# **Health Consultation**

Evaluation of Reduced Sulfur Compounds (RSCs) and Volatile Organic Compounds (VOCs) in Communities Near Graphic Packaging International, LLC. and Kalamazoo Water Reclamation Plant

KALAMAZOO, KALAMAZOO COUNTY, MICHIGAN

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#### **ACRONYMS AND ABBREVIATIONS**

ATSDR Agency for Toxic Substances and Disease Registry

CDES Chronic Disease Epidemiology Section (MDHHS)

CH<sub>4</sub>S Methanethiol (Methyl mercaptan)

**CNS** Central Nervous System

**CREG** Cancer Risk Evaluation Guide

EGLE Michigan Department of Environment, Great Lakes and Energy

(formerly MDEQ)

**EJScreen** Environmental Justice Screening and Mapping Tool

**EPA** United States Environmental Protection Agency

**GMAP** Geospatial Measurement of Air Pollution

**GPI** Graphic Packaging International, LLC

**H₂S** Hydrogen Sulfide

**HQ** Hazard Quotient

IARC International Agency for Research on Cancer

ITSL Interim Threshold Screening Level

KCHCS Kalamazoo County Health & Community Services Department

**KWRP** Kalamazoo Water Reclamation Plant

**LC** Lethal Concentration

**LD** Lethal Dose

**LOD** Limit of Detection

MDEQ Michigan Department of Environmental Quality

MDHHS Michigan Department of Health and Human Services

MDL Minimum Detection Limit

MRL Minimal Risk Level

MW Molecular Weight

NAAQS National Ambient Air Quality Standards

**ppb** Parts Per Billion

**ppm** Parts Per Million

**RIASL** Recommended Interim Action Screening Level

**RfC** Reference Concentration

**RL** Reporting Limit

**RSC** Reduced Sulfur Compound

**RSL** Regional Screening Level

SO<sub>2</sub> Sulfur Dioxide

**UF** Uncertainty Factor

**VOC** Volatile Organic Compound

#### **SUMMARY**

#### Introduction

For over a decade, residents in the Northside neighborhood of Kalamazoo have voiced concerns regarding foul odors and adverse health effects in their community. The nearby Graphic Packaging International, LLC (GPI) paper processing plant and Kalamazoo Water Reclamation Plant (KWRP) have been identified as potential sources of odors reported in this community. At the request of the Kalamazoo County Health & Community Services Department (KCHCS), the Michigan Department of Health and Human Services (MDHHS) evaluated ambient air monitoring and sample data in this Kalamazoo community.

Odorous chemicals related to paper mills and water treatment plants can include reduced sulfur compounds (RSCs), in particular hydrogen sulfide (H<sub>2</sub>S), and VOCs. H<sub>2</sub>S is a gas with a foul, pungent odor that can be smelled at very low concentrations in the air. H<sub>2</sub>S can cause eye, nose, and throat irritation, difficulty breathing in people with asthma, and transient (short-term) neurological effects like headaches, nausea, and tiredness depending on concentration and the amount of time a person is exposed. VOCs are a class of chemicals that can cause a variety of harmful health effects, depending on the chemical, the amount present in the air, and the amount of time a person is exposed. Many VOCs are also associated with odors. Some sensitive individuals may have transient health effects while breathing in environmental odors, but effects are not likely to be long-lasting once the odor is gone.

The purpose of this health consultation is to evaluate people's exposure to chemicals in the community surrounding GPI and KWRP and any potential health risks from that exposure. As a general disclaimer, this health consultation is not a medical evaluation or health study.

#### **Conclusions**

MDHHS has reached the following public health conclusions for people living in communities adjacent to GPI and KWRP:

#### Conclusion 1

Measured ambient air concentrations of  $H_2S$  in communities adjacent to GPI and KWRP present a public health hazard. People consistently breathing in maximum measured levels of  $H_2S$  for a lifetime may be at increased risk of nasal irritation that does not go away once the person stops breathing in  $H_2S$ .

Basis for Conclusion 1: Continuous combined H<sub>2</sub>S and reduced sulfur compound (RSC) sensors at several locations in the communities adjacent to GPI and KWRP reported concentrations that regularly exceeded EPA's Reference Concentration (RfC) of 1.4 ppb from September 2019 to December 2021.

Although these sensors cannot specifically identify  $H_2S$ , when individual RSCs were measured via speciated sampling,  $H_2S$  tended to be the primary RSC detected.

The RfC is a level below which there is minimal to no health risk for exposure over a lifetime. Several health-protective factors are incorporated into this value to increase the margin of protection over a lifetime of exposure. Exposure to levels that exceed an RfC will not necessarily cause an adverse health effect but may increase an individual's risk. Based on available toxicological data, exposure to these levels of H<sub>2</sub>S over a lifetime may result in an increased risk of nasal irritation.

There is not an urgent health risk related to short-term  $H_2S$  exposure at the levels measured in the communities adjacent to GPI and KWRP. Only a single 24-hour composite air canister sample (out of 71 total samples taken in the community) was higher than the ATSDR Acute Inhalation Minimal Risk Level (MRL) of 70 ppb. This sample was taken at Krom and Prouty Park in the Northside neighborhood in September 2021. All other monitoring and sampling data for  $H_2S$  from the Kalamazoo community were below 70 ppb.

More data will help to characterize not only the frequency and magnitude of these events, but also the industrial or atmospheric conditions that may lead to them.

Conclusion 2

Measured ambient air concentrations of  $H_2S$  and some VOCs in the communities adjacent to GPI and KWRP are at levels that people may detect as odors.

Basis for Conclusion 2: Community air concentrations of H<sub>2</sub>S are regularly higher than the odor threshold for H<sub>2</sub>S, sometimes by an order of magnitude. Additionally, limited sampling results have detected some odorous VOCs at levels higher than their odor thresholds by an order of magnitude. Odor thresholds represent a concentration of a chemical above which it can typically be detected via scent.

Conclusion 3

Based on available data, asthma prevalence and asthma-related hospitalization rates in the areas surrounding GPI and KWRP are not significantly higher than comparable measures for Michigan as a whole.

Basis for Conclusion 3: The data review of asthma prevalence and asthma hospitalization rates by the MDHHS Chronic Disease Epidemiology Section (CDES) provided a descriptive analysis of the occurrence of asthma in selected ZIP code

areas in the city of Kalamazoo and the state as a whole. These asthma measures are not significantly different or are significantly lower in each of the ZIP code areas when compared to the state as a whole.

### Conclusion 4

In communities adjacent to GPI and KWRP, measured ambient air concentrations of sulfur compounds other than  $H_2S$  present no apparent public health hazard for either short-term or long-term exposure.

Basis for Conclusion 4: Continuous RSC sensors at several locations adjacent to GPI and KWRP reported concentrations in community outdoor air up to 25 ppb. These sensors quantify total RSCs, including H<sub>2</sub>S, and do not speciate between different RSCs.

However, based on available canister samples analyzed for specific RSCs, it is likely that the continuous RSC sensors in the community are primarily measuring H<sub>2</sub>S.<sup>1</sup> Other than H<sub>2</sub>S, no measured RSC concentrations from these samples or measured sulfur compounds from other samples were higher than applicable health-based screening values.

Sulfur dioxide was measured in outdoor air at concentrations that did not exceed its primary National Ambient Air Quality Standards (NAAQS). Additionally, concentrations of sulfur dioxide that were measured in the community are comparable to typical background levels of sulfur dioxide in urban areas.

Other than H<sub>2</sub>S, sulfur compounds in the outdoor air near GPI and KWRP are not expected to increase risk of harmful health effects.

#### Conclusion 5

Measured ambient air concentrations of non-sulfur compounds, including VOCs, in communities adjacent to GPI and KWRP present no apparent public health hazard for either short-term or long-term exposure.

Basis for Conclusion 5: While air sampling in the communities adjacent to GPI and KWRP detected a variety of non-sulfur compounds, including VOCs, all were measured below their respective health-based screening values for short-term exposure.

For the majority of non-sulfur compounds detected in these samples, measured concentrations were also below respective health-based screening values for long-term exposure.

<sup>&</sup>lt;sup>1</sup> The majority of speciated RSC samples did not detect any RSCs other than H₂S. Carbon disulfide was detected in several community samples taken during the October 2020 and September 2021 investigations, at a maximum measurement of 7.4 ppb.

For the few compounds measured at levels above health screening values for long-term exposure, further analysis did not identify any potential public health risks as the higher concentrations were transient. Most of the measured concentrations higher than the screening levels were in grab samples (which are collected quickly at one instant), and these concentrations were not replicated in 24-hour composite samples (air samples collected over 24 hours) taken from the community.

Non-sulfur compounds in the outdoor air near GPI and KWRP are not expected to increase risk of harmful health effects.

#### Limitations

The following limitations apply to this evaluation:

- No continuous monitoring data specific for H<sub>2</sub>S is available. The most comprehensive source of data for Kalamazoo is from the City's continuous monitoring instruments, which measure total RSCs, one of which is H<sub>2</sub>S. Results for individual RSCs were only available from single point-in-time canister and Tedlar Bag samples.
- No long-term data was available for VOCs, and VOCs were evaluated via grab (instantaneous) samples and composite (up to 24-hour) samples only.
- Formaldehyde was detected on KWRP property, but not sampled offsite in the surrounding community.
- Due to the low number of reported asthma cases and hospitalizations in the community surrounding GPI and KWRP, asthma prevalence and hospitalization rates were calculated using grouped data for multiple ZIP codes and from multiple years and could not be stratified by race. This analysis only represents a descriptive review of asthma prevalence and hospitalizations and does not serve as evidence linking any environmental contaminant exposure with asthma.
- The test method used to measure ammonia has a detection limit that
  exceeds the health screening values for both short-term and longterm exposure to ammonia. As a result, this method cannot be used
  to determine whether ammonia concentrations are below its health
  screening values. However, available data from sanitary sewers
  indicates that ammonia levels in the community are unlikely to
  exceed its health screening values.

#### Recommendations

1) MDHHS recommends further actions relating to ambient air concentrations of H<sub>2</sub>S in the community near GPI and KWRP:

- a. Using EPA-approved instruments and methods, the amounts of  $H_2S$  being emitted to the ambient air that is attributable to GPI and KWRP should be quantified.
- b. Mitigating attributable sources to reduce H<sub>2</sub>S to levels below those that may present a public health hazard for the community.
- c. KWRP should continue to maintain its existing network of RSC sensors in Kalamazoo.
- 2) MDHHS recommends further monitoring and sampling for VOCs, including formaldehyde, in the community near GPI and KWRP using EPA-approved instruments and methods.
  - Sampling should be done with the goals of characterizing ambient air concentrations of VOCs, including potential seasonal variations.
  - Risk associated with detected VOCs in the community found at levels above chemical-specific health screening values should be assessed.
- 3) For community members with existing respiratory problems or sensitivity to odors, MDHHS recommends staying indoors and avoiding outdoor exercise or physical exertion when an environmental odor is present. MDHHS also recommends that people with asthma take their control and rescue medications as prescribed by their doctors. If you have questions about your own health, contact your health care provider.

For More Information

If you have immediate concerns about your health, please contact your health care provider. Please call MDHHS Division of Environmental Health at 1-800-648-6942 regarding this health consultation or about exposure to chemicals.

#### 1. PURPOSE AND HEALTH ISSUES

The Michigan Department of Health and Human Services (MDHHS) developed this health consultation at the request of community members and the Kalamazoo County Health and Community Services Department (KCHCS) to assess the potential public health impacts of chemicals in community ambient air near the Graphic Packaging International, LLC (GPI) facility and Kalamazoo Water Reclamation Plant (KWRP), both located in the city of Kalamazoo, Kalamazoo County, Michigan.

On August 3, 2020, MDHHS was contacted by KCHCS regarding community concerns that foul odors from the facilities were causing adverse health effects, including eye irritation and asthma. Residents that live near GPI and KWRP have also expressed concern about perceived increases in rates of cancer and respiratory illness in their community. There is also community concern about environmental injustice as the residents in communities adjacent to GPI and KWRP are predominantly African American and therefore would be disproportionately impacted by any adverse environmental exposures. KCHCS requested that MDHHS review available environmental monitoring and sampling data and address these concerns.

Air monitoring and/or sampling have been conducted by the city of Kalamazoo, GPI, the Michigan Department of Environment, Great Lakes, and Energy (EGLE), and the United States Environmental Protection Agency (EPA) to characterize ambient (outdoor) air quality in the communities adjacent to GPI and KWRP.

This Health Consultation serves as MDHHS's review of ambient air concentrations of chemical compounds in the community surrounding the GPI and KWRP facilities and evaluation of public health concerns from community exposure to the emissions.

## 2. SITE DESCRIPTION AND BACKGROUND

GPI is a company that manufactures a variety of paper-based packaging used for food and beverages, food service and dining, and personal care and pet care products.<sup>2</sup> GPI operates a recycled paper processing and manufacturing mill located at 1500 N. Pitcher Street in Kalamazoo, Michigan. The facility has been in operation since the 1920s.

KWRP is a wastewater treatment facility located at 1415 Harrison St. in Kalamazoo, Michigan, adjacent to the GPI facility. KWRP was built in 1955 and underwent significant upgrades in the 1980s. More than 150,000 Kalamazoo residents receive treatment services from KWRP, which also services industrial wastewater sources, including GPI.<sup>3</sup> See Figure 1 for a map showing the locations of GPI and KWRP.

<sup>&</sup>lt;sup>2</sup> https://www.graphicpkg.com/who-we-are/

<sup>&</sup>lt;sup>3</sup> https://www.kalamazoocity.org/docman/public-services/6187-kalamazoo-water-reclamation-plant-brochure/file

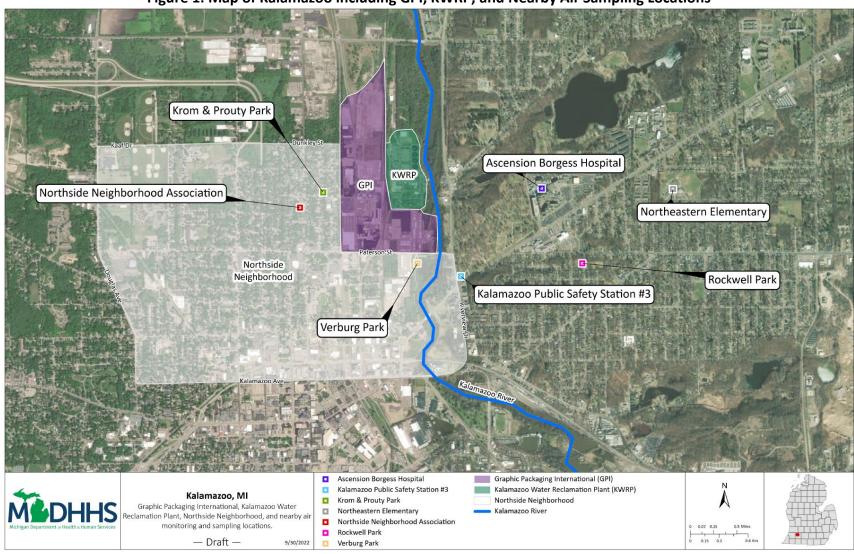


Figure 1: Map of Kalamazoo including GPI, KWRP, and Nearby Air Sampling Locations

From June 2010 to September 15, 2022, over 240 odor complaints have been received by EGLE, the city of Kalamazoo, and MDHHS (Table 1). Odor reports increased in frequency in 2020 and have remained regular since then.

Table 1: Summary of Total Odor Complaints Related to GPI or KWRP, as of September 15, 2022							
<b>Organization Receiving</b>	Organization Receiving Start date Number of						
Complaint		<b>Complaints Received</b>					
EGLE	June 2010	161					
City of Kalamazoo	June 2021	78					
MDHHS	June 2021	7					
	Total	246					

EGLE has cited GPI several times for odor violations dating back to 2012. These violations were based on odors that were observed by EGLE investigators and traced back to GPI as the source. EGLE has also cited GPI for violations related to GPI's plant expansions and calcite ash fallout reaching nearby communities (Appendix A-1).

In response to the odor complaints, GPI and the city of Kalamazoo commissioned independent environmental consultants to conduct several investigations to evaluate odors and chemicals in outdoor air near their facilities. These investigations primarily investigated concentrations of hydrogen sulfide (H<sub>2</sub>S) and other reduced sulfur compounds (RSCs) in the outdoor air. H<sub>2</sub>S is an RSC produced by the microbial breakdown of organic matter in anaerobic environments (those with little to no oxygen). It has a characteristic foul odor of rotten eggs and is commonly associated with odors produced by paper mills and wastewater treatment plants (ATSDR 2016). In addition to H<sub>2</sub>S and RSC monitoring efforts, some investigations measured outdoor air levels of non-sulfur compounds like VOCs and ammonia, which may also cause foul odors.

Additional monitoring efforts include continuous real-time RSC monitoring by GPI and the city of Kalamazoo. GPI is monitoring RSC concentrations at several on-site locations around their facility while the city of Kalamazoo is monitoring at several community locations around KWRP as well as in the community surrounding the facilities (Kalamazoo Odor Task Force 2021b). EGLE and EPA have also conducted chemical monitoring in the Kalamazoo area in response to the continued odor complaints.

## 2.1 Demographics

Recently, most odor-related complaints have originated from the Northside neighborhood, a community adjacent to west side of the GPI facilities (Figure 1). Northside is roughly bordered by the Kalamazoo River to the east, W Kalamazoo Ave to the south, Douglass Ave to the west, and Kaaf Dr and W Dunkley St to the north, with an estimated population of 6,257 (EPA 2020). The United States Environmental Protection Agency (EPA) Environmental Justice Screening and

Mapping Tool (EJScreen) provided the following demographic statistics for the Northside neighborhood:

- 81 percent are People of Color (84<sup>th</sup> percentile in US)
- 66 percent are low-income (92<sup>nd</sup> percentile)
- 22 percent have less than a high school education (81st percentile)

EJScreen also calculates EJ Indices (Environmental Justice Indices) for eleven environmental pollution factors. EJ Indices combine environmental factors, like air quality and proximity to known pollution sites, and demographic indicators to identify communities that may be experiencing environmental disparities. MDHHS used EJScreen to calculate EJ indices for the Northside neighborhood (Table 2). EJ Indices are based on a combination of demographic factors and environmental indices, like proximity to hazardous waste sites.

Table 2: EJ Indices for Northside, Kalamazoo as of February 3, 2022

011 CD1 dd1 <b>y</b> 3, 2022					
	Percentile in				
EJ Index	United States				
PM2.5	80				
Ozone	82				
NATA Diesel Particulate Matter	75				
NATA Air Toxics Cancer Risk	77				
NATA Respiratory Hazard Index	75				
Traffic Proximity and Volume	83				
Lead Paint Indicator	90				
Superfund Proximity	99 <sup>1</sup>				
RMP Proximity	90				
Hazardous Waste Proximity	82				
Wastewater Discharge Indicator	96				

PM=particulate matter

RMP=risk management plan facility

NATA=National Air Toxics Assessment

1 The Superfund Proximity index is skewed high as the Superfund site for the Kalamazoo River is incorrectly mapped at E Paterson St and Walbridge St, which is much closer to Northside.

Eight EJ indices for the Northside neighborhood meet or exceed the 80<sup>th</sup> percentile in the United States, indicating that the Northside neighborhood has a higher EJ index than 80 percent of the United States. The remaining three EJ indices calculated by EJScreen all exceed the 70<sup>th</sup> percentile in the United States. Full EJScreen results are available in Appendix A-2.

#### 3. INVESTIGATIONS OF ODOR-CAUSING CHEMICALS IN AMBIENT AIR

Several investigations were conducted to measure potential chemical sources of odors in the communities adjacent to GPI and KWRP. These investigations collected monitoring results and

air samples to determine the levels of various chemicals in the air, including H<sub>2</sub>S, RSCs, and VOCs. See below for brief summaries of each investigation. Summaries of sampling results are available in Appendices B (Hydrogen Sulfide and Reduced Sulfur Compounds) and C (Volatile Organic Compounds).

These investigations include several monitoring and sampling techniques that are not intended for regulatory purposes or quantification of specific contaminants. MDHHS analyzed all available data using a weight of evidence approach to identify potential health risks.

## 3.1 GPI Odor Investigation and H₂S Monitoring, July-September 2020

On 26 days from July 9, 2020-September 4, 2020, a contractor for GPI used a Jerome 631-X field analyzer to measure instantaneous  $H_2S$  concentrations at locations on GPI's property and in the community. This instrument uses gold film sensing technology and reports  $H_2S$  concentrations in parts per billion (ppb) with a limit of detection (LOD) of 3 ppb.<sup>4</sup> Concentrations are reported over intervals lasting 3-30 seconds.<sup>5</sup> GPI monitored at nineteen community locations during the investigation for a total of 988  $H_2S$  measurements.

The highest  $H_2S$  level reported by this instrument was 10 ppb. Of the 988 measurements, all but 8 measurements were below 5 ppb. For a map of monitoring locations and full  $H_2S$  monitoring results, see Appendices B-1 and B-2.

## 3.2 KWRP Odor Investigation, October-November 2020

From October 19-November 10, 2020, a contractor for KWRP conducted ambient air monitoring and sampling for RSCs and VOCs at 12 locations: six in the communities adjacent to GPI and KWRP and six within KWRP's sanitary collection sewer network (Kalamazoo Odor Task Force 2021a). KWRP measured real-time  $H_2S$  levels using Acrulog portable  $H_2S$  gas loggers. Ambient air samples were collected using canisters and air sampling bags, which were analyzed for RSCs, including  $H_2S$ , and VOCs. MDHHS used monitoring and sampling results from the six community locations to evaluate potential health risks. See Appendix B-3 for sampling locations from this investigation.

## H<sub>2</sub>S Gas Logger

The portable  $H_2S$  gas logger is an electronic device that instantly measures  $H_2S$  and outputs measurements to an electronic dataset. Two different gas loggers with differing sensitivities and logging intervals were used:

 PPB model: outputs H<sub>2</sub>S concentrations in ppb every 600 seconds with a minimum detection limit of 10 ppb.<sup>6</sup>

<sup>&</sup>lt;sup>4</sup> It should be noted that some readings from this instrument were reported to be below the instrument's LOD of 3 ppb.

https://www.brookfieldengineering.com/products/jerome/hydrogen-sulfide-analyzers/jerome-631-x

<sup>&</sup>lt;sup>6</sup> https://www.acrulog.com/wp-content/uploads/2019/04/Acrulog-H2S-PPB-Brochure.pdf

 Part Per Million (PPM) model: outputs H<sub>2</sub>S concentrations in ppm every 60 seconds with a minimum detection limit of 30 ppb.<sup>7</sup>

The ppm models were used to sample sanitary sewer locations, while the ppb models were used to sample community locations. Gas loggers in community locations were enclosed in plastic containers for the duration of the investigation. KWRP's contractor operated the community H<sub>2</sub>S gas loggers from October 19-November 10, 2020.

H<sub>2</sub>S concentrations were reported as 1-hour, 8-hour, 12-hour, and 24-hour averages. The majority of readings were non-detect (Kalamazoo Odor Task Force 2021a). Individual readings for the community locations did not exceed 10 ppb, the reported detection limit. Although there was a large percentage of non-detects, it was uncertain as to how those readings were incorporated into daily average summaries. For that reason, the calculated averages were not included in this evaluation. See Appendix B-4 for daily average results.

### **Canister Sampling**

KWRP collected composite samples using Silonite canisters, which are composed of stainless steel and coated with an ultra-inert ceramic layer. Canisters are placed in a sampling location and connected to a gas regulator, which draws in air over a specified length of time to create a composite sample.<sup>8</sup> Gas canisters can also be used to collect grab (instantaneous) samples. In this investigation, KWRP contractors collected 24-hour samples in each canister on three days (October 27, October 29, and November 4). Two canisters were collected during each sampling event: one to be analyzed for RSCs and the other for VOCs. Samples were analyzed for individual RSCs via test method ASTM D5504-12, and individual VOCs via EPA test method TO-15. ASTM D5504-12 and TO-15 are EPA's recommended test methods for quantification of RSCs and VOCs, respectively.

Of the analytes measured using ASTM D5504-12, only  $H_2S$  was detected regularly.  $H_2S$  concentrations ranged from non-detect to 32 ppb. Twenty-eight compounds were quantified via EPA test method TO-15. See Appendix B-5 for full ASTM D5504-12 results and Appendix C-1 for full TO-15 results. See Appendices D-1 and D-2 for full analyte lists for the ASTM D5504-12 and TO-15 methods, respectively.

#### **Bag Sampling**

KWRP collected grab (instantaneous) samples using Tedlar Polyvinyl Bags. Samples are collected by placing the bags in plastic chambers, connecting a squeeze bulb pump to the chamber, and squeezing the bulb, which forms a vacuum inside the chamber and fills the bag with air. As with the canister samples, bag samples were collected on October 27, October 29, and November 4 and were analyzed for RSCs and VOCs via test methods ASTM D5504-12 and TO-15, respectively.

<sup>&</sup>lt;sup>7</sup> https://www.acrulog.com/wp-content/uploads/2019/04/PPM-Brochure.pdf

<sup>8</sup> https://www.entechinst.com/silonite-vs-summa-canisters/

Of the analytes measured using ASTM D5504-12, only  $H_2S$  was detected regularly.  $H_2S$  concentrations ranged from non-detect to 11.5 ppb. Twenty-five compounds were quantified via EPA test method TO-15. See Appendix B-5 for full ASTM D5504-12 results and Appendix C-1 for full TO-15 results. See Appendices D-1 and D-2 for full analyte lists for the ASTM D5504-12 and TO-15 methods, respectively.

#### Ammonia Sampling

KWRP contractors collected air samples using sorbent tubes and pumps to analyze for ammonia concentrations. The sorbent tubes used in this investigation drew in air for 15 minutes at a rate of 0.5 L/min for a total of 7.5 L. Sorbent tubes were set up at the same locations as the canister and bag sampling, and samples were collected on November 5, 9, and 10, 2020. Samples were analyzed for ammonia using test method PE-IDH-037/OSHA ID-188, which has a detection limit of 5.56 ppm.<sup>9</sup>

Levels of ammonia for all samples collected from the community locations were either below the 5.56 ppm detection limit or outside the instrument's acceptable limits. For the samples collected from within KWRP's sanitary collection sewer network, samples from five locations (15 samples) were below the detection limit. The sixth location had one sample with an ammonia concentration of 5.65 ppm (the other two samples collected from this location were below the detection limit). Sampling results are further discussed in Appendix E-1.

## 3.3 City of Kalamazoo Continuous RSC Monitoring

The city of Kalamazoo has maintained nine Cairpol Cairsens RSC sensors within the KWRP complex and in the community since September 2019 (Kalamazoo Odor Task Force 2021b). Six of the nine instruments are located within KWRP or on its property, while the remaining three are located in the community (Gull & Riverview, Borgess Hospital, and Verburg Park). An additional three sensors were set up on January 20, 2021. The three instruments added in January 2021 (Northside Neighborhood Association, Krom & Prouty Park, and Rockwell Park) are all located in the community as well.

The instruments operate using amperometric technology to report combined RSCs, primarily  $H_2S$  and methanethiol (also known as methyl mercaptan and  $CH_4S$ ), with a maximum measuring limit of 1 ppm (1,000 ppb), a lower detection limit of 10 ppb, and a resolution of 1 ppb. As the sensors are highly cross-sensitive with other RSCs, the readings cannot be speciated. Therefore, the true composition of RSCs contributing to the readings cannot be obtained from these instruments.

MDHHS evaluated monitoring data from these instruments from September 2019-December 2021. The city of Kalamazoo reported that several sensors were affected by tampering, theft, and/or equipment malfunction, and worked with the instrument manufacturer to replace those sensors. MDHHS did not use any data that was suspected or confirmed to be affected by

<sup>9</sup> This method is the National Institute for Occupational Safety and Health (NIOSH)-recommended method for industrial hygiene. EPA recommends a different method for ambient air sampling of ammonia.

instrument error. A summary of sensor errors, as well as data results that were not considered to be reliable, is available in Appendix B-6.

Data from the Gull & Riverview and Borgess Hospital sensors were considered to be reliable for the duration of measurement. These results are further discussed in Section 5.1.1. See Appendix B-6 for sensor locations and a graph of results.

#### 3.4 EGLE Continuous Air Monitoring, April-May 2021

From April 13-May 25, 2021, EGLE measured RSC concentrations at two locations along Riverview Dr in Kalamazoo, east of KWRP. EGLE used identical amperometric monitoring instruments that the city of Kalamazoo uses for its continuous monitoring. The specifications of this instrument were previously discussed.

Daily average RSC concentrations from these sensors ranged from around 5-15 ppb. See Appendix B-7 for sensor locations used by EGLE and data results.

## 3.5 EPA Ambient Air Monitoring and VOC Sampling, May 2021

Scientists from the EPA visited Kalamazoo daily from May 11-13, 2021, to monitor for H<sub>2</sub>S and other compounds using EPA's geospatial measurement of air pollution (GMAP) vehicle. A GMAP vehicle is equipped with analyzers that measure chemical concentrations and a global positioning system (GPS) instrument. These instruments allow real-time monitoring and mapping of pollutants as the vehicle travels through an area.

EPA conducted a total of 33 mobile transects across three general areas: the Northside neighborhood and other community areas; near the GPI and KWRP facilities; and a more general 'scouting' area that included four local facilities - Textile Systems, Kalamazoo Metal Recyclers, Kaiser Aluminum, and Summit Polymers.

The GMAP vehicle that EPA used in Kalamazoo measures H<sub>2</sub>S using a cavity ringdown spectroscopy analyzer with a minimum detection limit (MDL) of 7.9 ppb and a reporting limit (RL) of 23.6 ppb. GMAP also monitors for methane, benzene, toluene, and p-xylene using a differential ultra-violet absorption spectrometer. See Appendix B-8 for full GMAP monitoring results, including mobile transects and paths.

EPA scientists also collected ambient air samples using six SUMMA canisters and two bottle-vacs (four composite and four grab) to be analyzed for VOCs via test method TO-15. Composite samples were run for 1 hour (2 samples) or 12 hours (2 samples). In addition, canister and bottle samples were characterized through a library search on all non-target or unknown peaks found in the sample in order to quantify any RSCs not included in the TO-15 test method. See Appendix C-2 for more information on canister locations and Appendix C-3 for full sampling results. See Appendix D-2 for full analyte lists for the EPA TO-15 method.

