer to the facility to identify if higher concentrations could be quantified and how accurately the reflect modeling for that area.

#### **IV. Child Health Considerations**

ATSDR recognizes that in communities faced with contamination of their air, water, soil, or food, the unique vulnerabilities of infants and children demand special emphasis. ATSDR is committed to evaluating the health impact of environmental contamination on children, and uses health guidelines in its investigations that are protective of children. Further characterization of ambient levels of manganese is needed to evaluate the impact of facility emissions on children's health in this community.

#### **V. Physical Hazards**

No physical hazards were identified in this evaluation.



**VI. Conclusions**

- Manganese was the only metal identified which warrants additional evaluation.
- Available data suggest that manganese exposures are higher for residents that live closer to the Eramet and Eveready facilities, however, to date there are only two monitoring locations in the area. The existing data are insufficient to adequately characterize the extent of exposure.
- Health outcomes due to manganese inhalation exposure at low levels have not been well documented; however, research suggests that subtle neurological effects may occur with chronic, low-level exposures.
- Very few studies exist that evaluate manganese exposure in sensitive populations and outside of occupational settings.

**VII. Recommendations**

- ATSDR and Ohio EPA should conduct additional ambient air sampling locations to measure exposure levels in communities impacted by manganese emissions.
- If supported by the results of the sampling conducted in the community (from recommendation 1), ATSDR should conduct a health study to measure impacts of manganese exposure on the health of area residents.