#### 3.6 GPI On-site Continuous Air Monitoring

Since August 2020, GPI has maintained 16 continuous RSC sensors at various locations around their facility, including some near the facility fence line and others closer to the facility. These are the same type of sensors used by the city of Kalamazoo for their continuous monitoring and used by EGLE for their monitoring in April 2021. MDHHS calculated daily averages for each sensor to determine RSC levels at GPI and near its fence line since January 2021. See Appendix B-9 for sensor locations and full results.

## 3.7 City of Kalamazoo Krom and Prouty Park Air Sampling, September 2021

The city of Kalamazoo conducted additional environmental air sampling in September 2021 at Krom and Prouty Park in response to the higher readings reported by the continuous RSC sensor at that location. As previously discussed, those higher readings were attributed to equipment error.

The Krom and Prouty Park sampling spanned from September 20-23, 2021 (Monday through Thursday) and included grab samples and 24-hour composite samples, both collected in canisters. Each day, two canisters were set up to collect 24-hour composite samples starting at 7:00AM. Grab samples were also taken in two-hour intervals starting at 7:00AM and ending at 7:00PM. Identical sampling was completed on each of the four days of sampling. The last 24-hour composite samples were retrieved at 7:00AM on Friday, September 24.

Canister samples were analyzed for RSCs, including H<sub>2</sub>S, via test method ASTM D5504-12, and VOCs via test method EPA TO-15 (ALS 2021). See Appendix B-10 for full RSC testing results and Appendix C-4 for full VOC testing results. See Appendix D-1 and D-2 for full analyte lists for the ASTM D5504-12 and EPA TO-15 methods, respectively.

### 3.8 EGLE Drone Investigation at KWRP, May 2022

On May 23 and 24, 2022, EGLE Air Quality Division completed an air monitoring investigation at KWRP to characterize levels of VOCs and other chemicals in the ambient air above the KWRP facilities. EGLE used a DR2000/DJI Inspire 2 drone with an onboard photoionization detector (PID) and other instruments to measure ambient air concentrations of total VOCs, formaldehyde, nitric oxide, SO<sub>2</sub>, and H<sub>2</sub>S.

Table 3: Instrument Specifications for May 2022 EGLE Drone Investigation at KWRP

<b>Chemical Species</b>	Instrument Type	Lower	Resolution	Time
		<b>Detection Limit</b>		Response
Total VOCs	Photoionization Detection (PID)	1 ppb	1 ppb	3 s
Hydrogen Sulfide	Electrochemical	7 ppb	1 ppb	35 s
Sulfur Dioxide	Electrochemical	10 ppb	1 ppb	20 s
Formaldehyde	Electrochemical	10 ppb	10 ppb	60 s
Nitric Oxide	Electrochemical	10 ppb	1 ppb	60 s

<sup>&</sup>lt;sup>10</sup> Although monitoring began in August 2020, data for several sensors was not available until 2021.

It is important to note that this investigation did not take any measurements in community ambient air. All measurements were taken within KWRP.

It should be noted that EGLE has indicated that the elevated measured concentrations of RSCs and VOCs from the May 23 sampling flights may have been skewed based on the presence of a truck near some flight paths. Combustion from emissions from the truck may include some of the compounds measured by the drone and therefore have contributed to the elevated concentrations.

See Appendix B-11 for a summary of maximum detections from the two days of monitoring.

#### 4. EXPOSURE EVALUATION AND CHEMICAL SCREENING ANALYSIS

In order for a hazardous substance to cause harm or injury, exposure must occur. To determine whether persons are, have been, or are likely to be exposed to contaminants, MDHHS evaluates the environmental and human components that could lead to human exposure, also known as an exposure pathway. An exposure pathway contains five elements:

- A source of contamination
- Contaminant transport through an environmental medium
- Point of exposure
- Route of human exposure
- Potentially exposed population

An exposure pathway is considered complete if there is evidence, or a high probability, that all five of these elements are, have been, or will be present at a site. It is considered either a potential or an incomplete pathway if there is a lower probability of exposure or there is no evidence that at least one of the elements above are, have been, or will be present. If there are no exposure possibilities, the pathway is eliminated from further evaluation. There must be clear evidence or a strong likelihood that people may be exposed to contaminants from a site in order for the site to pose a potential public health risk (ATSDR 2005).

## 4.1 Potential Emissions from Graphic Packaging International

The first part of the exposure pathway analysis is to identify a potential source. Paper mills, such as GPI, are associated with significant air pollution that can impact human health. Many air pollutants may be emitted as a result of paper mill operations (Dionne and Walker 2021), including sulfur oxides and VOCs. Sulfur compounds, including H<sub>2</sub>S, methyl mercaptan (methanethiol), and SO<sub>2</sub>, have been detected via on-site measurement of ambient air near pulp and paper mills (Tong et al. 2015; Scott et al. 2020). A paper mill in Edmundston, New Brunswick, Canada reported that it releases ammonia and chlorinated compounds (Dionne and Walker 2021). In a study investigating VOC emissions from a paper mill in Guangzhou, China, VOCs including alkanes, phenols, esters, benzenes, and ethers were detected in the ambient air at several on-site locations (Tong et al. 2015). Benzene, chloroform, toluene, xylenes,

dichlorodifluoromethane, and trichlorofluoromethane were detected in the community surrounding a large pulp paper mill (Glushchenko and Kadyseva 2021).

According to historical permit applications and National Emissions Inventory (NEI) data, GPI is known to emit a variety of pollutants including VOCs (Williams 2022).

Based on this information, GPI is a potential source of sulfur compounds and VOCs.

#### 4.2 Potential Emissions from the KWRP

Wastewater treatment plants, like KWRP, can emit sulfur compounds like H<sub>2</sub>S as a result of bacterial decomposition of organic matter in anaerobic environments (ATSDR 2016). Wastewater treatment plants are also associated with VOC emissions, including alkanes, alkenes, alcohols, esters, organic acids, and aromatic hydrocarbons. Processes like sludge treatment and anaerobic digestion release VOCs which can volatilize into ambient air. Most of these chemical classes have been detected in canister sampling at community locations near GPI and KWRP (see Appendices C-1, C-3, and C-4).

EGLE's May 2022 drone investigation provides further evidence that KWRP is a potential source of RSC and VOC emissions. Onboard chemical monitors measured concentrations of several chemicals, including total VOCs, H<sub>2</sub>S, and SO<sub>2</sub>, in the ambient air above KWRP buildings and structures and resulted in KWRP initiating actions to ensure worker safety. See Appendix B-11 for a summary of maximum measured concentrations from the investigation.

Based on this information, KWRP is a potential source of sulfur compounds and VOCs.

#### 4.3 Evidence of Community Exposure

MDHHS reviewed available ambient air monitoring and sampling data from the communities adjacent to GPI and KWRP to determine whether RSCs, VOCs, and other air pollutants known or suspected to be emitted by GPI and/or KWRP were detected. MDHHS also reviewed EGLE's odor complaint investigation reports.

## H<sub>2</sub>S and Reduced Sulfur Compounds

Continuous real-time monitoring instruments maintained by the city of Kalamazoo, EGLE, and GPI consistently detected RSCs in the ambient air at GPI, KWRP, and in the nearby community.

Community ambient air was also tested for RSCs via bag and canister samples, which were analyzed using the ASTM D5504-12 method. This method provides speciated results for a variety of RSCs. Other than H<sub>2</sub>S, the only RSC detected from these samples was carbon disulfide, which was measured in one 24-hour canister sample. Carbon disulfide and two disulfide compounds were also detected from several 24-hour canisters analyzed via EPA TO-15, a method intended to analyze for VOCs. No other RSCs were detected from these analyses.

Based on these results, it is likely that the real-time RSC sensors used by the city of Kalamazoo, GPI, and EGLE are predominantly detecting  $H_2S$ . It is unlikely that these sensors are detecting a significant amount of other RSCs, which were rarely detected by speciated sampling efforts.

## **Volatile Organic Compounds**

VOCs were detected from community ambient air sampling completed by the city of Kalamazoo and EPA. Canister and Tedlar Bag samples collected from the community had detectable levels of over 60 unique VOCs.

EGLE cross-referenced community ambient air sampling results from May and September 2021 with GPI's emission permit applications and the National Emission Inventory to identify VOCs that may have been emitted by GPI. The following VOCs are known to be emitted by GPI and were measured from air sampling results (Williams 2022):

- 2-Butanone (methyl ethyl ketone)
- 2-Ethyl-1-hexanol
- Acetaldehyde
- Benzene
- n-Butane
- Carbon disulfide
- Hexane
- n-Pentane
- Propene/propylene
- Toluene
- Vinyl acetate
- m- & p-Xylene

### EGLE Odor Investigations

As previously discussed, EGLE has issued several odor violations to GPI following investigations into community odor complaints. These violations were based on odors that were observed by EGLE investigators and traced back to GPI as the source.

Based on EGLE's investigations, residents near GPI have been impacted by odor-causing chemicals in the ambient air that were emitted by GPI. However, the exact chemicals resulting in the odors observed by community members and EGLE investigators are specifically identified. H<sub>2</sub>S, RSCs, and some VOCs are capable of causing odors.

#### 4.4 Exposure Pathways Analysis

MDHHS used available environmental sampling data and exposure information to determine whether a complete exposure pathway exists for GPI and/or KWRP.

As previously discussed, both GPI and KWRP represent potential sources of contamination based on their emissions of sulfur compounds, including H<sub>2</sub>S, and VOCs. Those substances are

emitted as gases into the outdoor air, potentially via stack emissions as a point-source (GPI), open-air clarifier volatilization (KWRP), or fugitive emissions (GPI and KWRP).

Emissions, whether point-source or fugitive, enter the ambient air where they can persist for varying durations of time. Once chemicals are released to the air, their movement can vary based on whether they are heavier or lighter than air. For example, denser chemicals, including H<sub>2</sub>S and many VOCs, may accumulate closer to the ground and not at higher elevations. Chemicals are also affected by meteorological conditions like wind, rain, and temperature. Chemicals tend to accumulate during atmospherically stable hours, like the evening and early morning.

As previously discussed, there is sufficient environmental monitoring and sampling data to conclude that emissions from GPI and KWRP have the potential to reach the nearby communities. The ambient air in those communities represent the point of exposure, where individuals may be exposed to contaminants.

The expected route of exposure to these contaminants is inhalation. RSCs and VOCs are emitted as gases and are expected to remain in the gaseous phase until they disperse. Small amounts of gaseous RSCs and VOCs may settle on the skin, causing dermal exposure, or be incidentally ingested while consuming food outdoors, causing oral exposure. However, these routes are not expected to cause significant exposure relative to inhalation.

Last, an exposure pathway requires a potentially exposed population. Potentially exposed populations to chemicals emitted by GPI and KWRP include adults and children who spend time outdoors in the communities near the plants. <sup>11</sup> As previously discussed, several residential neighborhoods are located near the plants.

Based on these conditions, MDHHS concludes that there is a completed exposure pathway for RSCs, and VOCs, and therefore ongoing potential for exposure.

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<sup>&</sup>lt;sup>11</sup> While adult workers at GPI and KWRP may also be exposed to chemicals emitted by GPI and KWRP, this assessment is focused on community exposures to the general public.

**Table 4: Exposure Pathway Summary** 

		Environmental	Exposure	Exposure Route of	Exposed		*
Chemical	Source	Medium	Point	concern	Population	Time Frame	Exposure*
Reduced Sulfur Compounds	GPI	Air	Ambient air in nearby	Inhalation	Adults Children	Past Present	Complete
Volatile Organic Compounds			communities		Workers	Future	
Reduced Sulfur Compounds	KWRP	Air	Ambient air in nearby communities	Inhalation	Adults Children Workers	Past Present Future	Complete
Volatile Organic Compounds			communities		Workers	ruture	

<sup>\*</sup>The exposure pathway is considered complete if there is evidence, or a high probability, that these elements are, have been, or will be present at a site (this indicates some level of exposure was likely).

Even if exposure occurs, it may not lead to harmful health effects. The likelihood that an individual may experience a harmful health effect, as well as the type and severity of that health effect, depends on several factors:

- Dose, or the amount of chemical that reaches the body;
- Exposure frequency (how often the individual is exposed) and duration (how long exposure happens when it occurs);
- Exposure pathway (breathing, eating, drinking, or dermal contact);
- Whether the individual is being exposed to a combination of contaminants with similar effects;
- Chemical and pharmacokinetic properties (how it passes through the body); and
- Personal characteristics of the exposed individual, like age, sex, nutritional factors, genetics, lifestyle, and health status.

### 4.5 Screening Evaluation of Ambient Air Monitoring and Sampling Data

MDHHS screened available community ambient air monitoring and sampling data to determine whether any chemicals or compounds were present at concentrations that could increase an individual's risk of adverse health effects.

Data screened for potential public health concerns include those results collected from the following investigations:

- KWRP Odor investigation, October-November 2020 (see Section 3.2)
- City of Kalamazoo Continuous Air Monitoring, September 2019-Present (see Section 3.3)
- EGLE Continuous Air Monitoring, April-May 2021 (see Section 3.4)
- EPA Ambient Air Monitoring and Sampling, May 2021 (see Section 3.5)
- City of Kalamazoo Krom and Prouty Park Investigation, September 2021 (see Section 3.7)

Data collected from GPI's continuous RSC sensors and EGLE's May 2022 drone investigation at KWRP were not screened against health-based screening values, as these data were collected from GPI and KWRP property, respectively.

As a first step in evaluating potential exposures, MDHHS compared air monitoring and sample concentrations to health-based screening values to identify chemicals of potential public health concern that may need more in-depth evaluation. Screening values represent concentrations of chemicals in the environment below which adverse health effects are unlikely, even among sensitive populations. If a screening value is exceeded, further investigation is necessary. Screening values are not thresholds for harmful health effects and concentrations higher than screening values do not indicate that health effects will occur.

Screening values used in this Health Consultation include:

- ATSDR Minimal Risk Levels (MRLs)
- ATSDR Cancer Risk Evaluation Guides (CREGs)
- EPA Reference Concentrations (RfCs)
- EGLE Interim Threshold Screening Levels (ITSLs)
- EGLE Residential Recommended Interim Action Screening Levels (RIASLs)<sup>12</sup>
- EPA Indoor Air Regional Screening Levels (RSLs)

## 4.5.1 Initial Screening

First, MDHHS screened measured chemical concentrations from environmental ambient air samples in the communities adjacent to GPI and KWRP using the most health-protective screening value for that chemical. For most measured chemicals in this investigation, the most health-protective screening value was protective against chronic or lifetime exposures. Chemicals for which no suitable screening values have been derived underwent further evaluation. Measured environmental chemical concentrations that did not exceed their most health-protective screening value were not considered to be public health concerns.

Most environmental chemicals detected in community ambient air were measured at concentrations below their most health protective screening values. The following chemicals were detected at concentrations that exceeded their most health protective screening value:

- 2-Ethylhexylacetate
- Acetaldehyde<sup>13</sup>
- Benzene
- Chloroform
- Formaldehyde
- Hexamethylcyclotrisiloxane

<sup>&</sup>lt;sup>12</sup> Although these screening values are intended for comparison with levels of chemicals in indoor residential air, MDHHS used them as a conservative approach for chemicals that lacked a more representative screening value. <sup>13</sup> Estimated result.

- H<sub>2</sub>S
- Isopropyl alcohol
- SO<sub>2</sub>
- Pyridine and pyridine-related compounds (including 2,6-lutidine and 2-ethylpyridine)

Ammonia was not detected, but the method used had a detection limit above the lowest screening value. These chemicals are discussed further in Section 5.

MDHHS was unable to identify suitable screening values for some chemicals measured in community air. These chemicals are discussed in greater detail in Section 4.5.2.

See Appendix E-1 for full results from the initial health screening of measured chemicals, including highest measured chemical concentrations and the screening value selected for each chemical.

4.5.2 Evaluation of Chemical Compounds Without Health-based Screening Values MDHHS was unable to identify health-based screening values for several chemical compounds identified in community ambient air samples near GPI and KWRP. These compounds were further evaluated to identify toxicity information and determine whether they may present a public health risk.

In order to evaluate these compounds, MDHHS compiled available toxicological information and data from published literature, chemical databases, and commercial Safety Data Sheets (SDSs). The following resources and databases were searched:

- ChemIDplus
- PubChem
- PubMed (search terms: chemical, CAS #)
- Google Scholar (same search terms as above)
- European Chemicals Agency (ECHA) chemical registration dossiers
- Sigma-Aldrich Safety Data Sheets

None of these chemicals had maximum measured concentrations that presented public health concerns.

Additional details on the evaluation of these chemicals can be found in Appendices E-2 and E-3.

### 5. PUBLIC HEALTH IMPLICATIONS

This section discusses potential public health impacts of chemicals measured in the communities adjacent to GPI and KWRP at concentrations that exceeded public health screening levels or were otherwise identified as requiring further evaluation.

The following chemicals are discussed in this section:

- H<sub>2</sub>S
- SO<sub>2</sub>
- 2-Ethylhexylacetate
- Ammonia
- Hexamethylcyclotrisiloxane
- Isopropyl alcohol
- Pyridine and pyridine-related compounds
- Acetaldehyde
- Benzene
- Chloroform

Additional discussions in this section include the potential public health impacts of environmental odors and the results of an investigation into asthma prevalence and asthmarelated hospitalization rates in the communities adjacent to GPI and KWRP. Potential health impacts from community and environmental stress and specific factors affecting children's health are also discussed.

## **5.1 Sulfur Compounds**

#### 5.1.1 Hydrogen Sulfide

 $H_2S$ , also known as hydrosulfuric acid, stink damp, sewer gas, and dihydrogen monosulfide, is a colorless gas at standard temperature and pressure with a characteristic rotten-egg odor. Its low melting point of -85.49°C indicates that it is predominantly in the gas phase. It has a variable odor threshold as low as 0.5 ppb, but high concentrations (150-200 ppm) can cause temporary olfactory fatigue, also known as olfactory nerve paralysis (ATSDR 2016).

H<sub>2</sub>S toxicity primarily targets the respiratory tract via inhalation exposure. No adverse health effects have been associated with oral or dermal exposure to H<sub>2</sub>S. For additional information on the toxicological effects of H<sub>2</sub>S, see Appendix E-4.

 $H_2S$  has industrial uses in the manufacturing of elemental sulfur and sulfuric acid. Natural sources of  $H_2S$  include swamps, bogs, volcanoes, and hot springs, while human sources include petroleum refineries, natural gas plants, landfills, paper mills, wastewater treatment plants, and tanneries.  $H_2S$  emissions may remain in the atmosphere for up to 42 days, where it may react with other chemicals to form  $SO_2$  and sulfates. Ambient air concentrations of  $H_2S$  from unpolluted areas range from 0.02-0.33 ppb, and levels in urban areas are generally below 1 ppb (ATSDR 2016).

 $H_2S$  concentrations in community ambient air were evaluated using an initial health screening value of 1.4 ppb, based on the EPA Chronic Inhalation RfC. The RfC was also used to assess public health risk from long-term exposure to  $H_2S$ . Additionally, the ATSDR Acute MRL was used to assess public health risk from short-term exposure to  $H_2S$ .

## 5.1.1.1 Public Health Conclusions for Long-term Exposure

To evaluate potential public health risks from long-term exposure to H<sub>2</sub>S, MDHHS evaluated continuous RSC monitoring data collected by the city of Kalamazoo and EGLE at community locations. Data from these sensors range in duration from 6 weeks to 2 years.

Continuous RSC monitoring data were compared to the EPA chronic inhalation RfC for  $H_2S$  of 0.002 mg/m³, equivalent to 1.4 ppb. <sup>14</sup> The RfC is based on an animal study that found nasal lesions in rats exposed to 30 or 80 ppm  $H_2S$  for 10 weeks and includes a 300-fold uncertainty factor (EPA 2003).

Average RSC concentrations indicate that RSC concentrations throughout the communities adjacent to GPI and KWRP regularly exceed the RfC. These concentrations result in hazard quotients (HQs) ranging from 3.2-8.3 (Table 5). HQs are the toxicity value ( $H_2S$  RfC) divided by the potential exposure concentration (average RSC concentration). They provide an indication of the magnitude of people's exposure. When a HQ is above 1, additional evaluation of the exposure is needed.

Table 5: Summary of Continuous RSC Monitoring Data and Hazard Quotients for Long-term Exposure

		Sampling	Average	Hazard
Investigation	Sampling Location	Duration <sup>15</sup>	RSCs (ppb)	Quotient
EGLE Riverview Dr	Riverview Dr (North)	6 weeks	6.4	4.6
RSC Monitoring	Riverview Dr (South)	6 weeks	9.6	6.9
City of Kalamazoo	Public Safety Station	2 years	11.6	8.3
Community RSC	#3			
Monitoring	Borgess Hospital	2 years	4.4	3.2
	Rockwell Park	11 months	9.7	7.0
	Krom and Prouty Park	7 months	8.4	6.1

It should be noted that these RSC sensors are highly cross-sensitive and will detect other RSCs in addition to  $H_2S$ . Due to this cross-sensitivity, the true concentration of  $H_2S$  from these measurements cannot be verified. However, speciated RSC canister sampling results taken from the communities adjacent to GPI and KWRP rarely measured RSCs other than  $H_2S$ .  $H_2S$  was detected in 31/71 (44 percent) of community ambient air samples analyzed for speciated RSCs,

 $<sup>^{14}</sup>$  Volume (ppb) = Volume (mg/m<sup>3</sup>) \* (Molar volume/Molecular mass) 0.002 mg/m<sup>3</sup> \* (24.45/34.0818) = 0.0014 ppm = 1.4 ppb

<sup>&</sup>lt;sup>15</sup> Running averages are based on over 2 years of data for the Borgess Hospital and Gull and Riverview public safety station locations (September 2019-December 2021), 11 months of data for the Rockwell Park location (February 2021-December 2021), and 7 months of data for the Krom and Prouty Park location (February-July; September-November).

while RSCs other than H<sub>2</sub>S were detected in only 1/71 samples.<sup>16</sup> Therefore, it is likely that the continuous RSC sensors are measuring predominantly H<sub>2</sub>S.

Combined RSC concentrations are consistently higher than the RfC for  $H_2S$ , up to nearly ten times higher, and the composition of RSCs measured by these sensors is expected to be predominantly  $H_2S$ . Therefore, true  $H_2S$  levels in the community likely exceed the RfC on a regular basis.  $H_2S$  concentrations in the communities adjacent to GPI and KWRP may have a higher lifetime exposure, assuming that concentrations measured during these investigations are representative of past or future concentrations.

The specific continuous RSC monitoring technology used in these monitoring efforts is not a method recommended by EPA or ATSDR for the purpose of risk assessment. The concentrations may be biased high, biased low, or variable over time. RSCs should be confirmed using an EPA recommended method. If environmental conditions in the community remain the same, residents' risk of respiratory effects, including nasal irritation, may increase.

5.1.1.2 Public Health Conclusions for Exposure to Transiently Higher Levels of  $H_2S$  MDHHS also evaluated  $H_2S$  measurements for the potential to increase risk of health effects from transiently higher levels of  $H_2S$ . To evaluate this exposure, MDHHS compared measured concentrations with ATSDR's Acute Inhalation MRL for H2S of 0.07 ppm (70 ppb).

The Acute MRL is intended to be protective against short, transient exposures to  $H_2S$ . It is based on a study that reported airway resistance and bronchial obstruction among people with asthma exposed to 2 ppm (2,000 ppb)  $H_2S$  for 30 minutes (ATSDR 2016). ATSDR considered this effect level to be a minimally adverse effect level as airway resistance and bronchial obstruction were observed in only 2/10 subjects. The MRL was calculated by applying an uncertainty factor of 27 (3 for use of a LOAEL, 3 for human variability, and 3 for database deficiencies due to the short exposure duration (30 minutes) of the study.

One 24-hour composite sample taken during the city of Kalamazoo's September 2021 Krom and Prouty Park sampling investigation contained  $H_2S$  at a concentration of 85 ppb, which exceeds the ATSDR Acute Inhalation MRL of 70 ppb (HQ=1.2). This finding was considered to be reliable and acceptable for the assessment of potential health risks. No other monitoring or sampling results for  $H_2S$  or RSCs exceeded the MRL at this location or at others in the community, including 70 short-term air samples analyzed for speciated RSCs.

The 85 ppb concentration of  $H_2S$  measured at Krom and Pouty in September 2021 indicates that  $H_2S$  concentrations in ambient air near GPI and KWRP may sporadically be higher than 70 ppb (Acute Inhalation MRL) during certain conditions. However, available data is not sufficient to characterize the frequency or magnitude of these exceedances. Additionally, it is not clear what

<sup>&</sup>lt;sup>16</sup> Sulfur compounds (1-methylethyl) (1,1-dimethylethyl)disulfide, bis(1-methylethyl)disulfide, and sulfur dioxide were also measured using EPA TO-15 analysis.

(if any) conditions caused the elevated concentrations measured in the September 2021 investigation, which were not observed in other  $H_2S$  investigations.

Possible contributing factors include atmospheric conditions (wind speed and direction) and changes in industrial processes at the two facilities. The canister was located at Krom and Prouty Park, which is directly west of GPI and KWRP. Winds out of the east could transport H<sub>2</sub>S emissions from these plants in the direction of the canister. Historical weather data<sup>17</sup> indicates that winds ranged from 5-20 mph and were consistently out of the south and south-southeast during the time when the sample was being collected (September 20, 2021 at 7am to September 21, 2021 at 7am). Therefore, wind conditions on that day would likely have transported emissions away from the canister.

It should also be noted that short-term RSC samples have limited seasonal variability – all samples were taken in fall or spring, while no samples were taken in summer or winter. Concentrations of many outdoor air contaminants peak in the summer and winter.

Based on the available data,  $H_2S$  concentrations in the communities adjacent to GPI and KWRP present no apparent public health hazard following exposure to transiently higher levels of  $H_2S$ . The 24-hour canister sample that exceeded the ATSDR Acute Inhalation MRL indicates that levels of  $H_2S$  in the community may briefly and sporadically exceed the MRL, which may increase the risk of respiratory effects in sensitive individuals. However, all other air samples and monitoring efforts indicate that  $H_2S$  concentrations are regularly below the Acute MRL. Additional data are needed to characterize the frequency and magnitude of these elevated  $H_2S$  events, as well as the conditions that cause them.

### Summary Table for H<sub>2</sub>S Screening Values Analysis

See below for a summary of H<sub>2</sub>S monitoring and sampling data and its health screening values (Table 6).

It is important to note that health screening values such as the ATSDR MRL and EPA RfC are intended for screening purposes only. Individuals who are exposed to concentrations of chemicals that exceed these values will not necessarily experience harmful health effects.

<sup>&</sup>lt;sup>17</sup> https://www.wunderground.com/history/daily/us/mi/portage/KAZO/date/2021-9-20

Table 6: Health Screening Value Analysis of H₂S in the Communities adjacent to GPI and KWRP

Kalamazoo H₂S Commun	ity Monitoring Data	1			Health Screening V	'alues	Concentrations				
Investigation Name (Duration)	Sampling Location	Sampling Type (Duration)	Relevant Findings		Туре	Value (ppb)	Exceed Screening Value? (Yes/No/ Indeterminate)				
City of Kalamazoo Odor			Range: ND-16 ppb	ATSDR Acute MRL	70	No					
Investigation (October-	locations	locations	locations	locations	locations		(56%)		EPA RfC	1.4	Yes
November 2020)		Canister (24-	Detections: 6/17	Range: ND-45 ppb	ATSDR Acute MRL	70	No				
		hour)	(35%)		EPA RfC	1.4	Yes				
EPA GMAP Monitoring (May 11-13, 2021)	Northside neighborhood;	Continuous monitoring	H <sub>2</sub> S was not detected 23.58 ppb.	ed above the instrument's RL of	ATSDR Acute MRL	70	No				
	GPI and KWRP (several hours property; four additional local facilities				EPA RfC	1.4	Indeterminate (Screening value below instrument RL)				
City of Kalamazoo Krom	Krom and Prouty	Canister (Grab)	Detections: 11/28	Range: ND-46 ppb	ATSDR Acute MRL	70	No				
and Prouty Park	Park (one		(39%)		EPA RfC	1.4	Yes				
Monitoring (September	location)			Canister (24-	Detections: 4/8	Range: ND-85 ppb	ATSDR Acute MRL	70	No		
20-23, 2021)		hour)	ur) (50%)	HQ=1.2	EPA RfC	1.4	Yes				
EGLE Riverview Dr RSC Monitoring (April-May 2021)	Two locations along Riverview Drive	Continuous monitoring (6 Weeks)	Average RSC Concentrations:  North Monitor: 6.4 ppb (HQ=4.6)		EPA RfC	1.4	Yes				
City of Kalamazoo	Several	Continuous	South Monitor: 9.6 Average RSC Conce	ppb (HQ=6.9) ntrations from 2019-2021:	EPA RfC	1.4	Yes				
Community RSC Monitoring (September 2019-ongoing)	community locations	monitoring (2 years)	Public Safety Station #3 (September 2019-December 2021): 11.63 ppb (HQ=8.3)  Borgess Hospital (September 2019-December 2021): 4.44 ppb (HQ=3.2)  Krom and Prouty Park (2021): 8.49 ppb (HQ=6.1)								
	1): 9.75 ppb (HQ=7.0)										

## 5.1.2 Sulfur Dioxide (SO<sub>2</sub>)

Sulfur dioxide is a colorless gas with a pungent odor. It is primarily released to the environment via the burning of fossil fuels but can also be contributed by natural processes such as volcanic activity. People are most commonly exposed to SO<sub>2</sub> via inhalation (ATSDR 1998a).

Extremely high concentrations of  $SO_2$  (100 ppm, or 100,000 ppb) are considered to be immediately dangerous to life and health. Long-term exposure to elevated  $SO_2$  (400-3,000 ppb) affected the lung function of workers, though these workers were also exposed to other chemicals. In particular, individuals with asthma were found to be sensitive to 250 ppb  $SO_2$  (ATSDR 1998a).

ATSDR has set an acute inhalation MRL of 10 ppb for  $SO_2$  based on evidence of slight bronchoconstriction after inhaling 100 ppb  $SO_2$ . No intermediate or chronic MRLs have been established for  $SO_2$  (ATSDR 1998a).

The EPA has set primary and secondary National Ambient Air Quality Standards (NAAQS) for SO<sub>2</sub>. The primary NAAQS are intended to protect public health including the health of sensitive populations, like people with asthma. SO<sub>2</sub> has a primary NAAQS of 75 ppb averaged over 1 hour. The secondary NAAQS protects public welfare including harm to animals, crops, and vegetation. Sulfur dioxide has a secondary NAAQS of 500 ppb over a 3-hour average (EPA 2021b). The NAAQS for SO<sub>2</sub> were last updated in 2019. No screening values for long-term exposure to SO<sub>2</sub> have been identified.

As the primary NAAQS standard for SO<sub>2</sub> was updated most recently and is protective of public health, including the health of sensitive populations, MDHHS chose the primary NAAQS standard as the health screening value for this assessment.

Sulfur dioxide was detected in samples from three locations during October 2020 odor monitoring investigation, at a maximum concentration of 27.1 ppb from a 24-hour canister sample. It should also be noted that the test method used for these samples (EPA TO-15) is not recommended for quantification of SO<sub>2</sub>.

Sulfur dioxide was not detected from any samples in the May 2021 or September 2021 sampling events. In total, SO<sub>2</sub> was detected in 16.25 percent of samples. The maximum measured SO<sub>2</sub> concentration was higher than the ATSDR Acute Inhalation MRL of 10 ppb. However, the maximum measured sulfur dioxide concentration was about three times lower than the primary NAAQS standard and about 18 times lower than the secondary NAAQS standard. Canister samples in May and September 2021 did not detect any SO<sub>2</sub>, indicating that the elevated levels detected in October 2020 may have been sporadic.

According to ATSDR, typical outdoor concentrations of  $SO_2$  in urban areas may range from 0-1 ppm (0-1,000 ppb) (ATSDR 1998a). Therefore, it is possible that  $SO_2$  measured from canister samples in the Kalamazoo community originated from general urban background sources as opposed to a specific source.

Based on the available data,  $SO_2$  in communities adjacent to GPI and KWRP does not appear to present a public health concern. No measured concentrations of  $SO_2$  exceeded the primary NAAQS for  $SO_2$ , and concentrations are in line with typical outdoor concentrations of  $SO_2$  in urban areas.

See below for a summary of measured SO<sub>2</sub> levels in community ambient air near GPI and KWRP (Table 7)

Table 7: Community Air Concentrations of Sulfur Dioxide (SO<sub>2</sub>) near GPI and KWRP

Investigation	Type of Sampling (Duration)	Number of Detections	Measured Exceedances (ppb)	Short-term Health Screening Value (ppb)	Long-term Health Screening Value (ppb)
KWRP October	Canister (24-hour)	9/18 (50%)	None	75	N/A
2020	Tedlar Bag (Grab)	4/18 (22%)	None	75	N/A
EPA May 2021	Canister (Grab, 1-hour, 12-hour)	0/8	None	75	N/A
KWRP	Canister (24-hour)	0/8	None	75	N/A
September 2021	Canister (Grab)	0/28	None	75	N/A
Percent	age of Total Samples with Detections:	16.25%			
Percent	age of Samples Exceeding Screening Value:	0%			

### **5.2 Non-Sulfur Compounds**

A variety of other compounds, primarily VOCs, were measured from short-term ambient air sampling in communities adjacent to GPI and KWRP. The majority of non-sulfur compounds measured in communities adjacent to GPI and KWRP were below preliminary or secondary screening values.

No non-sulfur compounds measured in the community were higher than short-term screening values. Four compounds were measured at concentrations higher than applicable long-term screening values or were otherwise identified as requiring further evaluation. These compounds are discussed in further detail below.

Four compounds were measured at concentrations higher than applicable cancer-based screening values and need further evaluation. These compounds are discussed in further detail in Section 5.3.

### 5.2.1 Ammonia (CAS #7664-41-7)

ATSDR has established the following MRLs for ammonia (ATSDR 2004):

- 1.7 ppm for Acute Inhalation exposure, based on mild irritation of the eyes, nose, and throat in humans exposed to ammonia gas for 2 hours.
- 0.1 ppm for Chronic Inhalation exposure, based on reported respiratory effects (cough, bronchitis, dyspnea, and others) reported by workers in a soda ash plant.

Ambient air samples were measured for ammonia during the October 2020 KWRP odor investigation. No samples collected in the community locations had detectable ammonia. Although the RL for the method, 5.56 ppm, was higher than both the Acute and Chronic MRLs for ammonia, only a single sample out of 18 samples taken from the sanitary sewer collection network had a detection for ammonia (5.65 ppm). If the source of any potential ammonia is in the sanitary sewer collection network, it is likely that concentrations would be higher there and lower in the ambient air. As only 1 out of 18 samples collected in the sanitary sewer had a detect of ammonia, it is not expected that there would be higher levels of ammonia in the ambient air in community locations. Additional sampling using a method with a lower RL would provide confirmation or would provide more appropriate data to evaluate, but is not recommended at this time.

## 5.2.2 Hexamethylcyclotrisiloxane (D3) (CAS #541-05-9)

D3 is a raw material used in the production of silicones and siloxane-based polymers. These materials may be used in cosmetics, medical devices, water-repellent coatings, and industrial lubricants and sealants. Limited toxicological data indicate that it may cause skin, eye, and respiratory irritation (ECHA, CAS #541-05-9, 2022).

No short-term health screening values have been established for D3. EGLE has derived an annual ITSL for D3 of 50  $\mu$ g/m³ (5 ppb) based on a 28-day gavage study in rats, which identified a LOAEL of 1,500 mg/kg D3 based on reduced body weights and food consumption (male rats only), increased liver weights, and increased hyaline droplets in the proximal tubule epithelium of the kidneys (males only) (MDNR 1992).¹8

Several D3 measurements from the October 2020 and September 2021 24-hour canister sampling, as well as the September 2021 grab canister sampling, exceeded EGLE's annual ITSL for D3. In total, D3 was detected in 30 samples (37.5 percent of all community air samples) and exceeded its screening value in 6 samples (7.5 percent of all community air samples).

The annual ITSL is intended for comparison with ambient air concentrations averaged over 1 year. As concentrations exceeded the ITSL in both October 2020 and September 2021, it is possible that community air concentrations of D3 would exceed the ITSL if averaged over 1 year.

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<sup>&</sup>lt;sup>18</sup> This ITSL is based on an oral toxicity study and includes oral route of exposure to inhalation route exposure extrapolation. While this extrapolation

However, it should be noted that D3 (as well as several other compounds that contain silicon) was only detected from Silonite canisters, which contain an internal layer of silica.<sup>19</sup> D3 was not detected in any Tedlar Bag samples or SUMMA canisters from the Kalamazoo community. Additionally, D3 is used in the production of silicones and siloxane-based polymers, and is therefore a potential breakdown product from silicone. Therefore, it is possible that detections of D3 and other silicon-based compounds resulted from the Silonite canister's unique silicon-based coating but there is no data available to confirm that scenario.

Based on the weight of evidence, D3 does not appear to present a health risk in communities adjacent to GPI and KWRP. Available data indicate that D3 levels in community air near GPI and KWRP occasionally exceed its health screening value. However, there is evidence that these detections are due to contamination unique to the sampling technology used in these studies.

Table 9: Community Air Concentrations of D3 near GPI and KWRP

	Type of		Measured	Short-term	Long-term Health
	Sampling	Number of	Exceedances	Health Screening	Screening Value
Investigation	(Duration)	Detections	(ppb)	Value (ppb)	(ppb)
	Silonite canister	10/18			
KWRP October	(24-hour)	(55.6%)	6.5, 9.1, 18.7	N/A	5
2020	Tedlar Bag				
	(Grab)	0/18	None	N/A	5
	SUMMA				
EPA May 2021	canister (Grab,				
	1-hour, 12-hour)	0/8	None	N/A	5
	Silonite canister	7/8			
KWRP	(24-hour)	(87.5%)	5.7	N/A	5
September 2021	Silonite canister	13/28			
	(Grab)	(46.4%)	5.5, 9.5	N/A	5
Percentage of Total Samples with					
Detections:		37.5%			
Percentage of Samples Exceeding					
	Screening Value:	7.5%			

#### 5.2.3 Isopropyl alcohol (CAS #67-63-0)

Isopropyl alcohol, also known as isopropanol, is a common cleaning solvent and disinfectant used in households, hospitals, and industry. High concentrations in the air may cause skin, eye, nose, and throat irritation, as well as drowsiness and headache. Isopropyl alcohol has not been identified as a carcinogen.

No short-term health screening values have been established for isopropyl alcohol. It has an EPA RSL for indoor air of 200  $\mu$ g/m³ (80 ppb) (EPA 2021a). Although the RSL of 80 ppb applies to indoor air concentrations of isopropyl alcohol, MDHHS used the RSL as a conservative health

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<sup>&</sup>lt;sup>19</sup> https://www.entechinst.com/silonite-vs-summa-canisters/

screening value for outdoor air concentrations in the absence of a more applicable screening value.

Samples with measured isopropyl alcohol exceeding 80 ppb were limited to three grab samples from the October 2020 investigation, which measured 146.5, 130.2, and 276.7 ppb. No other samples from this investigation (including all 24-hour samples) or the May 2021 or September 2021 investigations exceeded 80 ppb.

It is likely that the higher levels measured in the October 2020 Tedlar Bag samples were brief and transient. The 24-hour samples from the October 2020 investigation taken at the same time had a maximum measurement of 1.4 ppb, indicating that concentrations did not remain similarly high over a 24-hour day. Therefore, it is unlikely that isopropyl alcohol concentrations in community air regularly exceed 80 ppb.

It is also possible that the elevated measurements were due to laboratory contamination of Tedlar Bags, as isopropyl alcohol is a common laboratory cleaning agent.

Based on the weight of evidence, isopropyl alcohol is not likely to be a health risk for short-term or long-term health exposure in communities adjacent to GPI and KWRP.

Table 10: Community Air Concentrations of Isopropyl Alcohol near GPI and KWRP

			Measured	Short-term Health	Long-term Health	
	Type of Sampling	Number of	Exceedances	Screening	Screening	
Investigation	(Duration)	Detections	(ppb)	Value (ppb)	Value (ppb)	
	Silonite canister	2/18		N/A	80	
KWRP October 2020	(24-hour)	(11.1%)	None	N/A	80	
KWKP October 2020		6/18	130.2, 146.5,	N/A	80	
	Tedlar Bag (Grab)	(33.3%)	276.7	N/A	80	
	Silonite canister					
EPA May 2021	(Grab, 1-hour, 12-			N/A	80	
	hour)	0/8	None			
	Silonite canister			N/A	80	
KWRP September	(24-hour)	0/8	None	N/A	80	
2021	Silonite canister			N/A	80	
	(Grab)	0/28	None	N/A	80	
Percentage of	Percentage of Total Samples with					
	Detections:					
Percentage of	of Samples Exceeding		_			
	Screening Value:	3.75%				

#### 5.2.4 Pyridine (CAS #110-86-1) and pyridine-related compounds

Pyridine is a cyclic amine with a structure similar to benzene. It is a colorless to pale yellow liquid with an unpleasant odor. Pyridine is used as solvent and in the production of medicines, paints, dyes, adhesives, and insecticides. It is also formed naturally via environmental

degradation of organic materials. Pyridine is associated with a variety of harmful effects upon inhalation, including dizziness, headache, nausea, and shortness of breath. Dermal exposure can cause skin and eye irritation. Pyridine is also suspected of causing liver damage. The International Agency for Research on Cancer (IARC) considers pyridine to be possibly carcinogenic to humans based on sufficient evidence of carcinogenicity in experimental animals (PubChem 2022).

2,6-Lutidine and 2-ethylpyridine are alkylpyridines with dimethyl and ethyl substitutions.

No short-term health screening values have been established for pyridine. EGLE has derived an Annual ITSL of 3.5  $\mu$ g/m³ (1 ppb) for pyridine based on an EPA RfD of 1  $\mu$ g/kg/day. The RfD is based on a 90-day oral rat toxicity study with a critical effect of increased liver weight (MDEQ 2017).

No health screening values were identified for 2,6-lutidine or 2-ethylpyridine, and available data were insufficient to identify a secondary health screening value for either compound. Therefore, pyridine was identified as a suitable chemical surrogate and chemical concentrations of 2,6-lutidine and 2-ethylpyridine were compared to the Annual ITSL for pyridine. See Appendix E-1 for more information.

One grab canister sample from the September 2021 investigation contained pyridine at 3.7 ppb, 2,6-lutidine at 0.8 ppb, and 2-ethylpyridine at 0.7 ppb. The concentrations of these three compounds were combined as they were measured from the same sample, for a total concentration of 5.2 ppb. This concentration exceeds the EGLE annual ITSL of 1 ppb.

No other samples from any of the three investigations detected pyridine, 2,6-lutidine, or 2-ethylpyridine. Two 24-hour composite samples taken on the same day at the same location did not detect any pyridine-related compounds. Therefore, it is likely that the measurements of pyridine-related compounds were transient and not indicative of long-term, continuously elevated concentrations in the community.

Based on the weight of evidence, pyridine, 2,6-lutidine and 2-ethylpyridine are not likely to present a public health concern in the communities adjacent to GPI and KWRP.

Table 11: Community Air Concentrations of Pyridine, 2,6-Lutidine, and 2-Ethylpyridine near GPI and KWRP

		Number of	Combined	Short-term Health	Long-term Health
	Type of Sampling	Samples with	Concentrations	Screening Value	Screening
Investigation	(Duration)	Detections	(ppb)	(ppb)	Value (ppb)
KIA/DD Octobor	Silonite canister				
KWRP October	(24-hour)	0/18	ND	N/A	1
2020	Tedlar Bag (Grab)	0/18	ND	N/A	1
	Silonite canister				
EPA May 2021	(Grab, 1-hour, 12-				
	hour)	0/8	ND	N/A	1
	Silonite canister				
KWRP September	(24-hour)	0/8	ND	N/A	1
2021	Silonite canister	1/28			
	(Grab)	(3.5%)	5.2	N/A	1
Percentage of Total Samples with					
Detections:		1.25%			
Percentage o	f Samples Exceeding				
	Screening Value:	1.25%			

#### 5.3 Cancer Risks

Two compounds, benzene and chloroform, were measured in the communities adjacent to GPI and KWRP at concentrations that were higher than their respective ATSDR CREGs. CREGs are comparison values used to evaluate concentrations of carcinogenic chemicals in a population. They are based on theoretical estimates of cancer risk and represent concentrations estimated to potentially result in no more than one extra case of cancer in a population of one million similarly exposed people. Chemical concentrations exceeding a CREG do not mean that all or any individuals in an exposed population would be expected to develop cancer.

A third compound, acetaldehyde, was tentatively identified by one test method, EPA Method TO-15, and estimated at concentrations higher than its ATSDR CREG. As a conservative approach, acetaldehyde was also evaluated for potential cancer risks at the estimated concentrations.

Due to the conservative thresholds established by CREGs, some carcinogenic air pollutants in urban environments in the United States often are higher than the CREGs (Table 12). Many carcinogenic air pollutants are commonly emitted at low levels in vehicle exhaust and through industrial emissions. Ambient air concentrations of a pollutant higher than a CREG do not necessarily indicate elevated cancer risk from exposure to typical ambient air concentrations.

The three compounds that had average measured or estimated concentrations higher than their respective CREGs were compared with typical ambient air concentrations for those compounds as a first step to evaluate potential risks related to cancer (Table 12). Average concentrations were calculated for each compound using concentrations measured from composite samples of 1 hour or greater at the same sampling location. Non-detect

measurements were averaged using the standard EPA Method TO-15 highest allowable detection limit of 0.5 ppb (EPA 1999) as a conservative approach. See Appendix E-5 for details on average concentration calculations.

Table 12: Chemical Compounds Exceeding Cancer Risk Evaluation Guides (CREGs) in the Communities adjacent to GPI and KWRP

Chemical	Average Concentration (ppb)	Typical Ambient Air Concentration (ppb)	Typical Environmental Sources	ATSDR CREG (ppb)
Acetaldehyde	1.07 °	0.9 b	Motor vehicle exhaust <sup>c</sup> Industrial emissions <sup>c</sup> Paint/lacquers <sup>c</sup>	0.25
Benzene	0.57	0.26 <sup>b</sup> ; up to 1 <sup>d</sup>	Motor vehicle exhaust <sup>d</sup> Industrial emissions <sup>d</sup> Cigarette smoke <sup>d</sup>	0.04
Chloroform	0.23	0.2-0.5 <sup>e</sup>	Industrial emissions <sup>e</sup> Shower steam <sup>e</sup> Drinking water <sup>e</sup>	0.0089

<sup>&</sup>lt;sup>a</sup> Estimated result

The measured or estimated concentrations of these three chemicals are consistent with typical ambient air concentrations for urban areas in the United States. Acetaldehyde and benzene concentrations slightly exceed average concentrations reported by the EPA (2018) and were evaluated further using EPA cancer risk assessment methodology.

Lifetime exposure to the average estimated acetaldehyde concentration of 1.07 ppb presents an estimated cancer risk of approximately 4 extra cancer cases in a similarly exposed population of 1 million ( $4.25 \times 10^{-6}$ ). Lifetime exposure to the average measured benzene concentration of 0.57 ppb presents an estimated cancer risk of approximately 14 extra cancer cases in a similarly exposed population of 1 million ( $1.4 \times 10^{-5}$ ). For more details on how these values were calculated, see Appendix E-5.

For comparison, the American Cancer Society estimates that approximately 38.4 percent of people in the United States will develop some form of cancer in their lifetimes (ACS 2018). By comparison, if individuals in the communities adjacent to GPI and KWRP have a lifetime exposure to calculated average ambient air concentrations of acetaldehyde and benzene this may raise an individual's chances of developing cancer by a very small percentage (0.0004 percent and 0.0014 percent, respectively).

Therefore, this data does not indicate a concern for cancer risks.

<sup>&</sup>lt;sup>b</sup> EPA 2018

<sup>&</sup>lt;sup>c</sup> Sinharoy 2019

d ATSDR 2007

e ATSDR 2014

#### 5.4 Environmental Odors

Residents in the communities adjacent to GPI and KWRP have reported foul odors in their community since 2008. Since 2010, over 240 complaints have been reported to EGLE, the city of Kalamazoo, and MDHHS related to GPI and KWRP (Table 1).

Odors are caused by substances in the air that have a scent. When a sufficient concentration of an odor-causing chemical is inhaled through the nose, it stimulates olfactory nerves that cause the sensation of scent (Schiffman and Williams 2005). The concentration of a chemical or substance that can be detected via scent is called an odor threshold. When odors are particularly strong, unpleasant, or unwanted, they can become a nuisance and cause discomfort.

Environmental odors are odors in the outdoor air. They can cause discomfort and adversely impact an individual's quality of life, particularly if the odors are unpleasant, strong, and/or persistent. For example, residents are less able to exercise outdoors or visit a park if there are odors in the community, even if the levels are not high enough to cause health effects. Environmental odors may also permeate into a person's home or discourage people from opening their windows. Living in a community with persistent odors can contribute to chronic stress, which is associated with a variety of adverse health effects. Community and environmental stress are discussed further below.

Odors are also associated with a variety of transient health effects (Schiffman and Williams 2005):

- At levels near the odor threshold, odors can cause localized overstimulation of the olfactory nerves resulting in headaches, nausea, and vomiting.
- At levels one to two orders of magnitude above the odor threshold, odors can cause overstimulation of other cranial nerves which can cause irritation of the eyes, nose, or throat, which may include a burning sensation (burning eyes).
- Repeated exposure to odorous substances can cause respiratory effects in people with asthma.
- Previous exposure to high levels of an odor can make some people acutely sensitive to the substance in the future, reacting adversely to minimal concentrations of the substance.
- The aggregate effect of a mixture of odor-causing chemicals with similar scents can cause irritation, even if each individual substance is below its odor threshold.

Irritation usually resolves once the odor dissipates. However, in particularly sensitive people, some irritation may continue even after the odor is gone (ATSDR 2017a).

Health effects have also been reported in communities with levels of chemicals below those expected to cause irritation. Two community investigations found that residents experienced health effects from average daily exposures to 10 ppb H<sub>2</sub>S (Schiffman and Williams 2005).

MDHHS evaluated sampling data from the communities adjacent to GPI and KWRP to determine whether any concentrations of chemicals were above documented odor thresholds, with the goal of identifying chemicals that could cause odors.

MDHHS notes that it is difficult to quantitatively evaluate the potential for odor-related irritation health effects. As odor sensitivity varies from person to person, an individual that is particularly sensitive to odors may experience irritation or health effects from odors at concentrations below established or estimated odor thresholds. Similarly, many chemicals have several documented odor thresholds based on different methods or studies. As there is no authoritative source on chemical odor thresholds, and odor sensitivity varies greatly from person to person, MDHHS conservatively used the minimum reported odor threshold in order to identify any chemicals that could be causing environmental odors in the communities adjacent to GPI and KWRP.

#### 5.4.1 H<sub>2</sub>S and Other Sulfur Compounds

As previously discussed,  $H_2S$  has a distinct sulfuric odor similar to rotten eggs. People have varying abilities to detect  $H_2S$  in the air with odor thresholds ranging from 0.5-300 ppb (ATSDR 2016). This means that most people can detect  $H_2S$  at concentrations of 300 ppb or higher, but some people can detect  $H_2S$  at concentrations as low as 0.5 ppb.

Although it has a pungent odor that is detectable at low concentrations, people may be unable to detect H<sub>2</sub>S at higher concentrations (> 100 ppm, or 100,000 ppb) due to olfactory paralysis. Olfactory paralysis is the loss of the ability to perceive odors. It occurs when high concentrations of a chemical temporarily disable the nerves that detect odors. However, available monitoring and sampling data indicates that community air concentrations of H<sub>2</sub>S are well below those that could induce olfactory paralysis. People may also be unable to detect H<sub>2</sub>S due to olfactory fatigue, which is a similar condition that results in a gradual loss of sensitivity to an odor after continuous exposure (ATSDR 2016).

MDHHS found that community continuous RSC sensors regularly exceeded 0.5 ppb. All continuous sensors maintained by the city of Kalamazoo have reported 15-day average continuous RSC concentrations above 0.5 ppb — the lowest concentrations were detected in the Borgess Hospital sensors, which reported 15-day average concentrations around 2-4 ppb since March 2021. These results are further supported by EGLE's April 2021 continuous monitoring investigation, which consistently reported 15-day average concentrations between 6 and 11 ppb. Concentrations above 0.5 ppb were also reported from continuous sensors on GPI's property from January-August 2021.

None of the other sulfur compounds measured in the communities adjacent to GPI and KWRP were measured at concentrations that exceed their minimum reported odor threshold. Based on the available data, it is possible that elevated H<sub>2</sub>S levels in communities adjacent to GPI and KWRP are contributing to offensive odors and causing adverse health effects in particularly sensitive individuals. H<sub>2</sub>S levels regularly exceed the low end of the odor threshold range, and frequently exceed an order of magnitude above the odor threshold. H<sub>2</sub>S levels also

regularly exceed 10 ppb, a concentration of  $H_2S$  that was associated with odors and health effects in some community investigations (Schiffman and Williams 2005). These data indicate that  $H_2S$  in communities adjacent to GPI and KWRP has the potential to cause foul odors as well as transient health effects in particularly sensitive individuals.

5.4.2 Volatile Organic Compounds (VOCs) and Non-Sulfur Compounds
In addition to H<sub>2</sub>S, many VOCs are also responsible for causing odors. VOCs have odors that range from pleasant to pungent. In order to evaluate odor concerns related to VOCs, MDHHS compiled odor thresholds reported for each VOC detected in community air sampling. When multiple odor thresholds were reported for a chemical, MDHHS used the minimum reported odor threshold to compare with measured results.

Of the VOCs detected in community air sampling in in the area, the vast majority were measured at concentrations below their chemical-specific odor thresholds (Appendix E-6). VOCs measured above their respective odor thresholds are summarized below (Table 13) and discussed in Appendix E-7.

Table 13: Measured VOCs from Community Ambient Air Samples in Kalamazoo that Exceeded Minimum Odor Thresholds

Chemical	CAS#	October 2020 (ppb)	May 2021 (ppb)	September 2021 (ppb)	Odor Threshold (ppb)	Percentage of Samples Exceeding Odor Threshold
1-Butanol	71-36-3	1.4, 8.2	ND	2.1	1	3.75%
Acetaldehyde <sup>a</sup>	75-07-0	ND	ND	1.7, 2.4, 4.9	1.5	3.75%
Acetic acid	64-19-7	52.9	ND	<3.8	6	1.25%
Butanoic acid	107-92-6	ND	ND	2.4	0.19	1.25%
n-Butanal	123-72-8	ND	ND	1	0.67	1.25%
d-Limonene	5989-27-5	2.5	ND	ND	1.07	1.25%
				0.5, 0.5, 0.5,		
n-Nonanal	124-19-6	0.4, 2.4, 2.6	ND	0.7, 1.3, 1.3	0.34	11.25%

<sup>&</sup>lt;sup>a</sup> Acetaldehyde was tentatively identified and its concentration was estimated.

Based on the available data, it is possible that some environmental VOCs in the communities adjacent to GPI and KWRP are contributing to offensive odors. Several organic acids and aldehydes, which are known to cause odors at low concentrations, were measured at levels that exceeded reported odor thresholds. One chemical, n-nonanal, was measured above its odor threshold in 9 samples (11.25 percent of all samples), including some samples in October 2020 and September 2021. As previously discussed, environmental odors can cause adverse health effects beyond discomfort and annoyance, including nausea, headache, insomnia, and eye, nose, and throat irritation. People with asthma and other respiratory conditions may be more sensitive to environmental odors.

#### 5.5 Asthma Epidemiology

The MDHHS Chronic Disease Epidemiology Section (CDES) conducted a review of data for asthma prevalence and hospitalization rates in selected groups of ZIP codes located within the city of Kalamazoo, Michigan. The analyses were prepared in response to community concern that exposure to H<sub>2</sub>S and other air pollutants released from GPI and KWRP is resulting in asthma exacerbation. Research has shown that H<sub>2</sub>S exposure is linked with bronchial obstruction in people with asthma and that odors from H<sub>2</sub>S can exacerbate asthma symptoms (ATSDR 2016). The goal of this review was to determine if selected ZIP code areas surrounding GPI and KWRP in the city of Kalamazoo experienced significantly different asthma prevalence or hospitalization rates compared to the state of Michigan.

MDHHS received modeled emission contour lines for annual generic emissions from the GPI facility from EGLE (See Appendix F-1 for EGLE's emission modeling results), which suggested that ZIP codes 49004, 49007, and 49048 were the areas with air modelled to be the most influenced by emissions. Modelling suggested ZIP codes 49001, 49006, and 49008 would have air less influenced by the emissions estimated by EGLE. Therefore, these two regions of the city of Kalamazoo, each made up of three ZIP codes, were identified for the analysis of asthma prevalence and hospitalizations.

Below is a map of the ZIP codes used in the analyses: 49001, 49004, 49006, 49007, 49008, and 49048. The boundary of the city of Kalamazoo as well as the location of GPI are also indicated on the map.

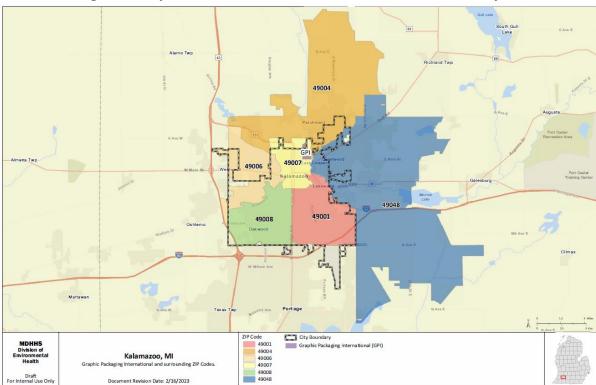


Figure 2: City of Kalamazoo ZIP Codes used in the Asthma Analyses

CDES utilized three sources for their analyses:

- MDHHS Health Data Warehouse to assess persistent asthma prevalence for 2019 for those enrolled in Medicaid
- Michigan Behavioral Risk Factor Surveys to assess adult lifetime and current asthma prevalence during 2016-2020
- Michigan Inpatient Database to assess asthma hospitalization rates during 2016-2019

For all three of these data analyses, statistical differences were determined using the 95-percent confidence intervals. Two measures are considered statistically significantly different if their 95-percent confidence intervals do not overlap. If the confidence intervals do overlap, the two rates are considered not statistically different.

CDES made the following observations from the results of their analyses:

- Persistent asthma prevalence among persons enrolled in Medicaid was either not significantly different or significantly lower for the ZIP code areas 49004+49007+49048 and 49001+49006+49008 compared to the state for all age groups.
- ZIP code area 49004+49007+49048 had significantly higher persistent asthma prevalence among Medicaid enrollees for age groups 0-64 years and 18-64 years compared to the ZIP code area 49001+49006+49008.
- There was no significant difference in adult lifetime or current asthma prevalence between ZIP code area 49004+49007+49048, ZIP code area 49001+49006+49008, and the state of Michigan.
- During 2016-2019, there was no significant difference in asthma hospitalization rates between ZIP code area 49004+49007+49048 and the state of Michigan. ZIP code area 49001+49006+49008 had significantly lower asthma hospitalization rates when compared to the state of Michigan during this time period.
- ZIP code area 49004+49007+49048 had significantly higher asthma hospitalization rates during 2017-2018 and 2018-2019 compared to ZIP code area 49001+49006+49008.

CDES notes that this review is subject to several limitations:

- Results of this investigation are based on surveillance data and not an epidemiologic research study of the relationship between asthma prevalence (or hospitalizations) and environmental contaminants. Therefore, these results cannot indicate whether asthma occurrence in the selected ZIP code areas are related to or caused by environmental contaminant exposures. If a statistical difference is observed among the results of these analyses, it does not necessarily mean that the difference is due to an environmental exposure.
- Analyses using small numbers of asthma cases or asthma hospitalizations result in imprecise measures. The small number of asthma cases and asthma hospitalizations in the selected ZIP code areas limited the types of analyses that could be conducted.