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## **Appendix A**

### **Area Map and Monitoring Locations**



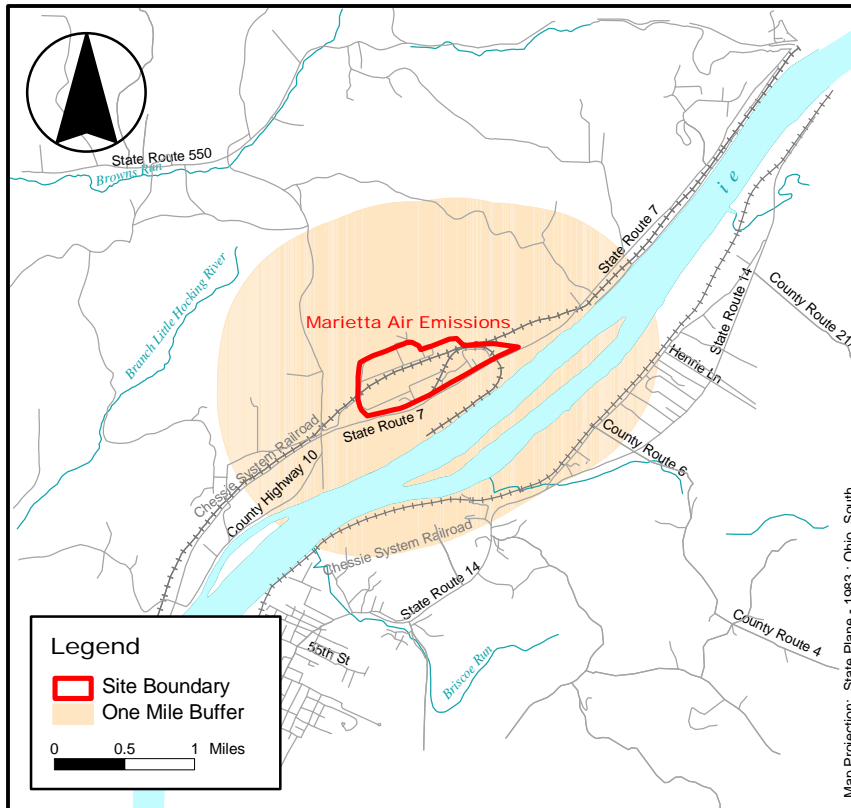
# Marietta Air Emissions

## Marietta, Ohio

# INTRO MAP



### Washington County, Ohio



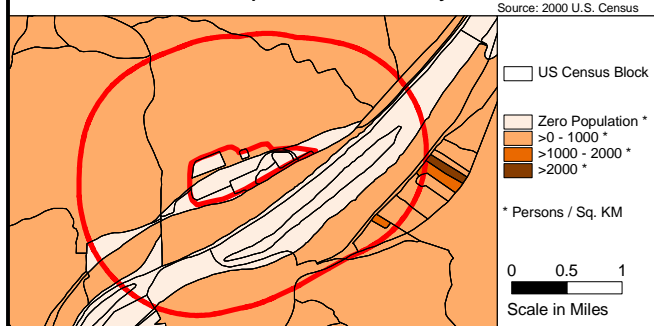
Base Map Source: 1995 TIGER/Line Files

### Demographic Statistics Within One Mile of Site\*

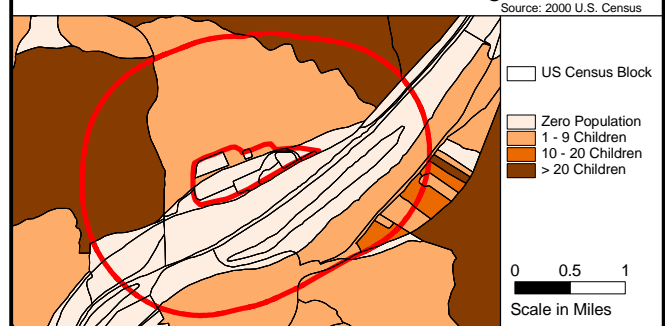
Total Population	539
White alone	534
Black alone	1
Am. Indian and Alaska Native alone	1
Asian alone	1
Native Hawaiian and Other Pacific Islander alone	0
Some other race alone	0
Two or More races	2
Hispanic or Latino	1
Children Aged 6 and Younger	56
Adults Aged 65 and Older	57
Females Aged 15 - 44	112
Total Housing Units	221

Demographics Statistics Source: 2000 US Census  
\*Calculated using an area-proportion spatial analysis technique