- The report is a descriptive review of asthma prevalence and hospitalization from surveillance data, it does not provide evidence that potential exposure to any environmental contaminant has resulted in higher or lower asthma prevalence and or hospitalization.
- When an individual's asthma is not well controlled, it can lead to more severe outcomes such as frequent hospitalizations.
- Increased or decreased asthma prevalence and hospitalization in an area during a period of time can occur by chance alone.

While the findings suggest that asthma measures are not significantly different or are significantly lower in each of the ZIP code areas when compared to the state, regional differences are observed when comparing the ZIP code areas to each other. Therefore, further investigation to understand these patterns is warranted.

See Appendix F-3 for the full results of CDES's analyses: Asthma Prevalence and Hospitalization Within Selected ZIP Code Areas in the City of Kalamazoo.

#### **5.6 Community and Environmental Stress**

Communities affected by environmental contamination often experience widespread chronic community stress. Stress can be defined as a physiological reaction that occurs when an individual feels threatened. These can be caused by particularly demanding or challenging situations, particularly those situations that challenge an individual's ability to cope. Stress can be acute, such as driving near a reckless driver, or chronic, like unsteady employment or relationship problems (ATSDR 2021a).

Stress related to environmental contamination most commonly presents as chronic stress. Chronic stress can cause many long-term, ongoing physiological effects, such as anxiety, headaches, trouble sleeping, and high blood pressure. If prolonged, these effects can also create a burden on our bodies, called allostatic load. It is suspected that heightened allostatic load can increase individual susceptibility to certain illnesses and risk of certain health effects (ATSDR 2021a).

Environmental contamination is often a major source of chronic stress. Environmental contamination can take many years to identify, address, and resolve, and there is often no clear beginning or end to a contamination event. Odors can further contribute to stress, especially if they are perceived to be uncontrollable or unpredictable (ATSDR 2021a).

Community stress is also caused by the significant uncertainty related to environmental contamination. Community members are often uncertain about what actions they can take to protect themselves, and what actions institutions can take to address the contamination. Additionally, scientific investigations into health risks may take years to provide results and conclusions. Conclusions regarding health risks are rarely definitive due to innate uncertainties

associated with environmental sampling and analysis techniques and variability in personal susceptibility to health effects from chemical exposures (ATSDR 2021a).

MDHHS is aware of significant community stress in Kalamazoo due to concerns that the GPI and KWRP facilities are contributing to environmental contamination. Community members have acknowledged the increased stress they have experienced based on their concerns that their health is being (or has already been) harmed by environmental contamination. They have also expressed frustration with persistent odors and environmental fallout in their community, which they believe are affecting their health and quality of life. The community has specifically voiced concern regarding the effects of environmental contamination on people with asthma.

MDHHS acknowledges that community stress in the Kalamazoo community will likely continue as long as community members are experiencing odors and potential transient health effects from those odors. To the extent possible, MDHHS encourages community members to seek out and adopt ways to manage their stress. Stress management strategies include eating a nutritious diet, getting enough sleep, and incorporating an exercise regimen (ATSDR 2021a).

#### 5.7 Children's Health

Children and adults have different health implications from exposure to environmental contaminants (ATSDR 2002). In general, children are at greater risk than adults to hazardous substances in the environment. Children are more likely to be exposed to environmental contaminants due to their unique behaviors: they are more likely to play outdoors, where air contaminants are more prevalent, and play or sit in dirt or soil; and they are more likely to put objects or their hands in their mouth that may have been contaminated by the environment.

Children also have physiological characteristics in addition to their behavior characteristics that can result in their being exposed to larger amounts of chemicals. They breathe more air per pound of body weight than adults. They also are shorter than adults, which makes them more likely to be exposed to chemicals in the air that accumulate near the ground (ATSDR 2021b).

Children's bodies can also be more susceptible to harmful exposures as there is evidence that they are less able to break down and remove toxic substances compared to adults. In addition, toxic exposures that occur during critical growth stages can permanently damage developing body and organ systems in children.

#### 6. CONCLUSIONS

MDHHS has reached the following public health conclusions for people living in communities adjacent to GPI and KWRP:

<u>Conclusion 1:</u> Measured ambient air concentrations of H<sub>2</sub>S in communities adjacent to GPI and KWRP present a public health hazard. People consistently breathing in maximum measured

levels of H<sub>2</sub>S for a lifetime may be at increased risk of nasal irritation that does not go away once the person stops breathing in H<sub>2</sub>S.

#### **Basis for Conclusion 1:**

Continuous combined H<sub>2</sub>S and reduced sulfur compound (RSC) sensors at several locations in the communities adjacent to GPI and KWRP reported concentrations that regularly exceeded EPA's Reference Concentration (RfC) of 1.4 ppb from September 2019 to December 2021. Although these sensors cannot specifically identify H<sub>2</sub>S, when individual RSCs were measured via speciated sampling, H<sub>2</sub>S tended to be the primary RSC detected.

The RfC is a level below which there is minimal to no health risk for exposure over a lifetime. Several health-protective factors are incorporated into this value to increase the margin of protection over a lifetime of exposure. Exposure to levels that exceed an RfC will not necessarily cause an adverse health effect but may increase an individual's risk. Based on available toxicological data, exposure to these levels of H<sub>2</sub>S over a lifetime may result in an increased risk of nasal irritation.

There is not an urgent health risk related to short-term H<sub>2</sub>S exposure at the levels measured in the communities adjacent to GPI and KWRP. Only a single 24-hour composite air canister sample (out of 71 total samples taken in the community) was higher than the ATSDR Acute Inhalation Minimal Risk Level (MRL) of 70 ppb. This sample was taken at Krom and Prouty Park in the Northside neighborhood in September 2021. All other monitoring and sampling data for H<sub>2</sub>S from the Kalamazoo community were below 70 ppb.

More data will help to characterize not only the frequency and magnitude of these events, but also the industrial or atmospheric conditions that may lead to them.

<u>Conclusion 2:</u> Measured ambient air concentrations of H<sub>2</sub>S and some VOCs in the communities adjacent to GPI and KWRP are at levels that people may detect as odors.

#### **Basis for Conclusion 2:**

Community air concentrations of  $H_2S$  are regularly higher than the odor threshold for  $H_2S$ , sometimes by an order of magnitude. Additionally, limited sampling results have detected some odorous VOCs at levels higher than their odor thresholds by an order of magnitude. Odor thresholds represent a concentration of a chemical above which it can typically be detected via scent.

<u>Conclusion 3:</u> Based on available data, asthma prevalence and asthma-related hospitalization rates in the areas surrounding GPI and KWRP are not significantly higher than comparable measures for Michigan as a whole.

#### **Basis for Conclusion 3:**

The data review of asthma prevalence and asthma hospitalization rates by the MDHHS Chronic Disease Epidemiology Section provided a descriptive analysis of the occurrence of asthma in selected ZIP code areas in the city of Kalamazoo and the state as a whole. These asthma measures are not significantly different or are significantly lower in each of the ZIP code areas when compared to the state as a whole.

<u>Conclusion 4:</u> In communities adjacent to GPI and KWRP, measured ambient air concentrations of sulfur compounds other than H2S present no apparent public health hazard for either short-term or long-term exposure.

#### **Basis for Conclusion 4:**

Continuous RSC sensors at several locations adjacent to GPI and KWRP reported concentrations in community outdoor air up to 25 ppb. These sensors quantify total RSCs, including  $H_2S$ , and do not speciate between different RSCs.

However, based on available canister samples analyzed for specific RSCs, it is likely that the continuous RSC sensors in the community are primarily measuring  $H_2S$ . Other than  $H_2S$ , no measured RSC concentrations from these samples or measured sulfur compounds from other samples were higher than applicable health-based screening values.

Sulfur dioxide was measured in outdoor air at concentrations that did not exceed its primary National Ambient Air Quality Standards (NAAQS). Additionally, concentrations of sulfur dioxide that were measured in the community are comparable to typical background levels of sulfur dioxide in urban areas.

Other than H<sub>2</sub>S, sulfur compounds in the outdoor air near GPI and KWRP are not expected to increase risk of harmful health effects.

<u>Conclusion 5:</u> Measured ambient air concentrations of non-sulfur compounds, including VOCs, in communities adjacent to GPI and KWRP present no apparent public health hazard for either short-term or long-term exposure.

#### **Basis for Conclusion 5:**

While air sampling in the communities adjacent to GPI and KWRP detected a variety of non-sulfur compounds, including VOCs, all were measured below their respective health-based screening values for short-term exposure.

For the majority of non-sulfur compounds detected in these samples, measured concentrations were also below respective health-based screening values for long-term exposure.

For the few compounds measured at levels above health screening values for long-term exposure, further analysis did not identify any potential public health risks as the higher concentrations were transient. Most of the measured concentrations higher than the screening levels were in grab samples (which are collected quickly at one instant), and these

concentrations were not replicated in 24-hour composite samples (air samples collected over 24 hours) taken from the community.

Non-sulfur compounds in the outdoor air near GPI and KWRP are not expected to increase risk of harmful health effects.

#### 7. LIMITATIONS

The following limitations apply to this evaluation:

- No continuous monitoring data specific for H<sub>2</sub>S is available. The most comprehensive source of data for Kalamazoo is from the City's continuous monitoring instruments, which measure total RSCs, one of which is H<sub>2</sub>S. Results for individual RSCs were only available from single point-in-time canister and Tedlar Bag samples.
- No long-term data was available for VOCs, and VOCs were evaluated via grab (instantaneous) samples and composite (up to 24-hour) samples only.
- Formaldehyde was detected on KWRP property, but not sampled offsite in the surrounding community.
- Due to the low number of reported asthma cases and hospitalizations in the community surrounding GPI and KWRP, asthma prevalence and hospitalization rates were calculated using grouped data for multiple ZIP codes and from multiple years and could not be stratified by race. This analysis only represents a descriptive review of asthma prevalence and hospitalizations and does not serve as evidence linking any environmental contaminant exposure with asthma.
- The test method used to measure ammonia has a detection limit that exceeds the
  health screening values for both short-term and long-term exposure to ammonia. As a
  result, this method cannot be used to determine whether ammonia concentrations are
  below its health screening values. However, available data from sanitary sewers
  indicates that ammonia levels in the community are unlikely to exceed its health
  screening values.

#### 8. RECOMMENDATIONS

- 1) MDHHS recommends further actions relating to ambient air concentrations of H₂S in the community near GPI and KWRP:
  - a. The amounts of  $H_2S$  and the potential sources of this pollutant should continue to be investigated using EPA-approved instruments and methods.
  - b. Mitigating attributable anthropogenic (man-made) sources to reduce  $H_2S$  to levels below those that may present a public health hazard for the community.
  - c. KWRP should continue to maintain its existing network of RSC sensors in Kalamazoo.

- 2) MDHHS recommends further monitoring and sampling for VOCs, including formaldehyde, in the community near GPI and KWRP using EPA-approved instruments and methods.
  - a. Sampling should be done with the goals of characterizing ambient air concentrations of VOCs, including potential seasonal variations.
  - b. Risk associated with detected VOCs in the community found at levels above chemical-specific health screening values should be assessed.
- 3) For community members with existing respiratory problems or sensitivity to odors, MDHHS recommends staying indoors and avoiding outdoor exercise or physical exertion when an environmental odor is present. MDHHS also recommends that people with asthma take their control and rescue medications as prescribed by their doctors. If you have guestions about your own health, contact your health care provider.

#### 9. PUBLIC HEALTH ACTION PLAN

- MDHHS will provide a copy of this Health Consultation to EGLE.
- MDHHS will continue to partner with EGLE and the City of Kalamazoo as EGLE continues its investigative work into air quality complaints in the community.
- MDHHS, EGLE, and the City of Kalamazoo will work together to continue to use available authorities to continue to reduce H<sub>2</sub>S concentrations originating from identified sources.
- MDHHS will develop a comprehensive community engagement and outreach plan to notify Kalamazoo residents of these findings. This plan may include public notification, community town halls and listening sessions, and the development of health education materials related to H<sub>2</sub>S, environmental odors, and the findings of this Health Consultation. Additional community outreach efforts may occur as new data becomes available.
- MDHHS will continue to evaluate monitoring and sampling results for the Kalamazoo area as new data becomes available.
- MDHHS will continue to evaluate the best available science regarding risks associated with reduced sulfur compound and volatile organic compound exposure, and asthmarelated outcomes.

If any individual has additional information or health concerns regarding this health consultation, please contact MDHHS Division of Environmental Health at 1-800-648-6942.

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#### 11. REPORT PREPARATION

The Michigan Department of Health and Human Services, Division of Environmental Health prepared this health consultation for the community and neighborhoods near Graphic Packaging International, LLC (GPI) and Kalamazoo Water Reclamation Plant (KWRP) located in Kalamazoo, Kalamazoo County, Michigan. This publication was made possible by a cooperative agreement (program #TS-23-0001) from the Agency for Toxic Substances and Disease Registry (ATSDR). Its contents are solely the responsibility of the authors and do not necessarily represent the official views of the ATSDR, or the U.S. Department of Health and Human Services.

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Toxicologist
Division of Environmental Health
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# **APPENDICES**

**Appendix A: Site Background Information** 

Appendix A-1: EGLE Violation Notices Issued to GPI as of June 14, 2022

Date of Violation		
Notice <sup>a</sup>	Rule/Permit Condition Violated	Reason
April 18, 2011	Renewable Operating Permit	Two stacks were below permitted limits
	(ROP)	and exceeded batch-per-day limits
December 20, 2012	R 336.1901 (Rule 901)	Odors were detected from GPI's K3
		Paper Machine.
October 20, 2014	R 336.1901 (Rule 901)	Odors were detected at the
		complainant's, which were determined
		to be from Graphic Packaging's
		wastewater treatment plant.
November 12, 2014	R 336.1901 (Rule 901)	Odors at the complainant's were traced
		back to the facility's wastewater
		treatment plant.
April 6, 2015	R 336.1901 (Rule 901) and	Analysis of fallout at complainant's
	General Condition 12, Section 1,	property shows that the Facility is the
	of MI-ROP-B1678-1678-2010b,	source.
	Section 1	
February 2, 2017	R 336.1901 (Rule 901) and	Strong and persistent odors were
	General Condition 12(b), Section	detected off-site
	1, of MI-ROP-B1678-2015	
April 5, 2017	R 336.1901 (Rule 901) and	Lab analysis of fallout at complainant's
	General Condition 12(b), Section	property shows that the Facility is the
1 26 2017	1, of MI-ROP-B1678-2015	source.
June 26, 2017	R 336.1901 (Rule 901) and	Strong and persistent odors were
	General Condition 12(b), Section	detected off-site
luna 20, 2017	1, of MI-ROP-B1678-2015	Character and an arcistant address ware
June 29, 2017	R 336.1901 (Rule 901) and General Condition 12(b), Section	Strong and persistent odors were detected off-site
	1, of MI-ROP-B1678-2015	detected off-site
April 17, 2018	R 336.1901 (Rule 901) and	Strong and persistent odors were
April 17, 2016	General Condition 12(b), Section	detected off-site
	1, of MI-ROP-B1678-2015	detected on site
May 14, 2019	R 336.1901 (Rule 901) and	Strong and persistent odors were
1110y 17, 2013	General Condition 12(b), Section	detected off-site
	1, of MI-ROP-B1678-2015	
November 20, 2020	R 336.1201 (Rule 201) and R	Facility began actual construction of
	336.2802(3) (Rule 1802, Subrule	footings and foundation for two new
	3)	boilers without a Permit to Install.
L	ı <i>'</i>	

<sup>&</sup>lt;sup>a</sup> A violation was also issued on April 19, 2013, due to a reporting error in GPI's ROP Certification Report. That report was subsequently resubmitted with the correct information.

# Appendix A-2: EPA Environmental Justice Screening and Mapping Tool (EJScreen) Results for Northside Neighborhood, Kalamazoo (February 3, 2022)

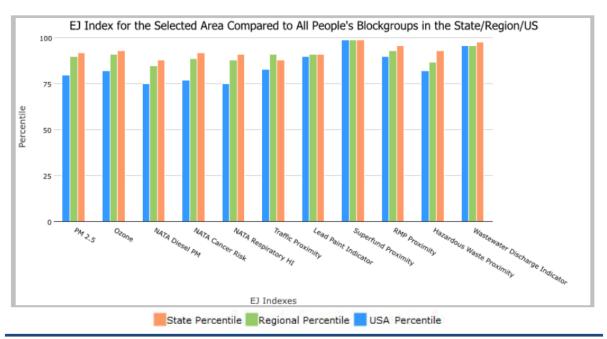


### **EJSCREEN Report (Version 2020)**



the User Specified Area, MICHIGAN, EPA Region 5
Approximate Population: 6,257
Input Area (sq. miles): 2.68

Selected Variables	State Percentile	EPA Region Percentile	USA Percentile
EJ Indexes			
EJ Index for PM2.5	92	90	80
EJ Index for Ozone	93	91	82
EJ Index for NATA* Diesel PM	88	85	75
EJ Index for NATA* Air Toxics Cancer Risk	92	89	77
EJ Index for NATA* Respiratory Hazard Index	91	88	75
EJ Index for Traffic Proximity and Volume	88	91	83
EJ Index for Lead Paint Indicator	91	91	90
EJ Index for Superfund Proximity	99	99	99
EJ Index for RMP Proximity	96	93	90
EJ Index for Hazardous Waste Proximity	93	87	82
EJ Index for Wastewater Discharge Indicator	98	96	96



This report shows the values for environmental and demographic indicators and EJSCREEN indexes. It shows environmental and demographic raw data (e.g., the estimated concentration of ozone in the air), and also shows what percentile each raw data value represents. These percentiles provide perspective on how the selected block group or buffer area compares to the entire state, EPA region, or nation. For example, if a given location is at the 95th percentile nationwide, this means that only 5 percent of the US population has a higher block group value than the average person in the location being analyzed. The years for which the data are available, and the methods used, vary across these indicators. Important caveats and uncertainties apply to this screening-level information, so it is essential to understand the limitations on appropriate interpretations and applications of these indicators. Please see EJSCREEN documentation for discussion of these issues before using reports.

February 03, 2022 1/3

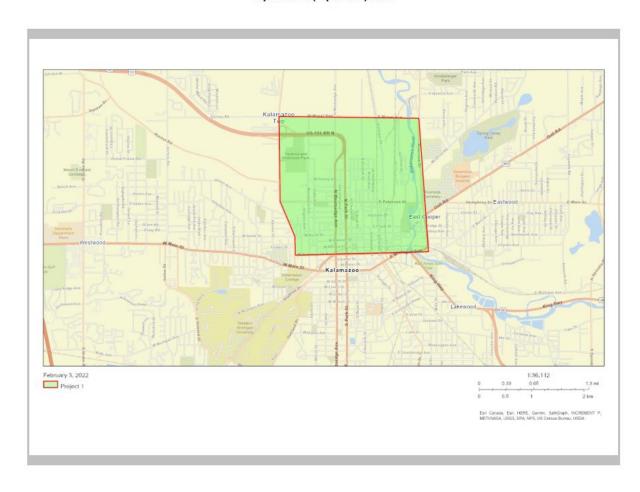


# **EJSCREEN Report (Version 2020)**



the User Specified Area, MICHIGAN, EPA Region 5

Approximate Population: 6,257 Input Area (sq. miles): 2.68



Sites reporting to EPA	
Superfund NPL	1
Hazardous Waste Treatment, Storage, and Disposal Facilities (TSDF)	0

February 03, 2022 2/3



### **EJSCREEN Report (Version 2020)**



the User Specified Area, MICHIGAN, EPA Region 5
Approximate Population: 6,257

Input Area (sq. miles): 2.68

Selected Variables		State Avg.	%ile in State	EPA Region Avg.	%ile in EPA Region	USA Avg.	%ile in USA
Environmental Indicators							
Particulate Matter (PM 2.5 in µg/m³)	7.93	8.11	44	8.4	30	8.55	30
Ozone (ppb)	44.8	43.1	83	43.8	59	42.9	69
NATA* Diesel PM (µg/m³)	0.286	0.338	48	0.446	<50th	0.478	<50th
NATA* Cancer Risk (lifetime risk per million)	25	24	57	26	<50th	32	<50th
NATA* Respiratory Hazard Index	0.29	0.29	54	0.34	<50th	0.44	<50th
Traffic Proximity and Volume (daily traffic count/distance to road)	830	650	76	530	84	750	78
Lead Paint Indicator (% Pre-1960 Housing)	0.68	0.38	79	0.38	80	0.28	87
Superfund Proximity (site count/km distance)	1.3	0.15	99	0.13	99	0.13	99
RMP Proximity (facility count/km distance)	1.7	0.53	92	0.83	85	0.74	87
Hazardous Waste Proximity (facility count/km distance)	2.1	1.2	81	2.4	65	5	67
Wastewater Discharge Indicator (toxicity-weighted concentration/m distance)	0.47	1.7	94	2.4	91	9.4	93
Demographic Indicators							
Demographic Index	73%	29%	93	28%	94	36%	91
People of Color Population	81%	25%	91	25%	91	39%	84
Low Income Population	66%	33%	90	30%	92	33%	92
Linguistically Isolated Population	0%	2%	63	2%	59	4%	45
Population With Less Than High School Education	22%	9%	91	10%	89	13%	81
Population Under 5 years of age	6%	6%	60	6%	56	6%	55
Population over 64 years of age	10%	16%	23	16%	27	15%	32

<sup>\*</sup> The National-Scale Air Toxics Assessment (NATA) is EPA's ongoing, comprehensive evaluation of air toxics in the United States. EPA developed the NATA to prioritize air toxics, emission sources, and locations of interest for further study. It is important to remember that NATA provides broad estimates of health risks over geographic areas of the country, not definitive risks to specific individuals or locations. More information on the NATA analysis can be found at: https://www.epa.gov/national-air-toxics-assessment.

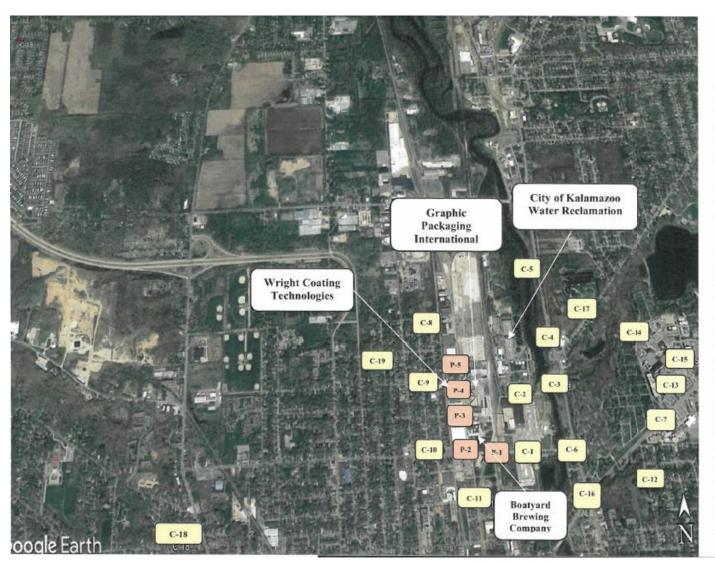
For additional information, see: www.epa.gov/environmentaljustice

EJSCREEN is a screening tool for pre-decisional use only. It can help identify areas that may warrant additional consideration, analysis, or outreach. It does not provide a basis for decision-making, but it may help identify potential areas of EJ concern. Users should keep in mind that screening tools are subject to substantial uncertainty in their demographic and environmental data, particularly when looking at small geographic areas. Important caveats and uncertainties apply to this screening-level information, so it is essential to understand the limitations on appropriate interpretations and applications of these indicators. Please see EJSCREEN documentation for discussion of these issues before using reports. This screening tool does not provide data on every environmental impact and demographic factor that may be relevant to a particular location. EJSCREEN outputs should be supplemented with additional information and local knowledge before taking any action to address potential EJ concerns.

February 03, 2022 3/3

Appendix B: Environmental Monitoring and Sampling Data from Investigations that Measured Hydrogen Sulfide and Reduced Sulfur Compounds, Kalamazoo, Michigan

Appendix B-1: GPI H<sub>2</sub>S Field Investigation Locations





RK No.	Location
	Perimeter
P-1	Paterson St & Walbridge St
P-2	Paterson St & Porter St
P-3	Graphic Packaging - Gate 2
P-4	Graphic Packaging - Gate 5
P-5	Graphic Packaging – Gate 6
	Community
C-1	Paterson St & Harrison St
C-2	Harrison St at WWT Plant gate
C-3	Kalamazoo River Watershed Council Parking Lot
C-4	Kalamazoo Township Parking Lot
C-5	Riverview Dr & Old Riverview Sav Rd
C-6	East side of Verburg Park Parking Lot
C-7	Kalamazoo County Juvenile Home Parking Lot
C-8	Dunkley St & Edwards St
C-9	Prouty St & Edwards St
C-10	Paterson S & Edwards St
C-11	Parsons St & Porter St
C-12	St. Mary Catholic Church Parking Lot
C-13	Borgress Medical Center Entrance Parking Lot
C-14	Neurosurgery of Kalamazoo Parking Lot
C-15	Borgress Medical Center at Lawrence Educational Center Parking Lot
C-16	E Paterson St & Riverview Dr. at Walgreens Parking Lot
C-17	Front Entrance of Mt Olivet Cemetery
C-18	1248 Blakeslee Street
C-19	Union St & E. Hopkins St.

Appendix B-2: GPI H₂S Field Investigation Results (July 9, 2020-September 4, 2020)

# Field Investigation Monitoring Results, Downwind

#### **Hydrogen Sulfide Concentration (ppb)** 7/9 7/10 7/13 7/14 7/20 7/22 7/29 8/4 8/7 8/10 8/12 8/13 8/17 8/21 8/26 8/27 9/1 9/4 7/16 7/24 7/28 7/30 8/5 8/18 8/25 9/3 Average Location 2 <1 <1 1 <1 <1 6 2 1 <1 C-1 4 3 10 1 2 <1 8 2 2 <1 1 4 2 2 3 1 4 3 C-2 2 2 <1 2 2 1 <1 1 2 <1 1 C-3 3 <1 1 1 2 1 <1 C-4 2 2 3 1 <1 1 <1 1 1 1 C-5 1 1 <1 <1 <1 1 1 <1 1 <1 1 <1 <1 1 2 C-6 1 <1 <1 <1 <1 <1 <1 <1 C-7 3 2 3 C-8 2 1 <1 1 C-9 <1 1 1 1 C-10 <1 <1 <1 <1 <1 2 C-11 <1 <1 <1 <1 C-12 <1 <1 <1 <1 <1 <1 C-13 1 <1 <1 <1 C-14 <1 <1 <1 <1 <1 C-15 <1 1 1 <1 C-16 <1 <1 <1 2 3 C-17 <1 <1 C-18 C-19

Some readings were reported to be below the instrument's limit of detection (LOD) of 3 ppb.

It is unclear from the investigation report whether blank boxes indicate that the location was not sampled or was below the LOD.

#### Field Investigation Monitoring Results, Upwind **Hydrogen Sulfide Concentration (ppb)** 7/9 7/16 7/24 9/4 7/10 7/13 7/14 7/20 7/22 7/28 7/29 8/4 8/5 8/10 8/13 8/17 8/18 8/21 8/25 8/26 8/27 9/1 9/3 Location 7/30 8/7 8/12 Average <1 <1 <1 <1 <1 <1 <1 <1 C-2 <1 2 3 <1 C-3 <1 <1 <1 <1 <1 <1 1 1 <1 <1 <1 <1 <1 <1 C-4 <1 <1 <1 <1 <1 <1 <1 C-5 <1 C-6 2 <1 <1 <1 <1 <1 <1 <1 <1 <1 1 <1 <1 <1 2 1 C-7 <1 1 <1 <1 <1 <1 <1 <1 <1 <1 <1 <1 <1 <1 <1 <1 1 2 <1 C-8 1 <1 1 1 <1 1 <1 <1 1 <1 <1 1 <1 <1 <1 <1 <1 <1 <1 <1 <1 C-9 2 <1 2 2 <1 <1 <1 2 <1 <1 <1 <1 <1 1 <1 <1 <1 1 1 C-10 2 1 <1 <1 <1 1 <1 <1 <1 <1 <1 2 <1 <1 <1 1 <1 C-11 6 <1 3 1 1 <1 <1 <1 <1 1 <1 <1 <1 <1 <1 <1 <1 <1 <1 1 2 1 C-12 2 2 <1 <1 <1 <1 <1 <1 <1 C-13 2 2 1 <1 <1 <1 <1 <1 <1 1 1 <1 1 <1 <1 2 <1 <1 <1 1 C-14 2 <1 <1 <1 <1 <1 <1 <1 <1 <1 1 <1 <1 1 <1 <1 1 2 1 C-15

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C-17

C-18

C-19

It is unclear from the investigation report whether blank boxes indicate that the location was not sampled or was below the LOD.

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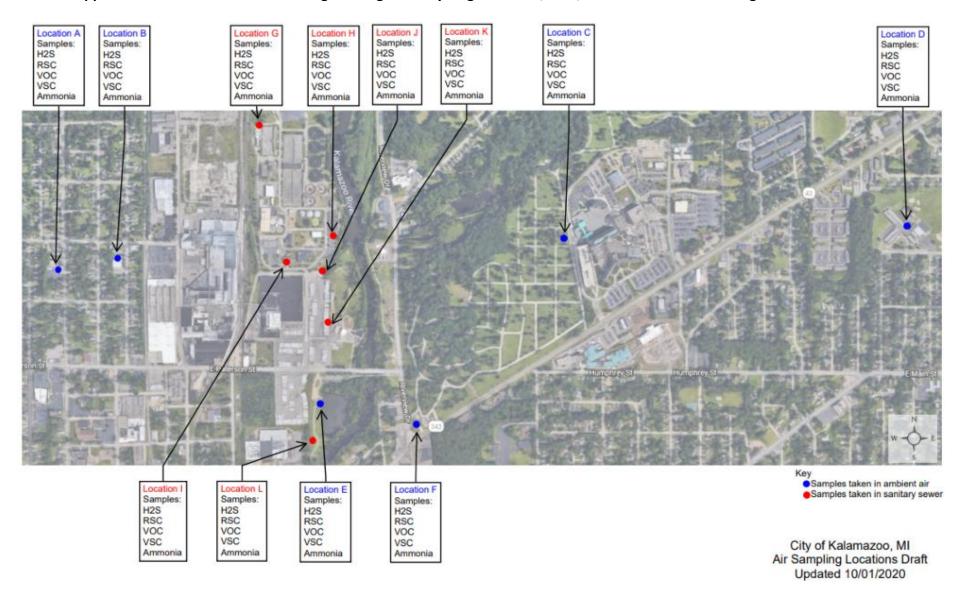
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Appendix B-3: KWRP Odor Monitoring Investigation: Hydrogen Sulfide, VOC, and Ammonia Monitoring Locations



Appendix B-4: KWRP Odor Monitoring Investigation: Portable H₂S Gas Logger Results (October 19, 2020-November 10, 2020)

Location	Location ID	Minimum Daily Average (ppb)	Maximum Daily Average (ppb)	Average (ppb)
Northside Neighborhood Association	А	0	0.07639	0.00736
Krom and Prouty Park	В	0	0.04861	0.00304
Borgess Hospital	С	0	0.06944	0.00868
Northeastern Elementary School	D	0	0.04861	0.00477
Verburg Park	E	0	0.24306	0.01884
Public Safety	F	0	0.04167	0.0026

These results were copied from the odor monitoring investigation report. They represent daily average  $H_2S$  concentrations for each day of sampling at several community locations. The minimum and maximum daily average columns represent the lowest and highest daily averages for each location. The overall average is an average of each of the 22 daily averages.

It should be noted that the instrument's reported minimum detection limit is 10 ppb. Therefore, it can be assumed that non-detect readings were reported as 0 ppb, though it is possible that true concentrations could have been up to 10 ppb. Additionally, it appears that average calculations incorporated non-detect readings as 0 ppb, as daily average readings were all below the minimum detection limit of 10 ppb.

# Appendix B-5: KWRP Odor Monitoring Investigation: Results for Hydrogen Sulfide and Other Sulfur Compounds

These samples were analyzed via ASTM D5504 for reduced sulfur compounds. Samples only had detections of hydrogen sulfide and carbon disulfide (one sample).

Figure B-5-1: Results from Tedlar Bag and Silonite Canisters Analyzed via ASTM D5504

		Hydrogen Sulfide (ppb)		
Location	Date	Silonite Canister	Tedlar Bag	
A North March Description	10/27	ND	11.5	
A. Northside Neighborhood Association	10/29	32	ND	
Association	11/4	ND	8.6	
	10/27	ND	10.8	
B. Krom and Prouty Park	10/29	10	ND	
	11/4	ND	9.3	
	10/27	ND	6.7	
C. Borgess Hospital	10/29	11.5	ND	
	11/4	ND	7.2	
D. Nowth ocetowe Florescetow.	10/27	23*	6.8	
D. Northeastern Elementary School	10/29	540**	ND	
3011001	11/4	13.6	5.4	
	10/27	ND	5.5	
E. Verburg Park	10/29	ND	ND	
	11/4	ND	5.9	
	10/27	ND	ND	
F. Public Safety	10/29	11.5	ND	
	11/4	ND	ND	

ND=non-detect

Detections are bolded

<sup>\*</sup>Carbon disulfide was also measured from this canister sample at 7.4 ppb.

<sup>\*\*</sup>This result was attributed to equipment malfunction.

Figure B-5-2: Results from Tedlar Bag and Silonite Canisters Analyzed via EPA Method TO-15

Chemical	CAS#	A. Northside Neighborhood Association	B. Krom and Prouty Park	C. Borgess Hospital	D. Northeastern Elementary School	E. Verburg Park	F. Public Safety	Screening Value (ppb)
(1-Methylethyl) (1,1-								
dimethylethyl)-								
disulfide	43022-60-2	ND	ND	ND	ND	ND	0.7	N/A
Bis(1-methylethyl)-								
disulfide	4253-89-8	ND	ND	ND	ND	ND	0.5	N/A
								EPA
Sulfur dioxide	7446-09-5	3.2-27.1	1.0	18.3	2.2-7.3	2.7	2.1	75 NAAQS

Tedlar Bag Results									
Chemical	CAS#	A. Northside Neighborhood Association	B. Krom and Prouty Park	C. Borgess Hospital	D. Northeastern Elementary School	E. Verburg Park	F. Public Safety	Screening Value (ppb)	
									EPA
Sulfur dioxide	7446-09-5	25.6	12.2	16.4	6.1	ND	ND	75	NAAQS

ND=non-detect

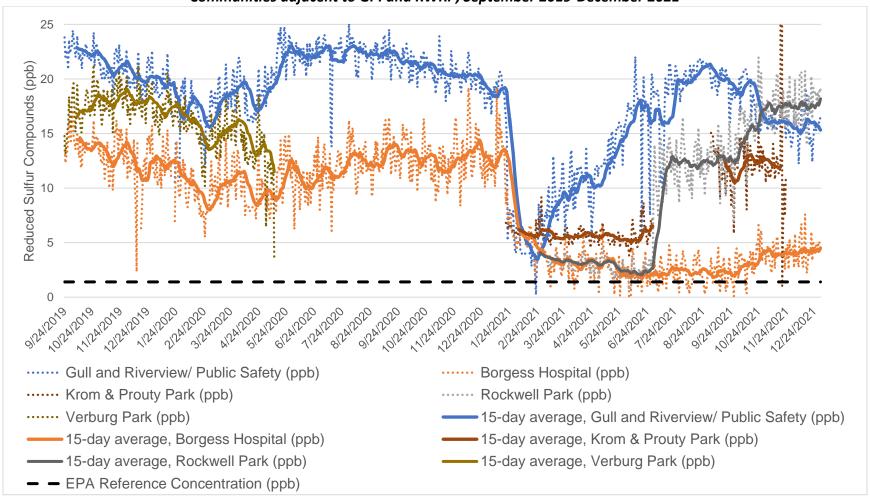
Appendix B-6: City of Kalamazoo Continuous RSC Monitoring Locations and Results



Figure B-6-1: Map of City of Kalamazoo Continuous RSC Sensors

Community Sensors: Borgess Hospital (4); Gull and Riverview Public Safety Station (11); Rockwell Park (15); Krom and Prouty Park (25); Verburg Park (near Gull and Riverview); and Northside Neighborhood Association (bottom left corner).

Figure B-6-2: Daily and 15-Day Average Combined Reduced Sulfur Compound (RSC) Concentrations (ppb) for Kalamazoo Communities adjacent to GPI and KWRP, September 2019-December 2021



This chart tracks daily average and 15-day average RSC concentrations reported by the city of Kalamazoo's community monitoring instruments. Dotted lines represent daily average measurements and solid lines represent the running 15-day average. The EPA Reference Concentration (RfC) of 1.4 ppb is also plotted.

Figure B-6-3: Summary of City of Kalamazoo Envirosuite Sensor Reliability, September 2019-December 2021

Sensor Location	Unreliable Date Ranges	Reason
	July 1-August 31, 2021	
Krom and Prouty Park	November 18-December 31, 2021	Equipment malfunction
Rockwell Park	January 20-February 12, 2021	Equipment malfunction
	All dates other than September 2019-	
Verburg Park	May 2020	Tampering and theft
Northside Neighborhood		
Association	All dates	Equipment malfunction

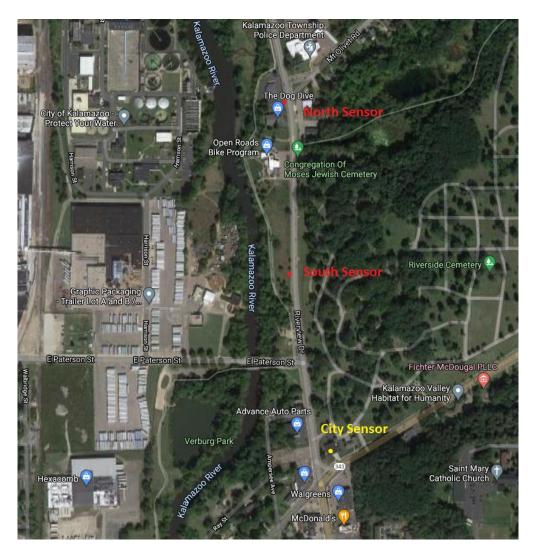
MDHHS received notification of sensor malfunctions by the city of Kalamazoo. Those malfunctions were confirmed by Envirosuite technicians. The city of Kalamazoo also notified MDHHS of the equipment tampering that occurred at Verburg Park.

Figure B-6-4: Annual and Running Average RSC Concentrations from Kalamazoo Community RSC Sensors, in ppb

	Gull and Riverview	Borgess Hospital	Krom & Prouty Park	Rockwell Park
2019	21.31	12.90	N/A	N/A
2020	20.38	11.53	N/A	N/A
2021	11.63	4.44	8.49	9.75
Running Average	18.05	9.75	8.49	9.75

# **Appendix B-7: EGLE Continuous RSC Monitoring Locations and Results**





25.000 20.000 15.000 RSCs (ppb) 10.000 5.000 0.000 24-Apr 25-Apr 28-Apr 29-Apr 30-Apr 1-May 2-May 3-May 4-May 5-Мау 7-Мау 9-Мау 10-May 11-May 12-May 14-May 16-May 18-May 20-May 22-May 23-May 24-May 25-May 20-Apr 22-Apr 13-May 17-May 21-May 26-Apr · · · · North Sensor Daily Avg (ppb) · · · · · City Sensor Daily Avg (ppb) South Sensor Daily Avg (ppb) North Sensor, 15-day (ppb) South Sensor, 15-day (ppb) City Sensor, 15-day (ppb) • ATSDR Intermediate MRL (ppb)

Figure B-7-2: Daily and 15-Day Average Combined RSC Concentrations (ppb) from 2021 EGLE Monitoring on Riverview Dr

Appendix B-8: EPA Geospatial Monitoring of Air Pollution (GMAP) Results from Kalamazoo Sampling, May 11-13, 2021



Figure B-8-2: Maximum one-second concentrations for contaminants measured from mobile transects near the community surrounding GPI and KWRP

Surre	anding or ra					
MOBILE MEASUREMENTS -	H <sub>2</sub> S	CH <sub>4</sub>	BEN	TOL	XYP	
MAY 11-13, 2021	(PPB)	(PPM)	(PPB)	(PPB)	(PPB)	FIGURE
ATSDR ACUTE (≤14 DAY) MRL	70	-	9	2000	2000	
ATSDR INTERMEDIATE (15-364 DAYS) MRL	20	-	6	-	600	
ATSDR CHRONIC (≥365 DAYS) MRL	-	-	3	1000	50	
GMAP MDL	7.86	0.00	4.80	3.69	4.05	
GMAP RL	23.58	0.00	24.00	18.45	20.25	
		max 1-sec	cond conce	entration		
210511_MA01	<rl< th=""><th>2.06</th><th><mdl< th=""><th><rl< th=""><th><rl< th=""><th>NA</th></rl<></th></rl<></th></mdl<></th></rl<>	2.06	<mdl< th=""><th><rl< th=""><th><rl< th=""><th>NA</th></rl<></th></rl<></th></mdl<>	<rl< th=""><th><rl< th=""><th>NA</th></rl<></th></rl<>	<rl< th=""><th>NA</th></rl<>	NA
210512_MA01	<rl< td=""><td>2.48</td><td><mdl< td=""><td><rl< td=""><td><mdl< td=""><td>NA</td></mdl<></td></rl<></td></mdl<></td></rl<>	2.48	<mdl< td=""><td><rl< td=""><td><mdl< td=""><td>NA</td></mdl<></td></rl<></td></mdl<>	<rl< td=""><td><mdl< td=""><td>NA</td></mdl<></td></rl<>	<mdl< td=""><td>NA</td></mdl<>	NA
210512_MA02	<rl< td=""><td>2.04</td><td><rl< td=""><td><rl< td=""><td><rl< td=""><td>NA</td></rl<></td></rl<></td></rl<></td></rl<>	2.04	<rl< td=""><td><rl< td=""><td><rl< td=""><td>NA</td></rl<></td></rl<></td></rl<>	<rl< td=""><td><rl< td=""><td>NA</td></rl<></td></rl<>	<rl< td=""><td>NA</td></rl<>	NA
210512_MA03	<rl< td=""><td>2.04</td><td><mdl< td=""><td><rl< td=""><td><rl< td=""><td>NA</td></rl<></td></rl<></td></mdl<></td></rl<>	2.04	<mdl< td=""><td><rl< td=""><td><rl< td=""><td>NA</td></rl<></td></rl<></td></mdl<>	<rl< td=""><td><rl< td=""><td>NA</td></rl<></td></rl<>	<rl< td=""><td>NA</td></rl<>	NA
210512_MA04	<rl< td=""><td>2.04</td><td><mdl< td=""><td><rl< td=""><td><mdl< td=""><td>NA</td></mdl<></td></rl<></td></mdl<></td></rl<>	2.04	<mdl< td=""><td><rl< td=""><td><mdl< td=""><td>NA</td></mdl<></td></rl<></td></mdl<>	<rl< td=""><td><mdl< td=""><td>NA</td></mdl<></td></rl<>	<mdl< td=""><td>NA</td></mdl<>	NA
210512_MA05	<rl< th=""><th>2.14</th><th><rl< th=""><th><rl< th=""><th><rl< th=""><th>NA</th></rl<></th></rl<></th></rl<></th></rl<>	2.14	<rl< th=""><th><rl< th=""><th><rl< th=""><th>NA</th></rl<></th></rl<></th></rl<>	<rl< th=""><th><rl< th=""><th>NA</th></rl<></th></rl<>	<rl< th=""><th>NA</th></rl<>	NA
210513_MA01	<mdl< td=""><td>2.53</td><td><mdl< td=""><td><rl< td=""><td><mdl< td=""><td>NA</td></mdl<></td></rl<></td></mdl<></td></mdl<>	2.53	<mdl< td=""><td><rl< td=""><td><mdl< td=""><td>NA</td></mdl<></td></rl<></td></mdl<>	<rl< td=""><td><mdl< td=""><td>NA</td></mdl<></td></rl<>	<mdl< td=""><td>NA</td></mdl<>	NA
210513_MA02	<rl< td=""><td>2.39</td><td><mdl< td=""><td><rl< td=""><td><mdl< td=""><td>NA</td></mdl<></td></rl<></td></mdl<></td></rl<>	2.39	<mdl< td=""><td><rl< td=""><td><mdl< td=""><td>NA</td></mdl<></td></rl<></td></mdl<>	<rl< td=""><td><mdl< td=""><td>NA</td></mdl<></td></rl<>	<mdl< td=""><td>NA</td></mdl<>	NA
210513_MA03	<rl< td=""><td>2.32</td><td><mdl< td=""><td><rl< td=""><td><mdl< td=""><td>NA</td></mdl<></td></rl<></td></mdl<></td></rl<>	2.32	<mdl< td=""><td><rl< td=""><td><mdl< td=""><td>NA</td></mdl<></td></rl<></td></mdl<>	<rl< td=""><td><mdl< td=""><td>NA</td></mdl<></td></rl<>	<mdl< td=""><td>NA</td></mdl<>	NA

Graphics Packaging & Water Reclamation Facility

Figure B-8-3: Mobile transects and paths driven near GPI and KWRP

Figure B-8-4: Maximum one-second concentrations for contaminants measured from mobile transects near GPI and KWRP

 $H_2S$ CH<sub>4</sub> BEN TOL XYP **MOBILE MEASUREMENTS -**(PPM) MAY 11-13, 2021 (PPB) (PPB) (PPB) (PPB) **FIGURE** ATSDR ACUTE (≤14 DAY) MRL 2000 2000 70 9 ATSDR INTERMEDIATE (15-364 DAYS) 600 20 6 MRL ATSDR CHRONIC (≥365 DAYS) MRL 3 1000 50 0.00 4.80 3.69 4.05 **GMAP MDL** 7.86 18.45 **GMAP RL** 23.58 0.00 24.00 20.25 NA 2.1 <MDL 210511\_MA01 <RL <RL <RL 2.17 <MDL NΑ 210511\_MA02 <RL <RL <RL NA 210511\_MA03 <RL 2.07 <MDL <RL <MDL NA 210511\_MA04 <RL 2.1 <MDL <RL <RL 210511 MA05 <RL <RL NA 2.36 <RL <RL <RL NA 210511 MA06 <MDL 2.25 <RL <RL NA 210512\_MA01 <RL 2.5 <MDL <MDL <MDL 210512\_MA02 2.32 <MDL <RL <MDL <RL NA NA 210512\_MA03 <RL 2.63 <MDL <RL <MDL 210512\_MA04 2.63 <MDL <RL <MDL NA <RL NA 210512\_MA05 2.12 <RL <MDL <RL <MDL <RL <MDL 210513 MA01 <RL 2.56 <MDL NA NA 210513\_MA02 2.34 <MDL <RL <MDL <RL NA 3.19 <MDL <RL <MDL 210513\_MA03 <RL 210513\_MA04 <RL 2.74 <MDL NA <RL <MDL



Figure B-8-6: Maximum one-second concentrations for contaminants measured from mobile transects during source scouting

MOBILE MEASUREMENTS – MAY 11-13, 2021	H <sub>2</sub> S (PPB)	CH₄ (PPM)	BEN (PPB)	TOL (PPB)	XYP (PPB)	FIGURE
ATSDR ACUTE (≤14 DAY) MRL	70	-	9	2000	2000	
ATSDR INTERMEDIATE (15-364 DAYS) MRL	20	-	6	-	600	
ATSDR CHRONIC (≥365 DAYS) MRL	-	-	3	1000	50	
GMAP MDL	7.86	0.00	4.80	3.69	4.05	
GMAP RL	23.58	0.00	24.00	18.45	20.25	
		max 1-sec	ond concentra	tion		
210511_MA01	<rl< td=""><td>2.05</td><td><rl< td=""><td><rl< td=""><td><rl< td=""><td>NA</td></rl<></td></rl<></td></rl<></td></rl<>	2.05	<rl< td=""><td><rl< td=""><td><rl< td=""><td>NA</td></rl<></td></rl<></td></rl<>	<rl< td=""><td><rl< td=""><td>NA</td></rl<></td></rl<>	<rl< td=""><td>NA</td></rl<>	NA
210511_MA02	<rl< td=""><td>2.05</td><td><mdl< td=""><td><rl< td=""><td><mdl< td=""><td>NA</td></mdl<></td></rl<></td></mdl<></td></rl<>	2.05	<mdl< td=""><td><rl< td=""><td><mdl< td=""><td>NA</td></mdl<></td></rl<></td></mdl<>	<rl< td=""><td><mdl< td=""><td>NA</td></mdl<></td></rl<>	<mdl< td=""><td>NA</td></mdl<>	NA
210511_MA03	<rl< td=""><td>2.09</td><td><rl< td=""><td><rl< td=""><td><rl< td=""><td>NA</td></rl<></td></rl<></td></rl<></td></rl<>	2.09	<rl< td=""><td><rl< td=""><td><rl< td=""><td>NA</td></rl<></td></rl<></td></rl<>	<rl< td=""><td><rl< td=""><td>NA</td></rl<></td></rl<>	<rl< td=""><td>NA</td></rl<>	NA
210511_MA04	<rl< td=""><td>2.09</td><td><rl< td=""><td><rl< td=""><td><rl< td=""><td>NA</td></rl<></td></rl<></td></rl<></td></rl<>	2.09	<rl< td=""><td><rl< td=""><td><rl< td=""><td>NA</td></rl<></td></rl<></td></rl<>	<rl< td=""><td><rl< td=""><td>NA</td></rl<></td></rl<>	<rl< td=""><td>NA</td></rl<>	NA
210511 84605	<rl< td=""><td>2.09</td><td><mdl< td=""><td><rl< td=""><td><rl< td=""><td>NA</td></rl<></td></rl<></td></mdl<></td></rl<>	2.09	<mdl< td=""><td><rl< td=""><td><rl< td=""><td>NA</td></rl<></td></rl<></td></mdl<>	<rl< td=""><td><rl< td=""><td>NA</td></rl<></td></rl<>	<rl< td=""><td>NA</td></rl<>	NA
210511_MA05	NIL.	2.03		-112		
*210511_MA06	29.3	2.11	<mdl< td=""><td><rl< td=""><td><rl< td=""><td>5</td></rl<></td></rl<></td></mdl<>	<rl< td=""><td><rl< td=""><td>5</td></rl<></td></rl<>	<rl< td=""><td>5</td></rl<>	5
_						5 NA
*210511_MA06	29.3	2.11	<mdl< td=""><td><rl< td=""><td><rl< td=""><td>_</td></rl<></td></rl<></td></mdl<>	<rl< td=""><td><rl< td=""><td>_</td></rl<></td></rl<>	<rl< td=""><td>_</td></rl<>	_

#### **Summary of Real-Time VOC Monitoring**

GMAP analysis measured methane in the communities adjacent to GPI and KWRP at concentrations of 2.04-2.53 ppm. Methane concentrations near GPI/KWRP and from scouting ranged from 2.07-3.19 ppm and 2.05-2.14 ppm, respectively. GMAP analysis did not measure benzene, toluene, or p-xylene at concentrations above their respective RLs.<sup>20</sup>

<sup>&</sup>lt;sup>20</sup> GMAP RLs for benzene, toluene, and p-xylene are 24.00, 18.45, and 20.25 ppb, respectively.

Appendix B-9: GPI Continuous RSC Sensor Locations and Results, 2021



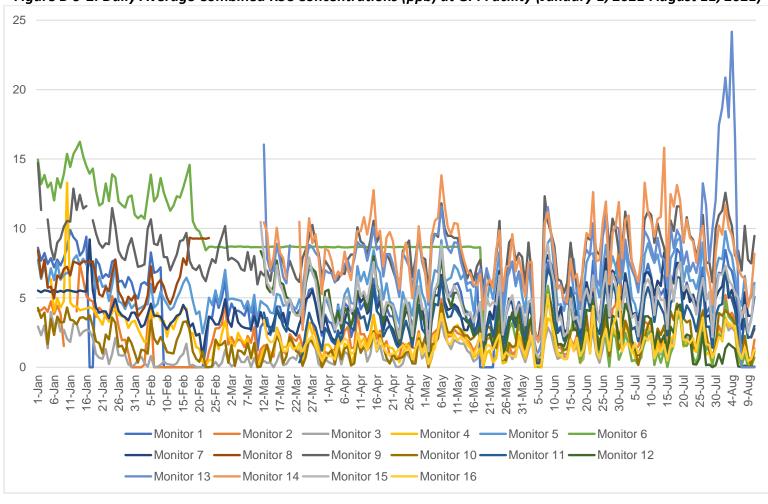


Figure B-9-2: Daily Average Combined RSC Concentrations (ppb) at GPI Facility (January 1, 2021-August 11, 2021)

**GPI On-site Continuous Monitoring: Average H₂S Results by Sensor** 

		13	16
Average H₂S 5.02 2.34 1.17 2.25 5.78 7.03 4.18 6.41 8.43 1.96 3.49 3.31 7.8	5 8.32	4.86 1	1.70

# Appendix B-10: September 2021 Krom and Prouty Park Investigation: Results from ASTM 5504-D Analysis of Silonite Canisters

Each canister in this investigation was analyzed for reduced sulfur compounds (RSCs) via ASTM 5504-D. Only hydrogen sulfide (H<sub>2</sub>S) was detected. No other RSCs were detected from these samples.

	H <sub>2</sub> S Concentration		
Date	Sample ID	Sample type	(ppb)
9/20/2021	Monday-Comp-1	24-hour Composite	85
9/20/2021	Monday-Comp-2	24-hour Composite	59
9/20/2021	Monday-Grab-0700	Grab	46
9/20/2021	Monday-Grab-0900	Grab	35
9/20/2021	Monday-Grab-1100	Grab	31
9/20/2021	Monday-Grab-1300	Grab	31
9/20/2021	Monday-Grab-1500	Grab	27
9/20/2021	Monday-Grab-1700	Grab	25
9/20/2021	Monday-Grab-1900	Grab	16
	Avera	ge of 9/20 Grab samples:	30.1
9/21/2021	Tuesday-Comp-1	24-hour Composite	7.4
9/21/2021	Tuesday-Comp-2	24-hour Composite	8.1
9/21/2021	Tuesday-Grab-0700	Grab	6.7
9/21/2021	Tuesday-Grab-0900	Grab	7.0
9/21/2021	Tuesday-Grab-1100	Grab	ND
9/21/2021	Tuesday-Grab-1300	Grab	ND
9/21/2021	Tuesday-Grab-1500	Grab	7.6
9/21/2021	Tuesday-Grab-1700	Grab	ND
9/21/2021	Tuesday-Grab-1900	Grab	6.9
	Avera	ge of 9/21 Grab samples:	7.9
9/22/2021	Wednesday	All samples	ND
9/23/2021	Thursday	All samples	ND

ND=non-detect

The naming of each grab canister sample indicates the time at which the sample was taken based on a 24-hour clock (e.g. 0700=7 AM; 1100=11 AM; 1700=5 PM).

Composite samples started at 7am on each collection day and ended at 7am the following day

Appendix B-11: May 2022 EGLE Drone Investigation, Maximum Ambient Air Concentrations of Measured Compounds at KWRP

Compound	Date	Maximum Measured
		Concentration (ppb)*
Formaldehyde	May 23	864
	May 24	104
Hydrogen Sulfide	May 23	698
	May 24	76
Sulfur Dioxide	May 23	309
	May 24	1,207
Nitric Oxide	May 23	1,009
	May 24	1,081
Total VOCs	May 23	749
	May 24	467

<sup>\*</sup>Maximum measured concentrations of several compounds were measured on May 23 at the Biosolids Holding location. EGLE reports that a truck was being loaded with biosolids at that location during the drone flyover. It is possible that combustion emissions from the truck contributed to the elevated levels measured by the drone on May 23.