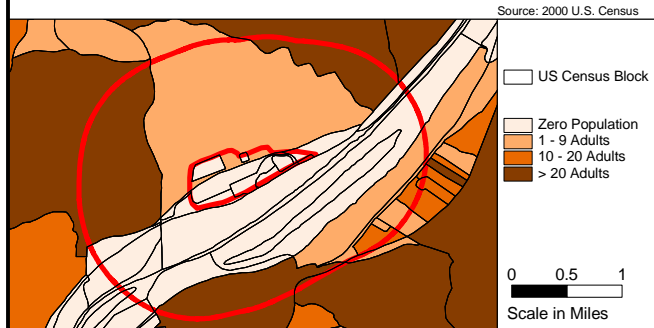
### Population Density



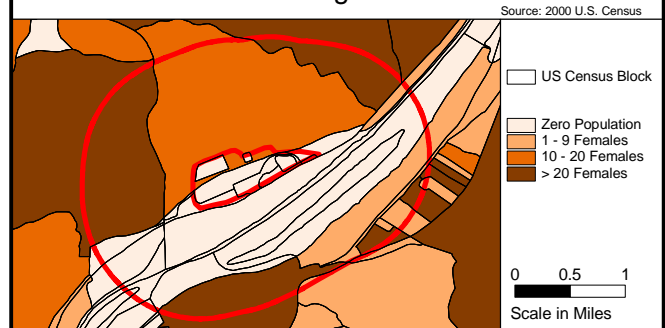
### Children 6 Years and Younger



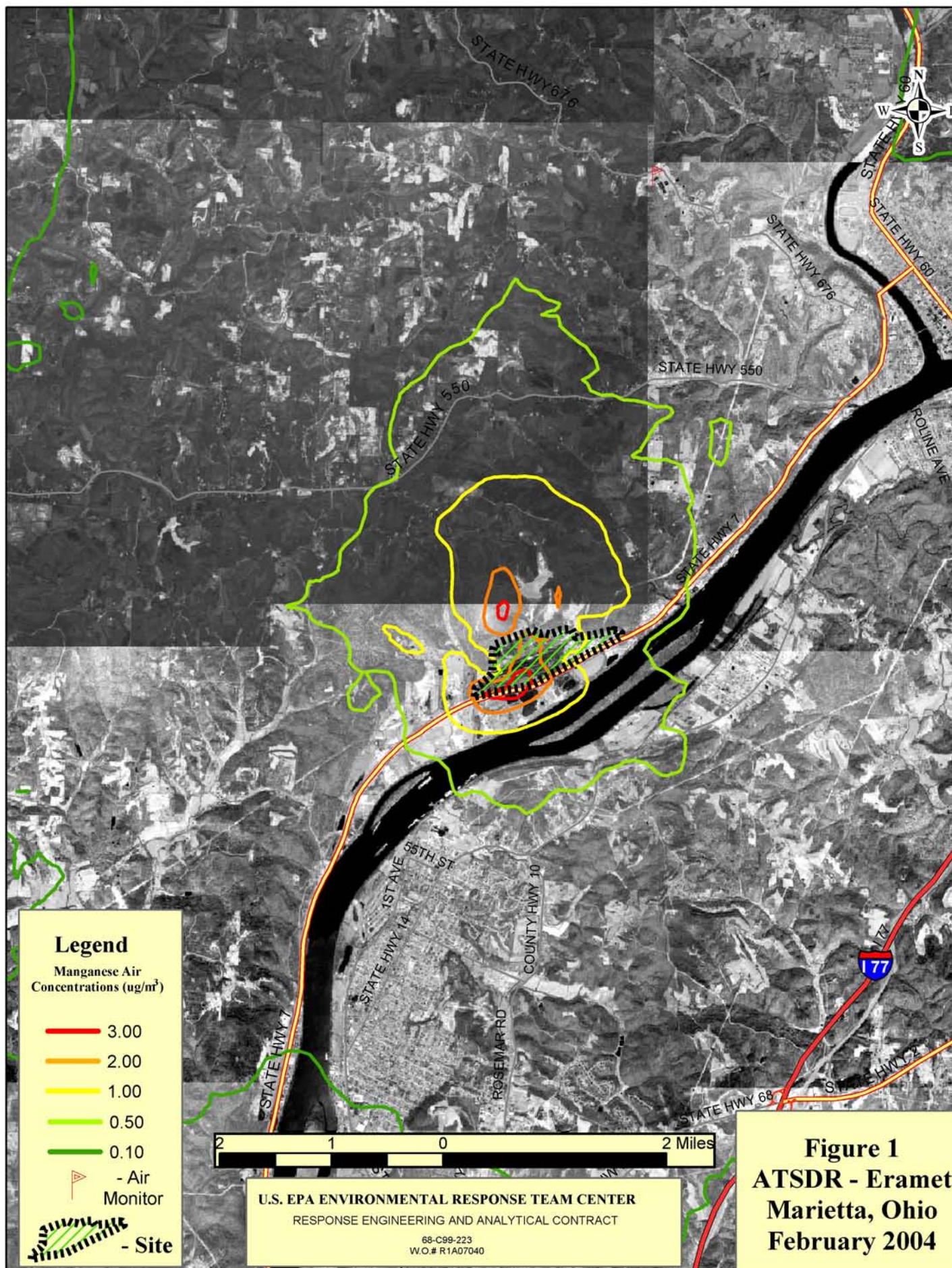
### Adults 65 Years and Older



### Females Aged 15 - 44









**Appendix B**  
**Air Modeling Maps**







**Appendix C**  
**Ambient Air Data**



Table 1. Air concentrations from the Washington County Career Center, 2003-2005 ( $\mu\text{g}/\text{m}^3$ )

2003	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sept	Oct	Nov	Dec
Arsenic	<b>0.0015</b>	<b>0.0012</b>	<b>0.0018</b>	<b>0.0021</b>	<b>0.0011</b>	<b>0.0026</b>	<b>0.0019</b>	<b>0.001</b>	<b>0.001</b>	<b>0.0021</b>	<b>0.0026</b>	<b>0.00097</b>
Beryllium	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.000027	BDL
Cadmium	0.00047	<b>0.00087</b>	<b>0.0067</b>	<b>0.002</b>	<b>0.0029</b>	<b>0.014</b>	<b>0.0016</b>	0.0006	<b>0.00073</b>	<b>0.0089</b>	0.0048	0.00031
Chromium	BDL	BDL	<b>0.004</b>	<b>0.0051</b>	BDL	<b>0.0041</b>	BDL	BDL	BDL	BDL	BDL	BDL
Lead	0.0086	0.0052	0.0046	0.012	0.0074	0.0071	0.0061	0.0044	0.0067	0.0077	0.01	0.0062
Manganese	<b>0.08</b>	<b>0.068</b>	<b>0.24</b>	<b>0.66</b>	<b>0.058</b>	<b>0.4</b>	<b>0.19</b>	<b>0.093</b>	<b>0.14</b>	<b>0.1</b>	<b>0.32</b>	<b>0.22</b>
Zinc	0.027	0.022	0.029	0.064	0.024	0.043	0.03	0.018	0.021	0.024	0.037	0.023
2004	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sept	Oct	Nov	Dec
Arsenic	<b>0.00083</b>	<b>0.00065</b>	<b>0.0016</b>	<b>0.001</b>	<b>0.001</b>	<b>0.0011</b>	<b>0.001</b>	<b>0.00051</b>	<b>0.00081</b>	<b>0.0026</b>	<b>0.0021</b>	<b>0.0014</b>
Beryllium	0.000022	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Cadmium	0.00015	0.00019	<b>0.0016</b>	<b>0.0074</b>	0.00022	<b>0.0032</b>	0.00041	0.00027	0.00034	<b>0.00064</b>	<b>0.0014</b>	<b>0.004</b>
Chromium	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Lead	0.0043	BDL	0.0058	BDL	0.01	0.0051	BDL	BDL	BDL	BDL	0.013	BDL
Manganese	0.022	<b>0.12</b>	<b>0.053</b>	<b>0.049</b>	<b>0.17</b>	<b>0.12</b>	<b>0.14</b>	0.028	0.036	<b>0.12</b>	<b>0.34</b>	0.039
Zinc	0.018	0.02	0.02	0.024	0.022	0.023	0.017	0.012	0.017	0.032	0.049	0.032
2005	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sept	Oct	Nov	Dec
Arsenic	<b>0.00066</b>	<b>0.00065</b>	<b>0.00057</b>	<b>0.00083</b>	<b>0.0015</b>	<b>0.00068</b>	<b>0.00067</b>	<b>0.0009</b>	<b>0.0026</b>	<b>0.0014</b>	<b>0.001</b>	NR
Beryllium	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Cadmium	0.00033	0.0006	0.00021	<b>0.00076</b>	0.0035	0.0017	0.00024	0.00025	<b>0.00065</b>	<b>0.0043</b>	0.00055	NR
Chromium	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Lead	BDL	BDL	BDL	BDL	0.0052	BDL	BDL	BDL	0.0054	0.004	0.005	NR
Manganese	0.019	<b>0.14</b>	<b>0.048</b>	0.017	<b>0.14</b>	<b>0.079</b>	0.023	<b>0.076</b>	<b>0.25</b>	<b>0.23</b>	<b>0.21</b>	NR
Zinc	0.023	0.035	0.022	0.018	0.023	0.021	0.022	0.021	0.039	0.028	0.028	NR

Table 2. Air concentrations from the Washington County Career Center, 2003-2005 ( $\mu\text{g}/\text{m}^3$ )

2005	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sept	Oct	Nov	Dec
Arsenic	<b>0.00093</b>	<b>0.00096</b>	<b>0.00095</b>	<b>0.0028</b>	<b>0.003</b>	<b>0.0013</b>	<b>0.0009</b>	<b>0.0012</b>	<b>0.0031</b>	<b>0.0012</b>	<b>0.00089</b>	NR
Beryllium	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	NR
Cadmium	<b>0.0015</b>	0.00036	<b>0.00061</b>	<b>0.00068</b>	<b>0.00077</b>	<b>0.0016</b>	0.00037	<b>0.0008</b>	<b>0.00089</b>	<b>0.00044</b>	<b>0.00028</b>	NR
Chromium	BDL	BDL	BDL	<b>0.0036</b>	BDL	BDL	BDL	<b>0.0034</b>	<b>0.0042</b>	BDL	BDL	NR
Lead	0.0054	0.0063	0.0039	0.0063	0.0094	BDL	0.0048	0.013	0.014	0.0086	0.0083	NR
Manganese	<b>0.1</b>	<b>0.22</b>	<b>0.12</b>	<b>0.44</b>	<b>0.75</b>	<b>0.4</b>	<b>0.31</b>	<b>0.69</b>	<b>0.79</b>	<b>0.34</b>	<b>0.46</b>	NR
Zinc	0.028	0.029	0.022	0.038	0.038	0.032	0.032	0.035	0.078	0.029	0.026	NR

$\mu\text{g}/\text{m}^3$  = micrograms of metal per cubic meter of air

BDL: the metal was present at a concentration below the detection limit of the sampling analysis method.

Highlighted, bolded cells are concentrations which exceeded the ATSDR and USEPA health-based screening levels