Appendix C: Environmental Sampling Data for Volatile Organic Compounds via EPA TO-15, Kalamazoo, Michigan

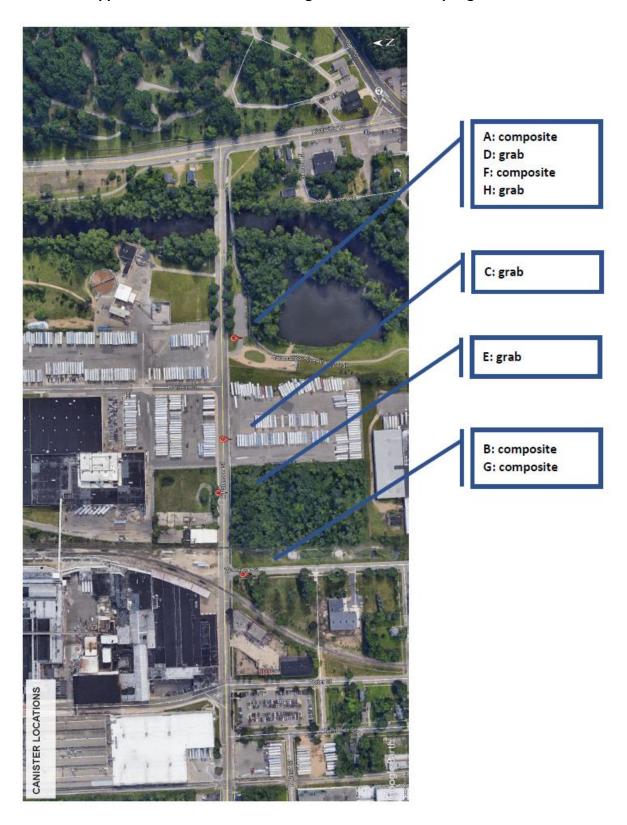
Appendix C-1: KWRP Odor Monitoring Investigation: EPA Method TO-15 Results, Silonite Canister and Tedlar Bag

Figure C-1-1: KWRP Odor Monitoring Investigation, Silonite Canister EPA TO-15 Results (ppb)											
Chemical	CAS#	A. Northside Neighborhood Association	B. Krom and Prouty Park	C. Borgess Hospital	D. Northeastern Elementary School	E. Verburg Park	F. Public Safety				
(1-Methylethyl) (1,1- dimethylethyl)disulfide	43022-60-2	ND	ND	ND	ND	ND	0.7				
1-Butanol	71-36-3	ND	ND	ND	ND	ND	1.4				
2-Butanone (methyl ethyl ketone)	78-93-3	ND	ND	ND	ND	ND	0.6				
2-Methylbutane	78-78-4	2.6-3.7	0.4-5.1	ND	1.5	2.6	2.0-2.8				
2-Methylpentane	107-83-5	ND	0.7-1.6	1.4	1.8	0.7-2.6	0.5-0.6				
2-Methylpropene	115-11-7	ND	ND	ND	ND	ND	0.9				
2,2,6-Trimethyloctane	62016-28-8	ND	0.4	0.9	ND	ND	ND				
3-Methylpentane	96-14-0	ND	1.6	ND	ND	ND	ND				
Acetic acid	64-19-7	ND	ND	ND	52.9	ND	ND				
Acetone	67-64-1	2.1	ND	1.6-3.9	4.6	1.7	6.3				
Benzene	71-43-2	0.7	ND	ND	0.7	ND	ND				
Bis(1- methylethyl)disulfide	4253-89-8	ND	ND	ND	ND	ND	0.5				
n-Butane	106-97-8	0.4-2.6	0.8-2.4	0.4-1.4	1.6	1.3-1.8	1.5-2.4				
Chlorodifluoromethane	75-45-6	ND	0.8	0.7	ND	ND	ND				
Dichlorodifluoromethane	75-71-8	0.6	0.5	0.4-0.7	0.5-0.6	0.4-0.5	0.4				
Ethanol	64-17-5	1.6-2.0	2.3-2.5	2.1-2.2	2.8	1.8	0.9-2.5				
Ethyl acetate	141-78-6	1.4	1.4-1.6	0.8	19.4	ND	0.8				
Hexamethyl- cyclotrisiloxane	541-05-9	0.2-4.7	0.4	9.1	0.3-18.7	0.3	1.8-6.5				
n-Hexane	110-54-3	ND	ND	ND	ND	0.5	ND				
Isobutane	75-28-5	ND	2.1	1.5	0.9	0.9	1.3				
Isopropyl alcohol	67-63-0	ND	1.0-1.2	1.0	1.4	ND	0.7				
n-Nonanal	124-19-6	ND	ND	ND	ND	0.4	ND				

Fi	Figure C-1-1: KWRP Odor Monitoring Investigation, Silonite Canister EPA TO-15 Results (ppb)												
Chemical	CAS#	A. Northside Neighborhood Association	B. Krom and Prouty Park	C. Borgess Hospital	D. Northeastern Elementary School	E. Verburg Park	F. Public Safety						
n-Pentane	109-66-0	0.7-1.1	0.6-1.9	0.7-1.0	0.9	0.7-0.8	0.9-1.3						
Propane	74-98-6	ND	1.6-2.8	1.1-2.2	ND	1.9-2.2	2.2-2.8						
Sulfur dioxide	7446-09-5	3.2-27.1	1.0	18.3	2.2-7.3	2.7	2.1						
Toluene	108-88-3	0.6	0.5-1.0	0.5	0.5	ND	0.5-0.6						
Trimethylsilanol	1066-40-6	0.6	ND	2.7	ND	ND	0.5						
o-Xylene	95-47-6	ND	0.5	ND	ND	ND	ND						

		A. Northside			D. Northeastern		
Chemical	CAS#	Neighborhood Association	B. Krom and Prouty Park	C. Borgess Hospital	Elementary School	E. Verburg Park	F. Public Safety
1-Butanol	71-36-3	8.2	ND	ND	ND	ND	ND
1,1-Difluoroethane	75-37-6	5.9	15.5	ND	ND	ND	ND
2-Butanone (methyl ethyl ketone)	78-93-3	44.1	19.7	ND	ND	ND	ND
2-Methylbutane	78-78-4	13.2-71.2	12.5-20.3	8.8	6.4	44.1	7.5-57.6
2-Methylpentane	107-83-5	5.1-5.4	8.2	ND	ND	ND	6.2-11.6
2,4-Dimethylheptane	2213-23-2	2.5	3.1-7.6	4.0-6.5	4.0-4.6	3.2-4.4	4.6-5.1
3-Methylpentane	96-14-0	ND	ND	ND	ND	ND	5.7
4-Methyloctane	2216-34-4	ND	ND	4.8	4.2	4.2	2.5-3.4
Acetone	67-64-1	ND	ND	13.5	5.5	7.6	ND
n-Butane	106-97-8	ND	ND	ND	ND	ND	32.0
Cyclohexanone	108-94-1	ND	ND	ND	ND	4.0	21.9
Ethanol	64-17-5	15.4-281.3	17-106.1	10.6-12.7	9.6	11.1-21.2	16.5-52.0
Ethyl acetate	141-78-6	36.1	9.4	ND	ND	5.0	18.9
n-Hexane	110-54-3	ND	ND	ND	ND	ND	5.4
Isobutane	75-28-5	5.9	ND	ND	ND	ND	5.9-8.4
Isopropyl alcohol	67-63-0	11.0-146.5	9.8-130.2	276.7	ND	5.3-38.7	65.1
d-Limonene	5989-27-5	ND	ND	ND	ND	2.5	ND
Methylcyclopentane	96-37-7	ND	ND	ND	ND	ND	4.6
n-Nonanal	124-19-6	2.6	2.4	ND	ND	ND	ND
n-Pentane	109-66-0	5.1-244.0	4.7-47.4	10.2	ND	13.2	14.9-44.1
Propene	115-07-1	ND	ND	14.5	ND	ND	ND
Sulfur dioxide	7446-09-5	25.6	12.2	16.4	6.1	ND	ND
Toluene	108-88-3	5.6-15.4	5.8-7.7	3.7	4.0	4.2-5.0	8.2-9.0
m-Xylene	108-38-3	ND	ND	ND	ND	ND	3.2
p-Xylene	106-42-3	3.0-4.4	ND	ND	ND	ND	3.5

Appendix C-2: EPA GMAP Investigation: Canister Sampling Locations



Appendix C-3: EPA GMAP Investigation: EPA Method TO-15 Results, Silonite Canisters (ppb)

		E Paters	E Paterson Rd Verburg Park			Walbridge St			
Chemical	CAS#	C (G)	E (G)	A (C-1h)	D (G)	F (C-12h)	Н (G)	B (C-1h)	G (C-12h)
2,2,4-Trimethylpentane	540-84-1	0.41	ND	ND	ND	ND	0.18	ND	ND
2-Butanone (methyl ethyl ketone)	78-93-3	0.44	ND	ND	ND	0.44	0.51	ND	ND
Benzene	71-43-2	0.15	ND	ND	ND	ND	0.24	ND	ND
Chloroform	67-66-3	ND	ND	ND	ND	0.17	0.16	ND	ND
Chloromethane	74-87-3	0.69	0.58	0.93	0.64	0.96	0.79	0.67	0.74
Dichlorodifluoromethane	75-71-8	2.3	2.3	2.2	2.3	2.2	2.3	2.2	2.2
m & p-Xylene	1330-20-7	1.2	ND	ND	ND	ND	1.2	ND	ND
Toluene	108-88-3	2.4	ND	0.71	ND	1.1	2.2	1.1	ND
Trichlorofluoromethane	75-69-4	1.1	ND	1.1	ND	1.1	1.1	ND	1.1

<sup>(</sup>G): grab sample

<sup>(</sup>C): composite sample, either 1-hour (C-1h) or 12-hour (C-12h)

Appendix C-4: KWRP Krom and Prouty Park Investigation: EPA Method TO-15 Results, Silonite Canisters (ppb)

Fi	Figure C-4-1: 24h Composite Canister Results											
		Sample Date										
Chemical	CAS#	9/20/2021	9/21/2021	9/22/2021	9/23/2021							
1-Butanol	71-36-3	ND	ND	ND	0.9							
2-Ethyl-1-hexanol	104-76-7	ND	0.5	0.9-1.0	ND							
2-Ethylhexylacetate	103-09-3	ND	ND	0.5-1.1	ND							
Acetaldehyde*	75-07-0	ND	4.9	ND	2.4							
Acetic acid	64-19-7	1.2-1.6	ND	ND	1.1-3.8							
Acetone	67-64-1	3.0-3.3	3.5-5.1	2.1-2.2	4.1-5.5							
Carbon disulfide	75-15-0	1.6	ND	ND	ND							
Dichlorodifluoromethane	75-71-8	0.6-0.7	ND	0.5	0.5							
Dimethylsilanediol	1066-42-8	ND	3.4	ND	ND							
Ethanol	64-17-5	ND	ND	ND	3.6							
Ethyl acetate	141-78-6	ND	1.7-2.0	ND	1.7-11.4							
Hexamethylcyclotrisiloxane	541-05-9	1.0	1.2-5.7	0.5-3.2	0.6-1.2							
Isopropyl alcohol	67-63-0	ND	ND	ND	1.0							
Methoxy-phenyl-oxime-	67160-14-9	ND	0.7	ND	ND							
n-Butanal	123-72-8	1.0	ND	ND	ND							
n-Nonanal	124-19-6	ND	ND	0.7	ND							
Propene	115-07-1	ND	ND	ND	1.5							
Propylene glycol	57-55-6	ND	ND	4.2	ND							

Figure C-4-2: Grab Canister Results								
		Sample Date						
Chemical	CAS#	9/20/2021	9/21/2021	9/22/2021	9/23/2021			
1,1-Difluoroethane	75-37-6	ND	3.7	ND	ND			
1,3,5-Trimethylbenzene	108-67-8	0.6	ND	ND	ND			
1-Butanol	71-36-3	2.1	ND	ND	ND			
2,6-Lutidine	108-48-5	0.8	ND	ND	ND			
2-Butanol	78-92-2	0.9	ND	ND	ND			
2-Butanone (MEK)	78-93-3	1.6	ND	ND	ND			
2-Ethyl-1-hexanol	104-76-7	0.6	1.1-1.7	ND	0.6			
2-Ethylhexylacetate	103-09-3	ND	2.3	ND	ND			
2-Ethylpyridine	100-71-0	0.7	ND	ND	ND			
2-Methylbutane	78-78-4	ND	ND	9.1-10.8	ND			
2-Methylpentane	107-83-5	0.8	1.8	1.2-1.3	ND			

<sup>\*</sup>Estimated result

Figure C-4-2: Grab Canister Results								
		Sample Date						
Chemical	CAS#	9/20/2021	9/21/2021	9/22/2021	9/23/2021			
2-Methylpyridine	109-06-8	2.5	ND	ND	ND			
3-Methylpentane	96-14-0	ND	ND	0.7	ND			
3-Methylpyridine	108-99-6	0.6	ND	ND	ND			
Acetaldehyde*	75-07-0	1.7	ND	ND	ND			
Acetic acid	64-19-7	1.1-3.8	ND	1.7	ND			
Acetic acid, ethenyl ester (Vinyl								
acetate)	108-05-4	ND	1.2	ND	ND			
Acetone	67-64-1	2.5-6.3	2.1-7.9	1.1-2.6	1.1-1.7			
Butanoic acid	107-92-6	ND	ND	2.4	ND			
Carbon disulfide	75-15-0	3.1	ND	2.1	ND			
Dichlorodifluoromethane	75-71-8	0.6-0.8	0.5-0.7	0.5-0.6	0.5-0.6			
Dimethyl disulfide	624-92-0	ND	ND	1.3	ND			
Ethanol	64-17-5	1.6-1.8	2.8-5.8	ND	ND			
Ethyl acetate	141-78-6	ND	69.4	0.7-3.3	ND			
Hexamethylcyclotrisiloxane	541-05-9	0.7-5.5	0.3-0.9	0.3-1.9	0.3-9.5			
Isobutane	75-28-5	1.1-5	ND	1-3.4	ND			
Isopropyl alcohol	67-63-0	0.9	4.5	ND	ND			
n-Butane	106-97-8	1.1-4.2	ND	4.6-10.5	ND			
n-Butyl acetate	123-86-4	0.6	ND	ND	ND			
n-Hexane	110-54-3	ND	ND	0.7	ND			
n-Nonanal	124-19-6	0.5	0.5	ND	0.5-1.3			
n-Pentane	109-66-0	0.8-1.2	8.1	1.5-5.1	ND			
p-Isopropyltoluene	99-87-6	ND	ND	1.5	ND			
Propane	74-98-6	1.8-2.2	ND	ND	ND			
Propene	115-07-1	1.9	5	ND	ND			
Pyridine	110-86-1	3.7	ND	ND	ND			
Toluene	108-88-3	1	2.1	ND	ND			
Trimethylsilanol	1066-40-6	7.6-11.1	7.9	ND	ND			
m-Xylene (1,3- Dimethylbenzene)	108-38-3	0.8-0.9	ND	ND	ND			

<sup>\*</sup> Estimated result

# Appendix D: Analyte Lists for Air Sampling Analysis Methods

Appendix D-1: Analyte List for ASTM Method D 5504-12

CAS#	Compound	
7783-06-4	Hydrogen Sulfide	
463-58-1	Carbonyl Sulfide	
74-93-1	Methyl Mercaptan	
75-08-1	Ethyl Mercaptan	
75-18-3	Dimethyl Sulfide	
75-15-0	Carbon Disulfide	
75-33-2	Isopropyl Mercaptan	
75-66-1	tert-Butyl Mercaptan	
107-03-9	n-Propyl Mercaptan	
624-89-5	Ethyl Methyl Sulfide	
110-02-1	Thiophene	
513-44-0	Isobutyl Mercaptan	
352-93-2	Diethyl Sulfide	
109-79-5	n-Butyl Mercaptan	
624-92-0	Dimethyl Disulfide	
616-44-4	3-Methylthiophene	
110-01-0	Tetrahydrothiophene	
638-02-8	2,5-Dimethylthiophene	
872-55-9	2-Ethylthiophene	
110-81-6	Diethyl Disulfide	

Appendix D-2: Analyte List for EPA Method TO-15

CAS#	Compound
115-07-1	Propene
75-71-8	Dichlorodifluoromethane (CFC 12)
74-87-3	Chloromethane
76-14-2	1,2-Dichloro-1,1,2,2-tetrafluoroethane (CFC 114)
75-01-4	Vinyl Chloride
106-99-0	1,3-Butadiene
74-83-9	Bromomethane
75-00-3	Chloroethane
64-17-5	Ethanol
75-05-8	Acetonitrile
107-02-8	Acrolein
67-64-1	Acetone
75-69-4	Trichlorofluoromethane
67-63-0	2-Propanol (Isopropyl Alcohol)
107-13-1	Acrylonitrile
75-35-4	1,1-Dichloroethene
75-09-2	Methylene Chloride
107-05-1	3-Chloro-1-propene (Allyl Chloride)
76-13-1	Trichlorotrifluoroethane
75-15-0	Carbon Disulfide
156-60-5	trans-1,2-Dichloroethene
75-34-3	1,1-Dichloroethane
1634-04-4	Methyl tert-Butyl Ether
108-05-4	Vinyl Acetate
78-93-3	2-Butanone (MEK)
156-59-2	cis-1,2-Dichloroethene
141-78-6	Ethyl Acetate
110-54-3	n-Hexane
67-66-3	Chloroform
109-99-9	Tetrahydrofuran (THF)
107-06-2	1,2-Dichloroethane
71-55-6	1,1,1-Trichloroethane
71-43-2	Benzene
56-23-5	Carbon Tetrachloride
110-82-7	Cyclohexane
78-87-5	1,2-Dichloropropane
75-27-4	Bromodichloromethane
79-01-6	Trichloroethene
123-91-1	1,4-Dioxane
80-62-6	Methyl Methacrylate
142-82-5	n-Heptane
10061-01-5	cis-1,3-Dichloropropene
108-10-1	4-Methyl-2-pentanone
10061-02-6	trans-1,3-Dichloropropene
79-00-5	1,1,2-Trichloroethane
108-88-3	Toluene
591-78-6	2-Hexanone
124-48-1	Dibromochloromethane
106-93-4	1,2-Dibromoethane
123-86-4	n-Butyl Acetate

CAS#	Compound
111-65-9	n-Octane
127-18-4	Tetrachloroethene
108-90-7	Chlorobenzene
100-41-4	Ethylbenzene
179601-23-1	m,p-Xylenes
75-25-2	Bromoform
100-42-5	Styrene
95-47-6	o-Xylene
111-84-2	n-Nonane
79-34-5	1,1,2,2-Tetrachloroethane
98-82-8	Cumene
80-56-8	alpha-Pinene
103-65-1	n-Propylbenzene
622-96-8	4-Ethyltoluene
108-67-8	1,3,5-Trimethylbenzene
95-63-6	1,2,4-Trimethylbenzene
100-44-7	Benzyl Chloride
541-73-1	1,3-Dichlorobenzene
106-46-7	1,4-Dichlorobenzene
95-50-1	1,2-Dichlorobenzene
5989-27-5	d-Limonene
96-12-8	1,2-Dibromo-3-chloropropane
120-82-1	1,2,4-Trichlorobenzene
91-20-3	Naphthalene
87-68-3	Hexachlorobutadiene

Appendix E: Screening an	d Evaluat	ion of Ch	nemicals I	Measured from	Community Am	bient Ai	r Sampl	es
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Appendix E-1: Initial Health Screening of Chemicals Measured in Community Ambient Air near GPI and KWRP

Chemical	CAS#	Highest detection (ppb)	S	creening value (ppb)	Highest detection over screening value?
(1-Methylethyl) (1,1-dimethylethyl)disulfide	43022-60-2	0.7		Annual ITSL <sup>2,</sup> (surrogate) <sup>7</sup>	No <sup>7</sup>
1,1-Difluoroethane	75-37-6	15.5	15,000	EPA RfC <sup>1</sup>	No
1,3,5-Trimethylbenzene	108-67-8	0.6	12	EPA RfC <sup>1</sup>	No
1-Butanol	71-36-3	8.2	115	EGLE Annual ITSL <sup>2</sup>	No
2,2,4-Trimethylpentane	540-84-1	0.41	3,500	EGLE 8-hour ITSL <sup>2</sup>	No
2,2,6-Trimethyloctane	62016-28-8	0.9		PPRTV RfC (surrogate) 11	No <sup>11</sup>
2,4-Dimethylheptane	2213-23-2	7.6		PPRTV RfC (surrogate) 11	No <sup>11</sup>
				, ,	No (individual chemical)/Yes
2,6-Lutidine	108-48-5	0.8	+	Annual ITSL <sup>2</sup> (surrogate) 10	(combined) <sup>10</sup>
2-Butanol	78-92-2	0.9	989	EGLE 8-hour ITSL <sup>2</sup>	No
2-Butanone (methyl ethyl ketone)	78-93-3	44.1	1,000	ATSDR Acute MRL <sup>3</sup>	No
2-Ethyl-1-hexanol	104-76-7	1.7	13	EGLE Annual ITSL <sup>2</sup>	No
2-Ethylhexylacetate	103-09-3	2.3	2	EGLE Annual ITSL <sup>2</sup>	Yes <sup>8</sup>
2-Ethylpyridine	100-71-0	0.7	1 EGLE	Annual ITSL² (surrogate) <sup>10</sup>	No (individual chemical)/Yes (combined) <sup>10</sup>
2-Methylbutane	78-78-4	10.8	5,996	EGLE 8-hour ITSL <sup>2</sup>	No
2-Methylpentane	107-83-5	11.6	4,992	EGLE 8-hour ITSL <sup>2</sup>	No
2-Methylpropene	115-11-7	0.9	47,924	EGLE Annual ITSL <sup>2</sup>	No
2-Methylpyridine	109-06-8	2.5	6.3	EGLE Annual ITSL <sup>2</sup>	No
3-Methylpentane	96-14-0	5.7	992	EGLE 8-hour ITSL <sup>2</sup>	No
3-Methylpyridine	108-99-6	0.6	21	EGLE Annual ITSL <sup>2</sup>	No
4-Methyloctane	2216-34-4	4.8	15 EPA	PPRTV RfC (surrogate) 11	No 11
Acetaldehyde*	75-07-0	4.9	0.25	ATSDR CREG <sup>3</sup>	Yes

					Highest detection over screening
Chemical	CAS#	Highest detection (ppb)	1	reening value (ppb)	value?
Acetic acid	64-19-7	52.9	488	EGLE 1-hour ITSL <sup>2</sup>	No
Acetic acid, ethenyl ester (Vinyl acetate)	108-05-4	1.2	10	ATSDR Intermediate MRL <sup>3</sup>	
Acetone	67-64-1	13.5	13,000	ATSDR Chronic MRL <sup>3</sup>	No
Ammonia		Non-detect (community locations) 5,650 (KWRP sanitary sewer location	100	ATSDR Chronic MRL <sup>3</sup>	N/A <sup>9</sup>
Benzene	71-43-2	0.7	0.04	ATSDR CREG <sup>3</sup>	No
Bis(1-methylethyl)disulfide	4253-89-8	0.5	4 EGLE	Annual ITSL <sup>2,</sup> (surrogate) <sup>7</sup>	No <sup>7</sup>
Butanoic acid	107-92-6	2.4	2.78	EGLE Annual ITSL <sup>2</sup>	No
Carbon disulfide	75-15-0	7.4	220	EPA RfC <sup>1</sup>	No
Chlorodifluoromethane	75-45-6	0.8	14,000	EPA RfC <sup>1</sup>	No
Chloroform	67-66-3	0.17	0.0089	ATSDR CREG <sup>3</sup>	No
Chloromethane	74-87-3	0.46	44	EPA RfC <sup>1</sup>	No
Cyclohexanone	108-94-1	21.9	199	EGLE 8-hr ITSL <sup>2</sup>	No
Dichlorodifluoromethane	75-71-8	0.8	66	EGLE Annual ITSL <sup>2</sup>	No
Dimethyl disulfide	624-92-0	1.3	4	EGLE Annual ITSL <sup>2</sup>	No
Dimethylsilanediol	1066-42-8	3.4	None av	ailable	N/A <sup>12</sup>
d-Limonene	5989-27-5	2.5	1121 pr ITSL	ovisional EGLE Annual	No <sup>13</sup>
Ethanol	64-17-5	281.3	10,000	EGLE RIASL⁴	No
Ethyl acetate	141-78-6	69.4	887	EGLE Annual ITSL <sup>2</sup>	No
Hexamethylcyclotrisiloxane	541-05-9	18.7	5	EGLE Annual ITSL <sup>2</sup>	Yes
Hydrogen Sulfide	7783-06-4	85	1.4	EPA RfC <sup>1</sup>	Yes
Isobutane	75-28-5	8.4	10,000	EGLE 8-hour ITSL <sup>2</sup>	No
Isopropyl alcohol	67-63-0	276.7	80	EPA Indoor Air RSL <sup>5</sup>	Yes

Chemical	CAS#	Highest detection (ppb)	Sci	creening value (ppb)	Highest detection over screening value?
m & p-Xylene	1330-20-7	0.28	23	EPA RfC (total xylenes) <sup>1</sup>	No No
Methoxy-phenyl-oxime-	67160-14-9	0.7	None av	, , ,	N/A <sup>14</sup>
Methylcyclopentane	96-37-7	4.6		E 24-hour ITSL	No <sup>15</sup>
m-Xylene (1,3-Dimethylbenzene)	108-38-3	3.2	23	EPA RfC (total xylenes) <sup>1</sup>	No
n-Butanal	123-72-8	1		Annual ITSL	No <sup>16</sup>
n-Butane	106-97-8	32	10,000		No
n-Butyl acetate	123-86-4	0.6	505	EGLE 8-hour ITSL <sup>2</sup>	No
n-Hexane	110-54-3	5.4	200	EPA RfC <sup>1</sup>	No
n-Nonanal	124-19-6	2.6	None available		N/A <sup>17</sup>
n-Pentane	109-66-0	244	5,996	EGLE 8-hour ITSL <sup>2</sup>	No
o-Xylene	95-47-6	0.5	23	EPA RfC (total xylenes) 1	No
p-Isopropyltoluene	99-87-6	1.5	1.82	EGLE Annual ITSL <sup>2</sup>	No
Propane	74-98-6	2.8	100000	O NIOSH 8-hour TWA REL	No <sup>18</sup>
Propene	115-07-1	14.5	4,995	EGLE 8-hour ITSL <sup>2</sup>	No
Propylene glycol	57-55-6	4.2	9	ATSDR Intermediate MRL <sup>3</sup>	
p-Xylene	106-42-3	4.4	23	EPA RfC (total xylenes) 1	No
Pyridine	110-86-1	3.7	1	EGLE Annual ITSL <sup>2</sup>	Yes
Sulfur dioxide	7446-09-5	27.1	75	EPA NAAQS <sup>6</sup>	Yes
Toluene	108-88-3	15.4	1,000	ATSDR Chronic MRL <sup>3</sup>	No
Trichlorofluoromethane	75-69-4	0.2	23	EGLE Annual ITSL <sup>2</sup>	No
Trimethylsilanol	1066-40-6	11.1	17	EGLE Annual ITSL <sup>2</sup>	No

<sup>\*</sup> Estimated result

<sup>&</sup>lt;sup>1</sup>EPA 2022

<sup>&</sup>lt;sup>2</sup>EGLE 2022

<sup>&</sup>lt;sup>3</sup>ATSDR 2022

<sup>&</sup>lt;sup>4</sup>EGLE 2020

<sup>&</sup>lt;sup>5</sup>EPA 2021a

#### <sup>6</sup>EPA 2021b

<sup>7</sup> Disulfide Compounds (1-Methylethyl) (1,1-dimethylethyl)disulfide (CAS #43022-60-2) Bis(1-methylethyl)disulfide (CAS #4253-89-8)

MDHHS was unable to identify any toxicological or epidemiological data for (1-methylethyl) (1,1-dimethylethyl)disulfide or bis(1-methylethyl)disulfide for the purposes of risk assessment and hazard characterization. MDHHS then searched for a structurally similar surrogate chemical with a health screening value or sufficient toxicity data.

(1-Methylethyl) (1,1-dimethylethyl)disulfide and bis(1-methylethyl)disulfide are structurally similar to dimethyl disulfide (CAS #624-92-0). Their structures differ only in that (1-methylethyl) (1,1-dimethylethyl)disulfide has longer saturated alkane chain substitutions on the disulfide center, which are not expected to contribute to toxicity. MDHHS considered dimethyl disulfide to be a sufficient surrogate chemical for the purpose of secondary health screening.

MDHHS used the Annual ITSL for dimethyl disulfide of 4 ppb (EGLE 2022) as a conservative approach to assess potential health risks from exposure to (1-methylethyl) (1,1-dimethylethyl)disulfide and bis(1-methylethyl)disulfide measured in community ambient air. (1-Methylethyl) (1,1-dimethylethyl)disulfide was measured in one grab sample at a concentration of 0.7 ppb and bis(1-methylethyl)disulfide was measured in one grab sample at a concentration of 0.5 ppb. Individually, these concentrations do not exceed the annual ITSL of 4 ppb for dimethyl disulfide.

As a conservative approach, MDHHS also combined the maximum detections for both disulfide compounds, as the maximum measurements for each compound were detected from the same odor monitoring investigation at the same location, and are being compared to the same screening value. The total concentration was 1.2 ppb, which is about 3 times below the Annual ITSL of 4 ppb.

## 8 2-Ethylhexylacetate (CAS #103-09-3)

2-Ethylhexylacetate is an acetate ester that is derived from hexanol. It is a solvent with a fruity, pleasant odor. 2-Ethylhexylacetate can cause moderate skin and eye irritation but is not associated with any other toxic effects (PubChem 2022).

No short-term health screening values have been identified for 2-ethylhexylacetate. EGLE has derived an annual ITSL for 2-ethylhexylacetate of  $15 \mu g/m^3$  (2 ppb) based on an acute oral toxicity study in rats that derived an LD<sub>50</sub> of 5.89 g/kg (MDNR 1993). No additional information was provided regarding the test protocol, rat body weights or inhalation rates, or any specific signs of toxicity.

It should be noted that this ITSL is extrapolated from an oral toxicity study and is based on effects that may be specific to oral ingestion of 2-ethylhexylacetate. As the exposure pathway of concern in this investigation is inhalation, harmful effects specific to oral ingestion of 2-ethylhexylacetate may not be relevant to the expected route of exposure to 2-ethylhexylacetate in this investigation.

2-Ethylhexylacetate was measured at 2.3 ppb from a grab canister sample taken during the September 2021 investigation, which can be considered equivalent to the EGLE annual ITSL of 2 ppb. No 24-hour composite samples taken during the September 2021 investigation measured 2-ethylhexylacetate above 2 ppb, and 2-ethylhexylacetate was not detected in the October 2020 investigation or the May 2021 EPA GMAP investigation. 2-Ethylhexylacetate was detected in three (3.75 percent) community air samples and was measured at levels exceeding its screening value in one (1.25 percent) sample.

Annual ITSLs are intended for comparison with exposures averaged over 1 year. As the only exceedance was detected in a grab sample and no 24-hour composite samples measured exceedances, concentrations of 2-ethylhexylacetate are not likely to exceed the annual ITSL over one year.

<sup>9</sup> Ammonia was not detected in air samples taken from the community; however, the detection limit was higher than the screening values. See section 5 for discussion of ammonia.

<sup>10</sup> Pyridine-related Compounds 2,6-Lutidine (CAS #108-48-5) 2-Ethylpyridine (CAS #100-71-0)

2,6-Lutidine is an alkylpyridine with two methyl groups. 2-Ethylpyridine is an alkylpyridine with one ethyl group.

Toxicological data on 2,6-lutidine and 2-ethylpyridine are limited. 2,6-Lutidine has oral and dermal  $LD_{50}$  values of 400 and 2,500 mg/kg, respectively, and an  $LC_{100}$  of 7,500 ppm (PubChem 2022). No toxicological data on 2-ethylpyridine were identified.

In the absence of a health screening value or sufficient toxicity data to assign a NOAEL for 2,6-lutidine or 2-ethylpyridine, MDHHS searched for a structurally similar surrogate chemical with a health screening value or sufficient toxicity data.

2,6-Lutidine and 2-ethylpyridine are structurally similar to pyridine (CAS #110-86-1). Their structures differ from pyridine only in that 2,6-lutidine has two methyl group substitutions and 2-ethylpyridine has an ethyl group substitution. Neither the methyl nor ethyl group substitutions are expected to contribute to toxicity. Additionally, structural similarity analysis indicates that 2,6-lutidine and 2-ethylpyridine both share an MCS

Tanimoto coefficients of 0.75 with pyridine, indicating that the structures have more shared structural features than unique (see Appendix E-3). MDHHS considered pyridine to be a sufficient surrogate chemical for the purpose of secondary health screening.

MDHHS used the Annual ITSL for pyridine of 1 ppb (EGLE 2022) as a conservative approach to assess potential health risks from exposure to 2,6-lutidine and 2-ethylpyridine measured in community ambient air. 2,6-Lutidine was measured at a maximum concentration of 0.8 ppb, and 2-Ethylpyridine was measured at a maximum concentration of 0.7 ppb. Individually, these concentrations do not exceed the annual ITSL of 1 ppb for pyridine. However, as both of the maximum measurements were detected from the same air sample and are being compared to the same screening value, MDHHS combined the two concentrations for a total concentration of 1.5 ppb. This concentration exceeds the annual ITSL of 1 ppb for pyridine.

Public health implications of this exceedance are discussed in Section 5.2.8.

<sup>11</sup> Branched Alkanes

2,2,6-Trimethyloctane (CAS #62016-28-8)

2,4-Dimethylheptane (CAS #2213-23-2)

4-Methyloctane (CAS #2216-34-4)

Three C9-C10 branched alkanes were detected in community ambient air samples near GPI and KWRP.

MDHHS was unable to identify any toxicological or epidemiological data for any of these specific branched alkanes for the purposes of risk assessment and hazard characterization.

The US EPA has established Provisional Peer-Reviewed Toxicity Values (PPRTVs) for several aliphatic hydrocarbon mixtures based on the number of carbons in each molecule. MDHHS selected the inhalation RfC of 0.1 mg/m³ (equivalent to 15 ppb²¹) for hydrocarbons ranging from C9-C18 for comparison with the branched alkanes detected near GPI and KWRP, as these alkanes ranged from C9-C10. This RfC is based on nasal goblet cell hypertrophy and adrenal hyperplasia in rats and mice exposed to concentrations of a hydrocarbon mixture (saturated, aliphatic, and alicyclic, C7-C12) for up to 2 years (EPA 2009).

As a conservative approach, the branched alkane with the highest molecular weight was used to convert the RfC to ppb.

 $<sup>^{21}</sup>$  0.1 mg/m<sup>3</sup> \* (24.45/128.257) = 0.015 ppm = 15 ppb

2,2,6-Trimethyloctane was measured in two 24-hour composite samples at a maximum concentration of 0.9 ppb. 2,4-Dimethylheptane was measured in over five grab samples at a maximum concentration of 7.6 ppb. 4-Methyloctane was measured in five grab samples at a maximum concentration of 4.8 ppb. None of the branched alkanes measured near GPI and KWRP exceeded the EPA's provisional RfC of 15 ppb.

As a conservative approach, MDHHS also calculated the sum of the maximum measurements for these three branched alkanes for comparison with the EPA PPRTV. The summed maximum concentrations of branched alkanes 2,2,6-trimethyloctane, 2,4-dimethylheptane, and 4-methyloctane is 13.3 ppb<sup>22</sup>, which is below the EPA PPRTV of 15 ppb.

Based on measured concentrations being below the EPA's provisional RfC for medium carbon range aliphatic hydrocarbons, 2,2,6-trimethyloctane, 2,4-dimethylheptane, and 4-methyloctane are not considered to present public health concerns in the communities adjacent to GPI and KWRP.

<sup>12</sup> Dimethylsilanediol (CAS #1066-42-8) See Appendix E-2.1

### <sup>13</sup> d-Limonene (CAS #5989-27-5)

d-Limonene is a cyclic monoterpene used commonly as a flavoring agent in food manufacturing. It is also used in industrial applications as a degreasing agent and as one of the components of turpentine. When released to air, d-limonene is expected to rapidly undergo gas-phase oxidation with estimated half-lives on the scale of minutes to hours. d-Limonene has been measured in indoor and outdoor air at various locations in Texas at concentrations ranging from 0.01-29 ppb (DEPA 2013).

Limited short-term inhalation toxicity data were available for d-limonene. Human volunteers exposed to 10, 225, and 450 mg/m³ d-limonene (approximately 1,794, 40,380, and 80,760 ppb²³) did not experience any irritation or central nervous system (CNS) effects. A statistically significant change in lung vital capacity among volunteers at the high exposure was not considered to be biologically significant. Mice exposed to 1,076 ppm (1,076,000 ppb) d-limonene had mild bronchoconstriction. No pulmonary or anesthetic effects were reported at 1,600 ppm, the highest concentration tested. A mixture of ozone (initially 4 ppm) and d-limonene (48 ppm) caused significant sensory irritation and reduced mean respiratory rate in mice (DEPA 2013).

 $<sup>^{22}</sup>$  0.9 + 7.6 + 4.8 = 13.3 ppb

<sup>&</sup>lt;sup>23</sup> Based on the equation: Concentration (mg/m<sup>3</sup>)  $\times$  (24.45/MW) = Concentration (ppm)  $\times$  1,000 = Concentration (ppb), and a MW of 136.2364 for d-limonene.

The Danish Environmental Protection Agency (DEPA) used the short-term inhalation study in human volunteers to assign an ambient air quality criterion of 4.5 mg/m<sup>3</sup> (807 ppb), which incorporated an uncertainty factor (UF) of 100 based on variations in biological sensitivity among humans and limited data on repeated-dose inhalation toxicity.

EGLE has assigned an annual ITSL for d-limonene of 6,250  $\mu$ g/m<sup>3</sup> (1,121 ppb) based on a chronic oral toxicity study in mice (EGLE 2016). There was a single detection of d-limonene in one grab sample, 2.5 ppb. That is more than 400 times below the annual ITSL.

MDHHS also compared the measured concentrations to the DEPA ambient air quality criterion of 807 ppb as a conservative approach to assess potential health risks from exposure to d-limonene in community ambient air. d-Limonene was measured in one grab sample at a concentration of 2.5 ppb. It was not detected in any other samples. The measured concentration of 2.5 ppb is more than 300 times below DEPA's ambient air quality criterion of 807 ppb.

Based on the weight of evidence, d-limonene is not considered to present a public health concern in the communities adjacent to GPI and KWRP.

<sup>14</sup> Methoxy-phenyl-oxime- (CAS #67160-14-9) See Appendix E-2.2

<sup>15</sup> Methylcyclopentane (CAS #96-37-7)

Methylcyclopentane is a cyclic alkane commonly used in organic synthesis and as an extraction solvent. It is also present in commercial hexane (PubChem 2022).

Limited toxicological data were identified for methylcyclopentane. In a two-generation reproductive toxicity study, male and female rats were exposed to 900, 3,000, and 9,000 ppm of a commercial hexane mixture containing 14 percent methylcyclopentane. Equivalent methylcyclopentane exposures were approximately 126, 420, and 1,260 ppm. Rats were exposed for 6 hours/day, 5 days/week over two generations. No reproductive effects were identified in rats exposed at any concentration, though reductions in body weight and body weight gain were measured in rats exposed to the high dose. Study authors identified a NOAEL of 3,000 ppm/6h/day (equivalent to 420 ppm methylcyclopentane) (PubChem 2022).

The NOAEL of 420 ppm methylcyclopentane was adjusted to 105 ppm (105,000 ppb) to account for less than daily exposure<sup>24</sup>. An uncertainty factor of 300 was applied to account for interspecies (rat-human; 10x) and intraspecies (human-human; 10x) variation and subchronic-chronic extrapolation (3x), resulting in a final screening value of 350 ppb.

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<sup>&</sup>lt;sup>24</sup> 420 ppm \* 6 hours/24 hours = 105 ppm

In a 90-day subchronic inhalation toxicity study, rats were exposed to 0, 290, 1,300, and 5,870 ppm methylcyclopentane vapor via whole body inhalation for 6 hours/day, 5 days/week over 13 weeks. Rats exposed to the high concentration showed exposure-related clinical signs, including salivation, rubbing, and increased organ weights (liver in both genders; kidney in females only). No other changes were observed. Study authors identified a NOAEL of 1,300 ppm/6h/day based on changes in liver and kidney weights at 5,870 ppm (Yang et al. 2014).

The NOAEL of 1,300 ppm methylcyclopentane was adjusted to 232 ppm (232,000 ppb) to account for less than daily exposure.<sup>25</sup> An uncertainty factor of 300 was applied to account for interspecies (rat-human; 10x) and intraspecies (human-human; 10x) variation and subchronic-chronic extrapolation (3x), resulting in a final screening value of 774 ppb.

EGLE has set a 24-hour ITSL of 700  $\mu$ g/m³ (203 ppb) for methylcyclopentane, matching the ITSL for n-hexane (EGLE 2010). Methylcyclopentane is often found as a component of commercial mixtures of hexane solvent. n-Hexane is a similar C6 compound that is expected to be more toxic than methylcyclopentane – therefore, basing the ITSL for methylcyclopentane on data for n-hexane is health-protective.

MDHHS selected EGLE's 24-hour ITSL of 203 ppb as a conservative approach to assess potential health risks from exposure to methylcyclopentane in community ambient air. Methylcyclopentane was measured in one grab sample at a concentration of 4.6 ppb. It was not detected in any other samples. The measured concentration is more than 40 times below the 24-hour ITSL developed by EGLE.

Based on the weight of evidence, methylcyclopentane is not considered to present a public health concern in the communities adjacent to GPI and KWRP.

<sup>16</sup> n-Butanal (CAS #123-72-8)

n-Butanal, also known as butyraldehyde, is a highly flammable, colorless gas with a characteristic pungent odor.

Butyraldehyde was evaluated by the Texas Commission on Environmental Quality (TCEQ) for the purpose of established health- and welfare-based exposure values (TCEQ 2015). TCEQ has established an acute (1 hour) exposure screening level (ESL) of 1,100 ppb based on a lack of adverse effects observed in human volunteers at that concentration. TCEQ also established a chronic ESL of 10 ppb based on hyperplasia, inflammation, and squamous metaplasia of the nasal tissues in rats and dogs (TCEQ 2015).

EGLE has established an annual ITSL of 7  $\mu$ g/m³ (2 ppb) for butyraldehyde based on a 14-week inhalation study in beagle dogs that identified a LOAEL of 125 ppm (EGLE 2017).

<sup>&</sup>lt;sup>25</sup> 1,300 ppm \* 6 hours/24 hours \*5 days/7 days = 232 ppm

As a conservative approach, MDHHS selected the annual ITSL of 2 ppb as the screening value for n-butanal. n-Butanal was measured in one grab sample at a concentration of 1.0 ppb. It was not detected in any other samples. This concentration is below both the acute and chronic ESLs established by TCEQ and EGLE's provisional annual ITSL. Based on the weight of evidence, n-butanal is not considered to present a public health concern in the communities adjacent to GPI and KWRP.

<sup>17</sup> n-Nonanal (CAS #124-19-6) See Appendix E-2.3.

### <sup>18</sup> Propane (CAS #74-98-6)

Propane is a colorless and odorless gas commonly used to produce liquefied petroleum gas. It is also used in the synthesis of chemicals. Propane has low toxicity via inhalation and is considered a simple asphyxiant (PubChem 2022). A simple asphyxiant is a gas that can displace oxygen and that lack of oxygen is the concern. Human volunteers exposed to up to 1,000 ppm propane for repeated 8-hour exposures did not experience any changes to clinical parameters or organ function. No health effects were noted in volunteers exposed to 10,000 ppm propane for 10 minutes, but volunteers exposed to 100,000 ppm propane for 10 minutes reported "distinct vertigo" (NRC 2012).

Because propane is a simple asphyxiant, occupational limits<sup>26</sup> can be informative when evaluating the levels measured in the community samples. The National Institute for Occupational Safety and Health (NIOSH) has a recommended exposure limit (REL) of 1000 ppm. This REL is intended to be used to compared to time-weighted averages of propane during an 8-hour work day.

Propane was measured in over five 24-hour composite samples and two grab samples at a maximum concentration of 2.8 ppb, which is more than 300,000 times lower than the REL of 1000 ppm (1,000,000 ppb).

Based on the weight of evidence, propane is not considered to present a public health concern in the communities adjacent to GPI and KWRP.

<sup>26</sup> In many cases occupational exposure limits would not be appropriate screening values to use to evaluate non-occupational exposures as occupational populations may not have sensitive populations, such as children or people that might have underlying health conditions.

#### Appendix E-2: Derivation of Secondary Screening Values and Summary Table

In the absence of an acceptable screening value and sufficient toxicity data for the target chemical, MDHHS derived secondary screening values based on available literature and data.

Some secondary screening values were based on toxicological data for a structurally similar surrogate chemical. Potential surrogates were evaluated on the basis of structure similarity, including shared functional groups and moieties. For each surrogate, a maximum common substructure (MCS) Tanimoto coefficient was calculated to further assess similarity. The Tanimoto coefficient indicates the proportion of structural features shared by two compounds compared to the number of total structures (unique and shared). Tanimoto coefficients range from 0-1, with values closer to 1 indicating more shared structural features (ChemMine 2022).

See below for writeups on the derivation of each secondary screening value used in this assessment.

#### Appendix E-2.1: Dimethylsilanediol (CAS #1066-42-8)

Dimethylsilanediol is an organosilicon compound. It is a silicon molecule with two methyl and two hydroxyl groups.

Limited toxicological data on dimethylsilanediol were identified. In an oral prenatal developmental toxicity study, pregnant rats (n=25) were administered 250, 500, and 1,000 mg/kg/day dimethylsilanediol in corn oil during days 6-19 of gestation (SEHSC 2013). Maternal findings were limited to statistically significant increases in mean liver weights in all treated groups. Fetuses from all treated groups had significantly lower mean body weights compared to controls. As statistically significant adverse effects were reported at all tested doses in both maternal and fetal rats, MDHHS identified a LOAEL of 250 mg/kg/day, the lowest tested dose. An uncertainty factor of 300 was applied to account for interspecies (rat-human; 10x) and intraspecies (human-human; 10x) variation and LOAEL to NOAEL extrapolation (3x), resulting in a final screening value of 0.83 mg/kg/day (830  $\mu$ g/kg/day).

The oral screening value was converted to an inhalation screening value by applying a standard adult body weight of 70 kg and a standard daily adult inhalation volume of 20 m<sup>3</sup> (EPA 2011).<sup>27</sup> The final inhalation screening value is 2,905  $\mu$ g/m<sup>3</sup> (738 ppb).

In a combined repeated dose toxicity study with the reproductive/developmental toxicity screening test, rats were administered 50, 250, or 500 mg/kg/day dimethylsilanediol via gavage (Dow Corning 2009). Rats in the male and female toxicity groups were exposed for 28 or 29 consecutive days, respectively, and evaluated for mortality, clinical signs of toxicity, and neurological effects via functional observational battery. Complete necropsies were then performed on males and toxicity group females, alongside hematology, serum chemistry, and organ weight analysis. Reproductive group females were treated for 14 days prior to mating, during mating, and through post-partum day 3, and were analyzed for several reproductive and developmental parameters. Following euthanasia, dams and pups were analyzed for external gross lesions. Organ-related effects were limited to hepatic protoporphyrinosis in 500 mg/kg/day males and periportal hepatocellular vacuolation in 500 mg/kg/day females in the toxicity group. These effects corresponded with increased liver weights in males and toxicity group females at 250 and 500 mg/kg/day. There were no treatment-related effects for any measured reproductive endpoints.

Based on the liver effects observed in male and female rats at 500 mg/kg/day, study authors identified a NOAEL of 250 mg/kg/day. An uncertainty factor of 100 was applied to account for interspecies (rat-human; 10x) and intraspecies (human-human; 10x) variation, resulting in a final screening value of 2.5 mg/kg/day (2,500  $\mu$ g/kg/day).

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 $<sup>^{27}</sup>$  830 µg/kg/day x 70 kg/20 m<sup>3</sup> = 2,905 µg/m<sup>3</sup>

The oral screening value was converted to an inhalation screening value by applying a standard adult body weight of 70 kg and a standard daily adult inhalation volume of 20 m<sup>3</sup> (EPA 2011).<sup>28</sup> The final inhalation screening value is 8,750  $\mu$ g/m<sup>3</sup> (2,321 ppb).

MDHHS selected the screening value of 738 ppb derived from the oral prenatal developmental toxicity study, as this study identified adverse effects at a lower concentration than the repeated dose toxicity study with the reproductive/developmental toxicity screening test. Dimethylsilanediol was measured in one composite sample at a concentration of 3.4 ppb. It was not detected in any other samples. The measured concentration is more than 200 times below the screening value of 738 ppb.

Based on the weight of evidence, dimethylsilanediol is not considered to present a public health concern in the communities adjacent to GPI and KWRP.

 $<sup>^{28}</sup>$  2,500 µg/kg/day x 70 kg/20 m<sup>3</sup> = 2,905 µg/m<sup>3</sup>

#### Appendix E-2.2: Methoxy-phenyl-oxime- (CAS #67160-14-9)

Methoxy-phenyl-oxime- is a benzene derivative with a ketoxime substitution consisting of oxime and methoxyl.

No toxicity data were identified for methoxy-phenyl-oxime-. A structural surrogate search identified methyl benzoate (CAS #93-58-3) as a potential surrogate. Methyl benzoate is a similar benzene derivative with a formic acid substitution. Additionally, structural similarity analysis indicates that methoxy-phenyl-oxime- and methyl benzoate have an MCS Tanimoto coefficient of 0.75, indicating that the structures have more shared structural features than unique (see Appendix E-3). MDHHS considered methyl benzoate to be a sufficient surrogate chemical for the purpose of secondary health screening.

No inhalation toxicity data were identified for methyl benzoate. An ECHA REACH registration dossier is available for methyl benzoate (ECHA 2022). ECHA has developed several derived no effect levels (DNELs) for methyl benzoate. DNELs indicate an exposure level below which a substance is not expected to present a human health hazard. As no repeated dose inhalation toxicity studies were identified for methyl benzoate, oral toxicity data from a surrogate compound were extrapolated to derive an inhalation DNEL.

MDHHS selected the inhalation DNEL for methyl benzoate for the general population<sup>29</sup> of 9.68 mg/m³ (1.73 ppm) to assess potential health risks from exposure to methoxy-phenyl-oxime-measured in community ambient air.

Methoxy-phenyl-oxime- was measured in one 24-hour composite sample at a concentration of 0.7 ppb. It was not detected in any other samples. The measured concentration of 0.7 ppb is more than 2,000 times below the selected screening value of 1.73 ppm (1,730 ppb).

Based on the weight of evidence, methoxy-phenyl-oxime- is not considered to present a public health concern in the communities adjacent to GPI and KWRP.

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<sup>&</sup>lt;sup>29</sup> ECHA develops different DNELs for the general population and for workers. General population DNELs incorporate additional safety factors and are more health-protective than worker DNELs.

#### Appendix E-2.3: n-Nonanal (CAS #124-19-6)

n-Nonanal, also known as nonaldehyde, is a colorless liquid with a floral odor. It is a common constituent of essential oils (PubChem 2022).

Limited toxicological data were available for n-nonanal. It has an LD<sub>50</sub> > 5 gm/kg and an LC > 9,500 mg/m $^3$ /4h (1,633 ppm), indicating that it is not acutely toxic (PubChem 2022). No repeated dose inhalation toxicity studies were identified.

An ECHA REACH registration dossier is available for n-nonanal (ECHA 2022). ECHA lists several DNELs for inhalation exposure to n-nonanal. As no repeated dose inhalation toxicity studies were identified for n-nonanal, oral toxicity data from a surrogate compound were extrapolated to derive an inhalation DNEL. MDHHS selected the inhalation DNEL for the general population of 6.1 mg/m³ (1.0 ppm) in order to screen concentrations of n-nonanal measured in community ambient air near GPI and KWRP.

n-Nonanal was measured in two 24-hour composite samples and over five grab samples at a maximum concentration of 2.6 ppb. The maximum concentration is two orders of magnitude below the DNEL of 1.0 ppm (1,000 ppb). Based on the weight of evidence, n-nonanal is not considered to present a public health concern in the communities adjacent to GPI and KWRP.

Appendix E-2.4: Summary Table of Secondary Screening Results

Secondary Screening Results for Chemicals Without Health-Based Screening Values						
Chemical/Class CAS# Maximum Measured Surrogate  Concentration (ppb) Secondary Screening Value (ppb) (if applicable)						
Dimethylsilanediol	1066-42-8	3.4	768	Adjusted LOAEL	N/A	
Methoxy-phenyl-oxime-	67160-14-9	0.7	1,730	ECHA DNEL	Methyl benzoate	
n-Nonanal	124-19-6	2.6	1,000	ECHA DNEL	N/A	

#### Appendix E-3: Compound Similarity Results for Selected Chemicals Measured in Community Ambient Air near GPI and KWRP

Figure E-3-1: Compound Similarity Results for 2,6-Lutidine and Pyridine

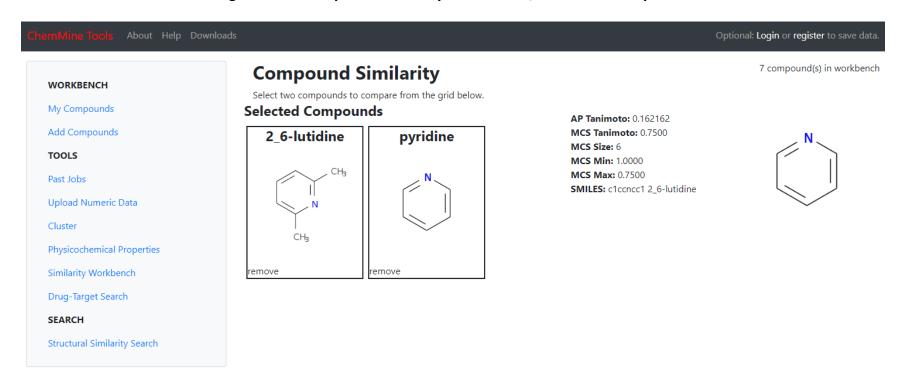


Figure E-3-2: Compound Similarity Results for 2-Ethylpyridine and Pyridine

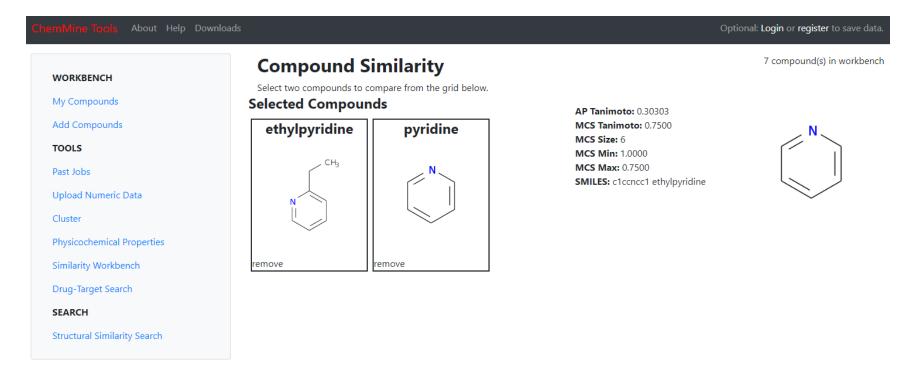
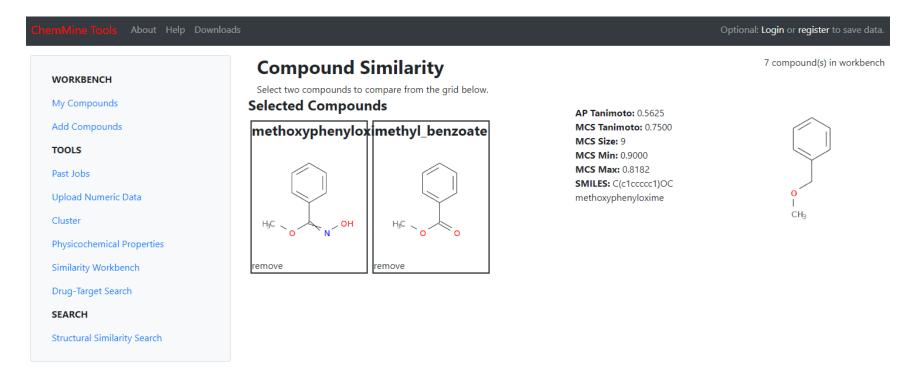


Figure E-3-3: Compound Similarity Results Methoxy-phenyl-oxime- and Methyl Benzoate



#### Appendix E-4: Toxicological Review of Hydrogen Sulfide (H<sub>2</sub>S)

While many of the community concerns have been discussed in other areas of the health consultation (Public Health Implications section, which includes an evaluation of people's exposure to the measured chemicals, discussion of environmental odors, and a summary of asthma prevalence and asthma-related hospitalization rates in communities adjacent to GPI and KWRP), this appendix discusses additional health outcomes that have been linked to H<sub>2</sub>S exposure in humans and health effects observed in laboratory animals.

#### Acute Toxicity

Acute (short-term) toxicity to  $H_2S$  generally presents as irritation of the nose, throat, and eyes and transient neurological effects such as nausea, headaches, dizziness, and fatigue. At higher concentrations, respiratory distress and fainting can occur. Rabbits exposed to 72 ppm  $H_2S$  for 1.5 hours fell unconscious. These effects tend to subside quickly after the exposure ends. Exposure to extremely high concentrations of  $H_2S$  ( $\geq 500$  ppm) can result in death due to respiratory failure (ATSDR 2016).

#### Intermediate and Chronic Toxicity (including systemic toxicity)

Long-term exposure to  $H_2S$  and RSCs is generally associated with adverse respiratory effects. Rats exposed to 30 and 80 ppm  $H_2S$  for up to 6 hours/day, 5 days/week for 90 days showed significant olfactory neuron loss and increased incidence of nasal lesions. Studies of communities located near sources of  $H_2S$  pollution have found increased rates of nasal irritation, cough, shortness of breath, worsened asthma symptoms, and altered lung function. Occupational studies of workers presumed to have increased exposure to  $H_2S$  were found to have increased prevalence of obstructive lung disease, shortness of breath and wheezing (ATSDR 2016).

Long-term exposure to  $H_2S$  has also been associated with adverse neurological effects. Workers in the shale industry exposed to >20 ppm  $H_2S$  daily had neurological effects including fatigue, loss of appetite, headache, poor memory, and dizziness. Memory loss and poor concentrations were reported in a study of sewer workers exposed to approximately 9 ppm  $H_2S$ . An ATSDR study of residents in Dakota City, Nebraska did not find significant differences in performance on neurobehavioral tests in residents chronically exposed to  $\geq$ 90 ppb  $H_2S$ . Rats and mice exposed to up to 80 ppm  $H_2S$  for 6 hours/day, 5 days/week for 90 days did not display any signs of treatment-related neurotoxicity or neurological effects (ATSDR 2016).

#### Carcinogenicity and Mutagenicity

No animal studies were available regarding the inhalation carcinogenicity of  $H_2S$ . An epidemiological study of individuals living downwind of natural gas refineries did not find increased cancer risk.  $H_2S$  is not classified as a carcinogen by the IARC or by EPA. Additionally,  $H_2S$  was not mutagenic in a bacterial reverse mutation assay (ATSDR 2016).

Reproductive and Developmental Toxicity

In animal studies,  $H_2S$  has not been associated with reproductive or developmental toxicity. Rats and mice exposed to up to 80 ppm  $H_2S$  for up to 6 hours/day and 5 days/week for 90 days did not display any treatment-related adverse effects on reproductive organs. In a developmental toxicity study, pregnant rats exposed to up to 75 ppm  $H_2S$  for up to 7 hours/day during gestation did not display any adverse reproductive effects other than increased parturition time, which was not statistically analyzed. A second reproductive toxicity study exposed rats to up to 80 ppm  $H_2S$  for 6 hours/day, 7 days/week for 2 weeks prior to mating, throughout mating, and from gestation days 0-19. No significant alterations in any reproductive or developmental parameters were noted (ATSDR 2016).

#### Asthma-related Effects

 $H_2S$  may cause more adverse respiratory effects in people with asthma. Individuals with asthma exposed to 2 ppm  $H_2S$  for 30 minutes had increased airway resistance and possible bronchial obstruction, which can contribute to difficulty breathing. In a 2004 study, people who lived near industrial sources of  $H_2S$  were more likely to visit the hospital for asthma the day after high  $H_2S$  levels were measured in community air. Another study found a weak association between atmospheric  $H_2S$  levels and individuals needing treatment for asthma (ATSDR 2016).

#### Odor-related Effects

The odors caused by  $H_2S$  can also trigger asthma symptoms in the absence of irritant or chemical effects. Repeated exposure to chemicals with foul odors, like  $H_2S$ , can trigger asthma exacerbations (commonly known as asthma attacks) and other health effects (Schiffman and Williams 2005).

#### **Appendix E-5: Cancer Risk Assessment Calculations**

#### **Average Concentration Calculations**

Average concentrations of acetaldehyde, benzene, and chloroform were calculated for the purposes of cancer risk assessment. Measured or estimated concentrations were averaged from all composite samples taken in the same location. Locations were selected that had the highest detected concentrations of each compound.

Acetaldehyde was tentatively identified by test method EPA Method TO-15, which provided estimated concentrations. Some of these estimated concentrations were higher than the ATSDR CREG for acetaldehyde. As a conservative approach, acetaldehyde was evaluated for potential cancer risks at the estimated concentrations.

For non-detect measurements, MDHHS was unable to use analyte-specific and instrument-specific minimum detection limits (MDLs) as no analyte-specific MDLs were provided in any laboratory analysis results. The results from the 2021 EPA GMAP study included an analyte-specific reporting limit (RL) for chloroform, which was used in the absence of an MDL. Use of the RL may result in higher calculated averages than use of the MDL, and therefore, would result in a more conservative evaluation. For acetaldehyde and benzene, the EPA TO-15 maximum acceptable detection limit of 0.5 ppb (EPA 1999) was used.

Chemical	Study	Sample Location	Total Samples	Measurements (ppb)	Number of Non-detect Measurements	MDL or RL (ppb)	Average Concentr	ation
Circinical	Study	Location	Janipics	(ppo)	ivicasurements	ILL (PPD)	ppb	μg/m³
Acetaldehyde	2020 KWRP 2021 KWRP	Krom and Prouty Park	11	4.9, 2.4	9	0.5	1.07	1.93
,		Northeastern Elementary		,				
Benzene	2020 KWRP	School	3	0.7 <sup>30</sup>	2	0.5	0.57	1.81
Chloroform	2021 GMAP	Verburg Park	2	0.17	1	0.2931	0.23	1.12

#### Cancer Risk Calculations

Chemicals that were measured or estimated at concentrations higher than their respective CREG values and an average concentration higher than typical urban background concentrations for that chemical were included in the cancer risk calculations. This applied to both acetaldehyde and benzene, which had average concentrations that exceeded typical urban background concentrations. As the average concentration for chloroform (0.23 ppb) was

<sup>&</sup>lt;sup>30</sup> Benzene was also detected at lower concentrations in the May 2021 canister samples. The maximum detection, 0.7 ppb, was used to be health-protective.

<sup>&</sup>lt;sup>31</sup> This value represents the RL for this analyte. The measurement of 0.17 ppb was below the RL, and therefore is an estimated result.

consistent with typical urban background concentrations (0.2-0.5 ppb [ATSDR 2014]), cancer risk calculations were not completed.

Estimated cancer risks were calculated by multiplying the average concentration of each chemical by their respective inhalation unit risk (IUR) factors. IURs are calculated by the EPA and used to evaluate cancer risk from lifetime exposure to chemicals that can cause cancer. IURs used in this analysis were retrieved from the EPA IRIS database (EPA 2022).

Below is the equation used to calculate cancer risk:

Cancer risk = 
$$C (\mu g/m^3) \times IUR$$

Where:

C = Average concentration of chemical (in  $\mu g/m^3$ ) IUR= Inhalation Unit Risk Factor (in  $(\mu g/m^3)^{-1}$ )

Estimated cancer risk based on levels of acetaldehyde and benzene measured or estimated in the communities adjacent to GPI and KWRP are in the table below.

Chemical	C (μg/m³)	IUR ((μg/m³)-1)	Estimated cancer Risk
			Extra 4 cases of cancer in a similarly
			exposed population of one million (4.3E-
Acetaldehyde	1.93	2.20E-06	06)
			Extra 14 cases of cancer in a similarly
			exposed population of one million (14E-
Benzene	1.81	7.80E-06	06)

Appendix E-6: Odor Threshold Analysis of Chemicals Measured in Community Ambient Air near GPI and KWRP

		Highest detection	Odor Threshold	
Chemical	CAS#	(ppb)	(ppb)	Odor Threshold Source
(1-Methylethyl) (1,1-				
dimethylethyl)disulfide	43022-60-2	0.7	Unknown	
1,1-Difluoroethane	75-37-6	15.5	Odorless	NJH 2008
1,3,5-Trimethylbenzene	108-67-8	0.6	2,400	NJH 2003
1-Butanol	71-36-3	8.2	1	WebWiser 2022
2,2,4-Trimethylpentane	540-84-1	0.41	Unknown	EPA 2000
2,2,6-Trimethyloctane	62016-28-8	0.9	Unknown	
2,4-Dimethylheptane	2213-23-2	7.6	Unknown	
2,6-Lutidine	108-48-5	0.8	Unknown	
2-Butanol	78-92-2	0.9	43,000	WebWiser 2022
2-Butanone (methyl ethyl				
ketone)	78-93-3	44.1	5,400	ATSDR 2020
2-Ethyl-1-hexanol	104-76-7	1.7	75	Wakayama et al. 2019
2-Ethylhexylacetate	103-09-3	2.3	72.4	PubChem 2022
2-Ethylpyridine	100-71-0	0.7	Unknown	
2-Methylbutane	78-78-4	10.8	1,300	Chemical Book 2022
2-Methylpentane	107-83-5	11.6	7,000	Nagata 2003
2-Methylpropene	115-11-7	0.9	Unknown	
2-Methylpyridine	109-06-8	2.5	50	PubChem 2022
3-Methylpentane	96-14-0	5.7	8,900	Nagata 2003
3-Methylpyridine	108-99-6	0.6	Unknown	
4-Methyloctane	2216-34-4	4.8	Unknown	
Acetaldehyde*	75-07-0	4.9	1.5	Nagata 2003
Acetic acid	64-19-7	52.9	6	Nagata 2003
Acetic acid, ethenyl ester				
(Vinyl acetate)	108-05-4	1.2	120	NRC 2013
Acetone	67-64-1	13.5	13,000	WebWiser 2022

		Highest detection	Odor Threshold	
Chemical	CAS#	(ppb)	(ppb)	<b>Odor Threshold Source</b>
Benzene	71-43-2	0.7	1,500	ATSDR 2007
Bis(1-methylethyl)disulfide	4253-89-8	0.5	Unknown	
Butanoic acid	107-92-6	2.4	0.19	Nagata 2003
Carbon disulfide	75-15-0	7.4	20	ATSDR 1996
Chlorodifluoromethane	75-45-6	0.8	Unknown	
Chloroform	67-66-3	0.17	8,500	ATSDR 1997
Chloromethane	74-87-3	0.46	10,000	ATSDR 1998b
Cyclohexanone	108-94-1	21.9	880	WebWiser 2022
Dichlorodifluoromethane	75-71-8	0.8	Odorless	WebWiser 2022
Dimethyl disulfide	624-92-0	1.3	2.2	Nagata 2003
Dimethylsilanediol	1066-42-8	3.4	Unknown	
d-Limonene	5989-27-5	2.5	1.07	DEPA 2013
Ethanol	64-17-5	281.3	520	Nagata 2003
Ethyl acetate	141-78-6	69.4	3,900	WebWiser 2022
Hexamethylcyclotrisiloxane	541-05-9	18.7	Unknown	
Hydrogen sulfide	7783-06-4	85	0.5	ATSDR 2016
Isobutane	75-28-5	8.4	Unknown	
Isopropyl alcohol	67-63-0	276.7	40,000	NRC 1984
m & p-Xylene	1330-20-7	0.28	81	EPA 1992 <sup>1</sup>
Methoxy-phenyl-oxime-	67160-14-9	0.7	Unknown	
Methylcyclopentane	96-37-7	4.6	1,700	Nagata 2003
m-Xylene (1,3- Dimethylbenzene)	108-38-3	3.2	81	EPA 1992 <sup>1</sup>
n-Butanal	123-72-8	1	0.67	Nagata 2003
n-Butane	106-97-8	32	1,200	WebWiser 2022
n-Butyl acetate	123-86-4	0.6	700	OSHA 1992
n-Hexane	110-54-3	5.4	1,500	Nagata 2003
n-Nonanal	124-19-6	2.6	0.34	Nagata 2003

		Highest detection	Odor Threshold	
Chemical	CAS#	(ppb)	(ppb)	Odor Threshold Source
n-Pentane	109-66-0	244	1,400	Nagata 2003
o-Xylene	95-47-6	0.5	81	EPA 1992 <sup>1</sup>
p-Isopropyltoluene	99-87-6	1.5	57	Chemical Book 2022
Propane	74-98-6	2.8	1,500,000	Nagata 2003
Propene	115-07-1	14.5	23,000	NJ 2017
Propylene glycol	57-55-6	4.2	Odorless	NJ 2009
p-Xylene	106-42-3	4.4	81	EPA 1992 <sup>1</sup>
Pyridine	110-86-1	3.7	21	WebWiser 2022
Sulfur dioxide	7446-09-5	27.1	670	NRC 2010
Toluene	108-88-3	15.4	2,900	ATSDR 2017b
Trichlorofluoromethane	75-69-4	0.2	20%	PubChem 2022
Trimethylsilanol	1066-40-6	11.1	Unknown	

<sup>\*</sup> Estimated result

<sup>&</sup>lt;sup>1</sup>The minimum odor threshold of 81 ppb identified for m-xylene was used for all xylene isomers.

## Appendix E-7: Discussion of Volatile Organic Compounds that Exceeded Respective Minimum Odor Thresholds

#### 1-Butanol, CAS #71-36-3

1-Butanol has a rancid, sweet odor (PubChem 2022). MDHHS identified a minimum odor threshold of 1 ppb (WebWiser 2022). 1-Butanol was measured above its minimum odor threshold in 3.75 percent of all samples measured for VOCs. The highest measured concentration was 8.2 ppb from the October 2020 investigation. It was not detected in any samples from the May 2021 investigation.

#### Acetaldehyde, CAS #75-07-0

Acetaldehyde has a pungent, suffocating odor that has been described as pleasant and fruity in low concentrations (PubChem 2022). MDHHS identified a minimum odor threshold of 1.5 ppb (Nagata 2003). Acetaldehyde was measured above its minimum odor threshold in 3.75 percent of all samples measured for VOCs. The highest measured concentration was 4.9 ppb from the September 2021 investigation. It was not detected in any samples from the October 2020 or May 2021 investigations.

#### Acetic acid, CAS #64-19-7

Acetic acid has a sour, vinegar-like odor (PubChem 2022). MDHHS identified a minimum odor threshold of 6 ppb (Nagata 2003). Acetic acid was measured above its minimum odor threshold in one sample from the October 2020 investigation which had a measured concentration of 52.9 ppb. It was not detected in any samples from the May 2021 investigation and was not detected above 3.8 ppb in the September 2021 investigation.

#### Ammonia, CAS #7664-41-7

KWRP conducted ammonia monitoring during its October 2020 investigation. While no samples contained measurable amounts of ammonia, the method reporting limit (RL) was 5.56 ppm which exceeds the lower end of the odor threshold for ammonia (5 ppm) (NRC 2008). Only one sample collected from the sanitary sewer network, out of 18 samples, had detectable ammonia at 5.65 ppm and no samples from community locations had detectable ammonia. If the sanitary sewer network is the source of the odors, it is likely that, if present, ammonia was not higher than 5 ppm. However, due to the higher RL, it cannot be confirmed whether ammonia is contributing to environmental odors near GPI and KWRP.

#### Butanoic acid, CAS #107-92-6

Butanoic acid has a penetrating, rancid odor (PubChem 2022). MDHHS identified a minimum odor threshold of 0.19 ppb (Nagata 2003). Butanoic acid was measured above its minimum odor threshold in one sample from the September 2021 investigation which had a measured concentration of 2.4 ppb. It was not detected in any samples from the October 2020 or May 2021 investigations.

#### n-Butanal, CAS #123-72-8

n-Butanal (also known as butyraldehyde) has a pungent, aldehydic odor (PubChem 2022). MDHHS identified a minimum odor threshold of 0.67 ppb (Nagata 2003). N-Butanal was measured above its minimum odor threshold in one sample from the September 2021 investigation which had a measured concentration of 1 ppb. It was not detected in any samples from the October 2020 or May 2021 investigations.

#### d-Limonene, CAS #5989-27-5

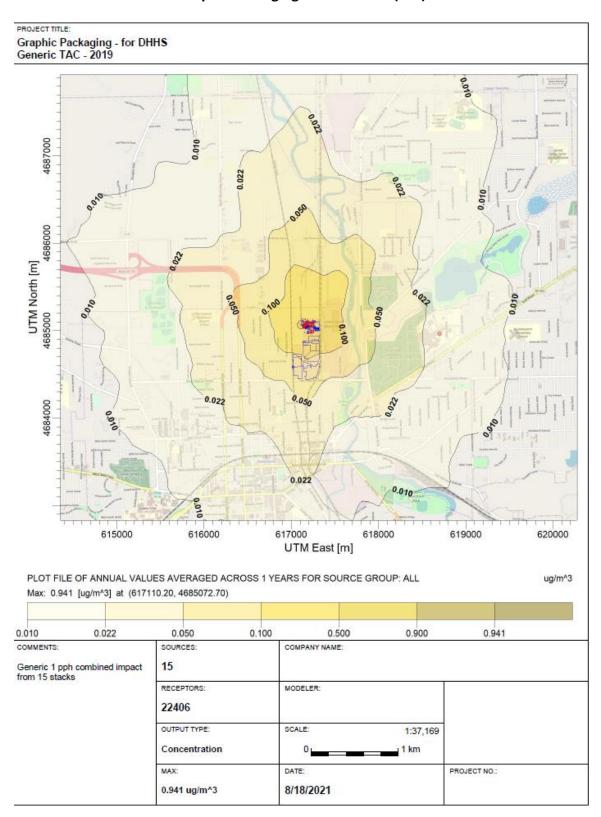
d-Limonene has a characteristic citrus odor (DEPA 2013). MDHHS identified a minimum odor threshold of 1.07 ppb (DEPA 2013). d-Limonene was measured above its minimum odor threshold in one sample from the October 2020 investigation which had a measured concentration of 2.5 ppb. It was not detected in any samples from the September 2021 or May 2021 investigations.

#### n-Nonanal, CAS #124-19-6

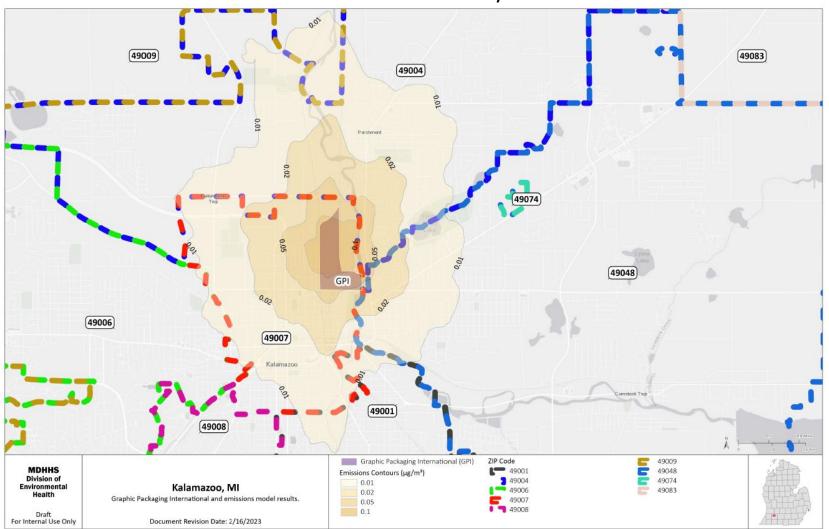
n-Nonanal has a rancid, sweet odor (PubChem 2022). MDHHS identified a minimum odor threshold of 1 ppb (WebWiser 2022). N-Nonanal was measured above its minimum odor threshold in 11.25 percent of all samples measured for VOCs. The highest measured concentration was 2.6 ppb from the October 2020 investigation. It was not detected in any samples from the May 2021 investigation.

# Appendix F: Data from Chronic Disease Epidemiology Section (CDES) Review of Asthma Prevalence and Hospitalization Rates in Kalamazoo

Appendix F-1: EGLE Modeled Emission Contour Lines for Annual Generic Emissions from Graphic Packaging International (GPI)



Appendix F-2: EGLE Modeled Emission Contour Lines for Annual Generic Emissions from Graphic Packaging International (GPI) with ZIP Code Overlay



# Appendix F-3: Asthma Prevalence and Hospitalization Within Selected ZIP Code Areas in the City of Kalamazoo

### Summary

This asthma data review was initiated as a result of resident concerns within the city of Kalamazoo, and not as a result of any documented cluster of asthma cases. This report provides asthma prevalence and hospitalization rates for selected groups of ZIP codes within the city of Kalamazoo compared to the state of Michigan.

- Persistent asthma prevalence among persons enrolled in Medicaid was either not significantly different or significantly lower for the ZIP code areas 49004+49007+49048 and 49001+49006+49008 compared to the state for all age groups.
- ZIP code area 49004+49007+49048 had significantly higher persistent asthma prevalence among Medicaid enrollees for age groups 0-64 years and 18-64 years compared to the ZIP code area 49001+49006+49008.
- There was no significant difference in adult lifetime or current asthma prevalence between ZIP code area 49004+49007+49048, ZIP code area 49001+49006+49008, and the state of Michigan.
- During 2016-2019, there was no significant difference in asthma hospitalization rates between ZIP code area 49004+49007+49048 and the state of Michigan. ZIP code area 49001+49006+49008 had significantly lower asthma hospitalization rates when compared to the state of Michigan during this time period.
- ZIP code area 49004+49007+49048 had significantly higher asthma hospitalization rates during 2017-2018 and 2018-2019 compared to ZIP code area 49001+49006+49008.

## **Background**

The Michigan Department of Health and Human Services' (MDHHS) Chronic Disease Epidemiology Section (CDES) conducted a review of data for asthma prevalence and hospitalization rates in selected groups of ZIP codes located within the city of Kalamazoo, Michigan. The analyses were prepared in response to community concern that exposure to H<sub>2</sub>S and other air pollutants released from Graphic Packaging International, LLC (GPI) and the Kalamazoo Water Reclamation Plant (KWRP) is resulting in asthma exacerbation. The goal of this review was to determine if selected ZIP code areas surrounding GPI and KWRP in the city of Kalamazoo experienced significantly different asthma prevalence or hospitalization rates compared to the state of Michigan.

#### Methods

MDHHS Division of Environmental Health evaluated modeled emission contour lines developed by the Michigan Department of Environment, Great Lakes and Energy (EGLE) for generic emissions from the GPI facility to determine the regions of the city of Kalamazoo where there was an emission influence on air quality. Two regions of the city of Kalamazoo, each made up of three ZIP codes each, were identified for the analysis of asthma prevalence and hospitalizations. The first region (49004, 49007, 49048) was modelled by EGLE to show a larger emission influence on the air in that location, while the second region (49001, 49006, 49008) showed less emission influence. Note that ZIP code 49007 is where both GPI and KWRP are located.

Data from three sources were used for the following analysis.

- 1. MDHHS Health Data Warehouse: Medicaid persistent asthma prevalence for 2019 was calculated for ZIP code area 49004+49007+49048, ZIP code area 49001+49006+49008, and the state. The population for this analysis was identified from the Michigan Medicaid beneficiary and administrative claims data from 2019. The analysis included people who had continuous Medicaid enrollment (11+ months in 2019), full Medicaid coverage, and no other insurance. Both fee-for-service and managed care beneficiaries were included. Medicaid persistent asthma prevalence measures are accompanied by 95-percent confidence intervals. Prevalence of persistent asthma was the percentage of beneficiaries in the identified population who meet the Healthcare Effectiveness Data and Information Set (HEDIS®) definition of persistent asthma defined below.
  - Persistent asthma prevalence: Health care utilization consistent with the diagnosis of asthma was defined according to HEDIS® specifications; in the year of the prevalence measurement, having (1) ≥4 asthma medication dispensing events OR (2) ≥1 emergency department visits for asthma OR (3) ≥1 hospitalization for asthma OR (4) ≥4 outpatient visits for asthma and ≥2 asthma medication dispensing events (National Committee for Quality Assurance. Appropriate Medications for People with Asthma. HEDIS® 2019, Volume 2: Technical Specifications. Washington, DC; 2019).
- 2. <u>Michigan Behavioral Risk Factor Survey (MiBRFS):</u> Adult lifetime and current asthma prevalence was calculated using data from the MiBRFS. MiBRFS is a statewide telephone survey of Michigan adults aged 18 years and older and is part of the national Behavioral Risk Factor Surveillance System coordinated by the Centers for Disease Control and Prevention. Five years of survey data, 2016-2020, were combined to obtain prevalence measures for the two ZIP code areas and the state of Michigan. Lifetime and current asthma prevalence measures are accompanied by their 95-percent confidence intervals. The following describe how the prevalence measures are defined.
  - Adult lifetime asthma is the proportion of Michigan adults who reported that they were ever told by a doctor, nurse, or other health care professional that they had asthma.
  - Current asthma is the proportion of Michigan adults who reported that they still have asthma.

3. Michigan Inpatient Database (MIDB): Asthma hospitalization data for 2016-2019 were obtained from the Michigan Health and Hospital Association's MIDB. An asthma hospitalization was defined as an inpatient stay with a primary discharge diagnosis of asthma (International Classification of Disease, Version 10, Clinical Modification; ICD-10-CM=J45.XX). These data represent the number of hospitalizations for asthma, not the number of persons with a hospitalization for asthma. Overlapping two-year rates were calculated and are presented per 10,000 population for the two ZIP code areas and the state of Michigan as a whole. Rates were age-adjusted to the US standard population to account for differences in the age distribution of the geographies being compared. Rates are accompanied by their 95-percent confidence intervals.

For all three of these data analyses, statistical differences were determined using the 95-percent confidence intervals. Two measures are considered statistically significantly different if their 95-percent confidence intervals do not overlap. If the confidence intervals do overlap, the two rates are considered not statistically different.

#### Limitations

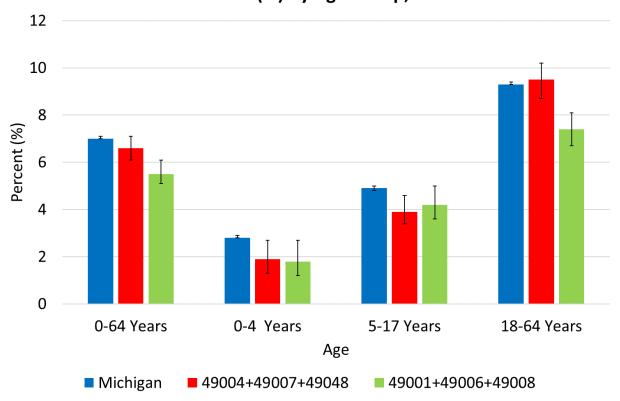
- Results of this investigation are based on surveillance data and not an epidemiologic research study of the relationship between asthma prevalence (or hospitalizations) and environmental contaminants. Therefore, these results cannot indicate whether asthma occurrence in the selected ZIP code areas are related to or caused by environmental contaminant exposures. If a statistical difference is observed among the results of these analyses, it does not necessarily mean that the difference is due to an environmental exposure.
- The small number of asthma cases and asthma hospitalizations in the selected ZIP code areas limited the types of analyses that could be conducted. First, multiple years of data were combined for the analysis of asthma prevalence measures from the MiBRFS and asthma hospitalization rates from the MIDB. Second, analysis by individual ZIP codes could not be conducted. Lastly, analysis by race group could not be conducted. Analyses using small numbers of asthma cases or asthma hospitalizations result in imprecise measures.

#### Results

The following data tables and figures provide the results of the analyses from the three datasets: 1) MDHHS Health Data Warehouse, 2) MiBRFS, and 3) MIDB. For each, the data are first presented in a graph form and secondly in tabular form. A summary of findings is provided after each set of results.

# 1. Medicaid Persistent Asthma Prevalence among Persons 0-64 Years Enrolled in Medicaid (Source: MDHHS Health Data Warehouse)

Figure 1. Age-adjusted<sup>1</sup> Medicaid Persistent Asthma<sup>2,3</sup> Prevalence (%) by Age Group, 2019



<sup>&</sup>lt;sup>1</sup>Age-adjusted to the 2000 US Standard Population

Note: For some prevalence measures, the lower or upper bound of the 95-percent confidence interval equals the prevalence measure due to rounding.

<sup>&</sup>lt;sup>2</sup>Based on annual NCQA HEDIS® definition

<sup>&</sup>lt;sup>3</sup>MDHHS Health Data Warehouse, 2019

Table 1. Age-Adjusted <sup>1</sup> Medicaid Persistent Asthma <sup>2,3</sup> Prevalence by Age Group, 2019					
	Count	Percent (%)	Lower 95%	Upper 95%	
			Confidence	Confidence	
			Limit <sup>4</sup> (%)	Limit <sup>4</sup> (%)	
Michigan					
0-64 years	106,781	7.0	7.0	7.1	
0-4 years	5,192	2.8	2.8	2.9	
5-17 years	25,028	4.9	4.8	5.0	
18-64 years	76,561	9.3	9.3	9.4	
49004+49007+49048					
0-64 years	758	6.6	6.1	7.1	
0-4 years	28	1.9	1.3	2.7	
5-17 years	156	3.9	3.4	4.6	
18-64 years	574	9.5	8.7	10.2	
49001+49006+49008					
0-64 years	560	5.5	5.1	6.0	
0-4 years	24	1.8	1.2	2.7	
5-17 years	154	4.2	3.6	5.0	
18-64 years	382	7.4	6.7	8.1	

<sup>&</sup>lt;sup>1</sup>Age-adjusted to the 2000 US Standard Population

#### **Summary of Findings**

- There was no significant difference in persistent asthma prevalence between the ZIP code area 49004+49007+49048 and the state of Michigan among age group 0-64 years or 18-64 years enrolled in Medicaid. Persistent asthma prevalence was significantly lower in the ZIP code area 49004+49007+49048 compared to the state for age groups 0-4 years and 5-17 years.
- ZIP code area 49001+49006+49008 had significantly lower persistent asthma prevalence among Medicaid enrollees in age groups 0-64 years, 0-4 years, and 18-64 years compared to the state; there was no significant difference in the prevalence measure for those 5-17 years.
- The ZIP code area 49004+49007+49048 had significantly higher persistent asthma prevalence among Medicaid enrollees for age groups 0-64 years and 18-64 years compared to the ZIP code area 49001+49006+49008, while the prevalence for all other age groups was not significantly different between the two ZIP code areas.

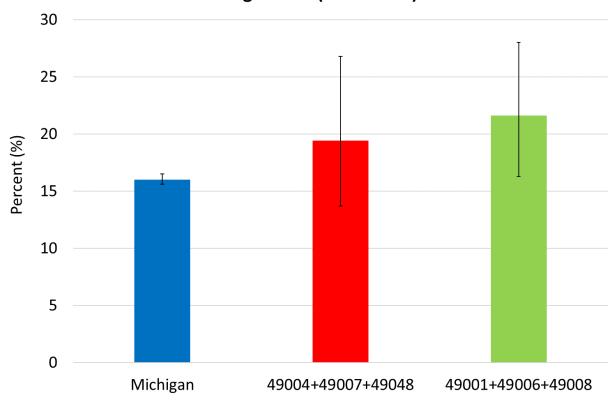
<sup>&</sup>lt;sup>2</sup>Based on annual NCQA HEDIS® definition

<sup>&</sup>lt;sup>3</sup>MDHHS Health Data Warehouse, 2019

<sup>&</sup>lt;sup>4</sup>For some prevalence measures, the lower or upper bound of the 95-percent confidence interval equals the prevalence measure due to rounding.

# 2. Lifetime and Current Asthma Prevalence among Adults (Source: MiBRFS)

Figure 2. Lifetime Asthma<sup>1</sup> Prevalence (%) Among Adults (2016-2020)

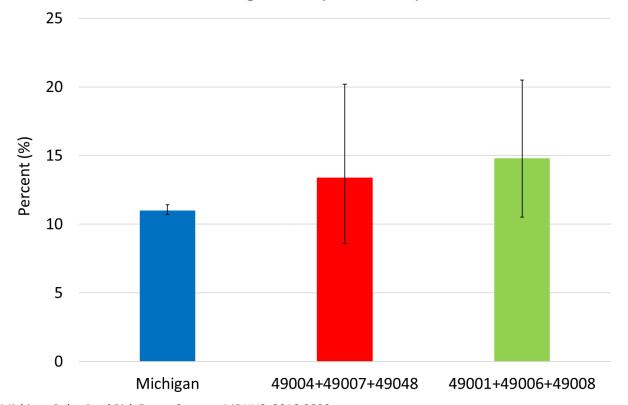


<sup>&</sup>lt;sup>1</sup>Michigan Behavioral Risk Factor Surveys, MDHHS, 2016-2020

Table 2. Lifetime Asthma <sup>1</sup> Prevalence (%) Among Adults (2016-2020)						
	Percent (%)	Lower 95%	Upper 95%			
		Confidence	Confidence			
		Limit (%)	Limit (%)			
Michigan	16.0	15.6	16.5			
49004+49007+49048	19.4	13.7	26.8			
49001+49006+49008	21.6	16.3	28.0			

<sup>&</sup>lt;sup>1</sup>Michigan Behavioral Risk Factor Surveys, MDHHS, 2016-2020

Figure 3. Current Asthma<sup>1</sup> Prevalence (%) Among Adults (2016-2020)



<sup>&</sup>lt;sup>1</sup>Michigan Behavioral Risk Factor Surveys, MDHHS, 2016-2020

Table 3. Current Asthma <sup>1</sup> Prevalence (%) Among Adults (2016-2020)						
	Percent (%)  Lower 95%  Confidence  Limit (%)  Upper 95%  Confidence  Limit (%)					
Michigan	11.0	10.7	11.4			
49004+49007+49048	13.4	8.6	20.2			
49001+49006+49008	14.8	10.5	20.5			

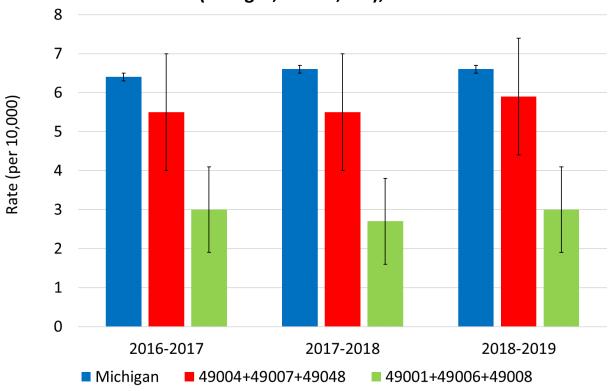
<sup>&</sup>lt;sup>1</sup>Michigan Behavioral Risk Factor Surveys, MDHHS, 2016-2020

#### **Summary of Findings**

- There was no significant difference in adult lifetime asthma prevalence between ZIP code area 49004+49007+49048, ZIP code area 49001+49006+49008, and the state of Michigan.
- There was no significant difference in adult current asthma prevalence between ZIP code area 49004+49007+49048, ZIP code area 49001+49006+49008, and the state of Michigan.

## 3. Asthma Hospitalization Rates, All Ages (Source: MIDB)

Figure 4. Age Adjusted<sup>1</sup> Asthma Hospitalization Rates<sup>2</sup> (All Ages, Per 10,000), 2016-2019



<sup>&</sup>lt;sup>1</sup>Age-adjusted to the 2000 US Standard Population

<sup>&</sup>lt;sup>2</sup>Michigan Inpatient Database, 2016-2019, MDHHS

Table 4. Age Adjusted <sup>1</sup> Asthma Hospitalization Rates <sup>2</sup>								
	(All Ages, Per 10,000), 2016-2019							
	Count	Count Rate per 10,000 Lower 95% U						
			Confidence	Confidence				
			Limit	Limit				
Michigan								
2016-2017	12,046	6.4	6.3	6.5				
2017-2018	12,253	6.6	6.5	6.7				
2018-2019	12,230	6.6	6.5	6.7				
49004+49007+49048								
2016-2017	57	5.5	4.0	7.0				
2017-2018	56	5.5	4.0	7.0				
2018-2019	59	5.9	4.4	7.4				
49001+49006+49008								
2016-2017	38	3.4	2.3	4.5				
2017-2018	32	2.7	1.6	3.8				
2018-2019	33	3.0	1.9	4.1				

<sup>&</sup>lt;sup>1</sup>Age-adjusted to the 2000 US Standard Population

#### **Summary of Findings**

- During 2016-2019, there was no significant difference in asthma hospitalization rates between ZIP code area 49004+49007+49048 and the state of Michigan.
- ZIP code area 49001+49006+49008 had significantly lower asthma hospitalization rates when compared to the state of Michigan during this time period.
- ZIP code area 49004+49007+49048 had significantly higher asthma hospitalization rates during 2017-2018 and 2018-2019 compared to ZIP code area 49001+49006+49008. The asthma hospitalization rates for 2016-2017 were not significantly different between the two ZIP code areas.

<sup>&</sup>lt;sup>2</sup>Michigan Inpatient Database, 2016-2019, MDHHS

#### Conclusion

This data review of asthma prevalence and asthma hospitalization rates provides a descriptive analysis of the occurrence of asthma in selected ZIP code areas in the city of Kalamazoo and the state as a whole. While asthma measures are not significantly different or are significantly lower in each of the ZIP code areas when compared to the state, regional differences are observed when comparing the ZIP code areas to each other. Therefore, further investigation to understand these patterns is warranted.

It is important to consider, however, the limitations of the analyses when evaluating the findings. Since this report is a descriptive review of asthma prevalence and hospitalization from surveillance data, it does not provide evidence that potential exposure to any environmental contaminant has resulted in higher or lower asthma prevalence or hospitalization. It is also worth noting that when an individual's asthma is not well controlled, it can lead to more severe outcomes such as frequent hospitalizations. Lastly, increased or decreased asthma prevalence and hospitalization in an area during a period of time can occur by chance alone.