MICHIGAN DEPARTMENT OF
ENVIRONMENT, GREAT LAKES, AND ENERGY

Modeling of H_2S Emissions and Impacts for the City of Kalamazoo

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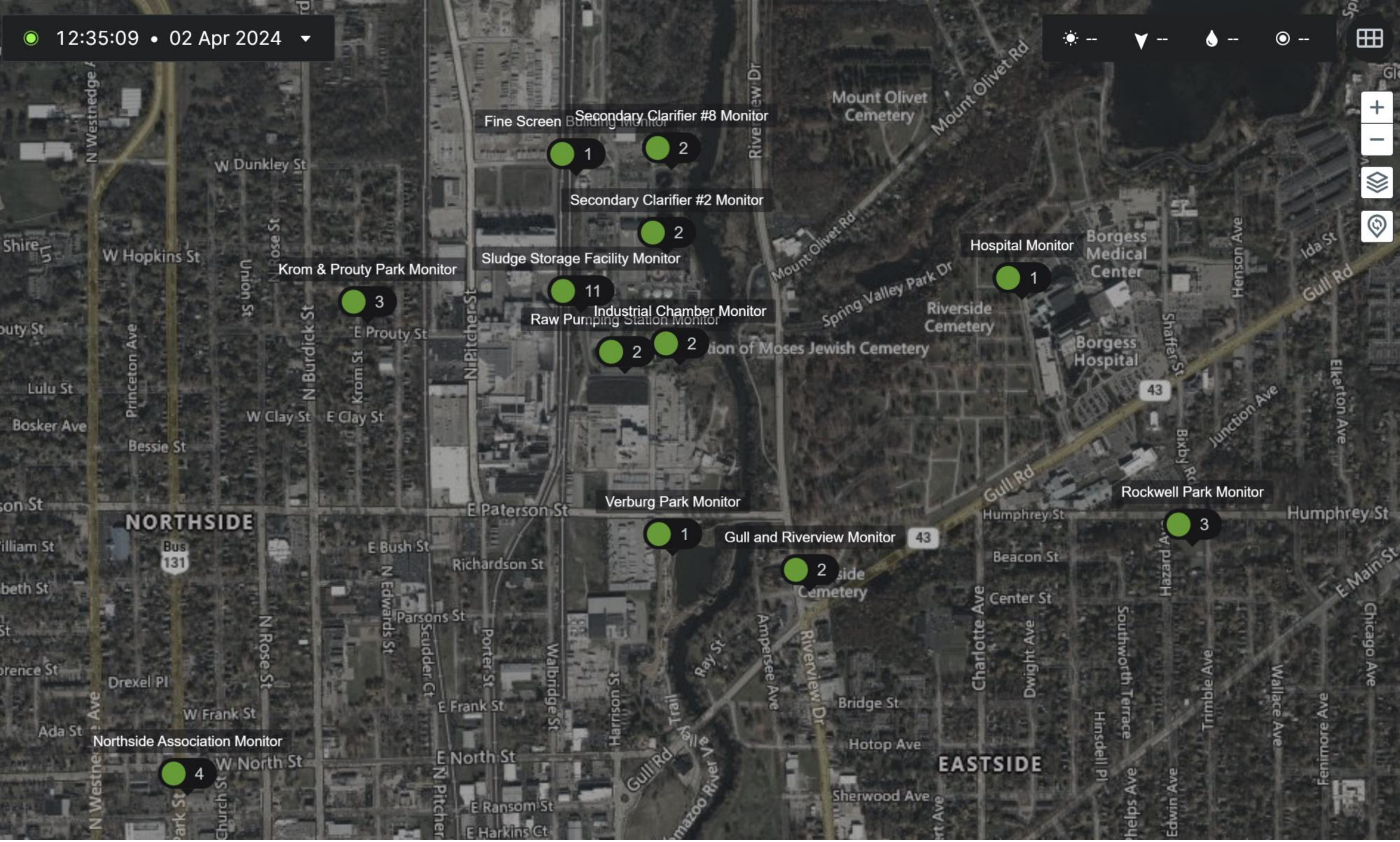
Background

- Hydrogen Sulfide (H_2S) is a reduced sulfur compound (RSC) with an odor threshold of a few ppb. The EPA Reference Concentration (RfC) for long-term health effects is 1.4 ppb.
- In Kalamazoo, Michigan the Kalamazoo Water Reclamation Plant (KWRP) and a paper mill run by Graphic Packaging International (GPI) are known sources of H_2S.
- The Michigan Department of Health and Human Services concluded that health effects at neighborhoods near GPI and KWRP are likely due to long-term exposure to H_2S > RfC.
- Since 2019, both GPI and the City of Kalamazoo have run networks of Envirosuite eNose sensors for RSC/H_2S detection.
- Sensor range: 0-1000 ppb; Limit of Detection: 10 ppb; measurement frequency: 1 minute.



City of Kalamazoo H_2S Sensor Network

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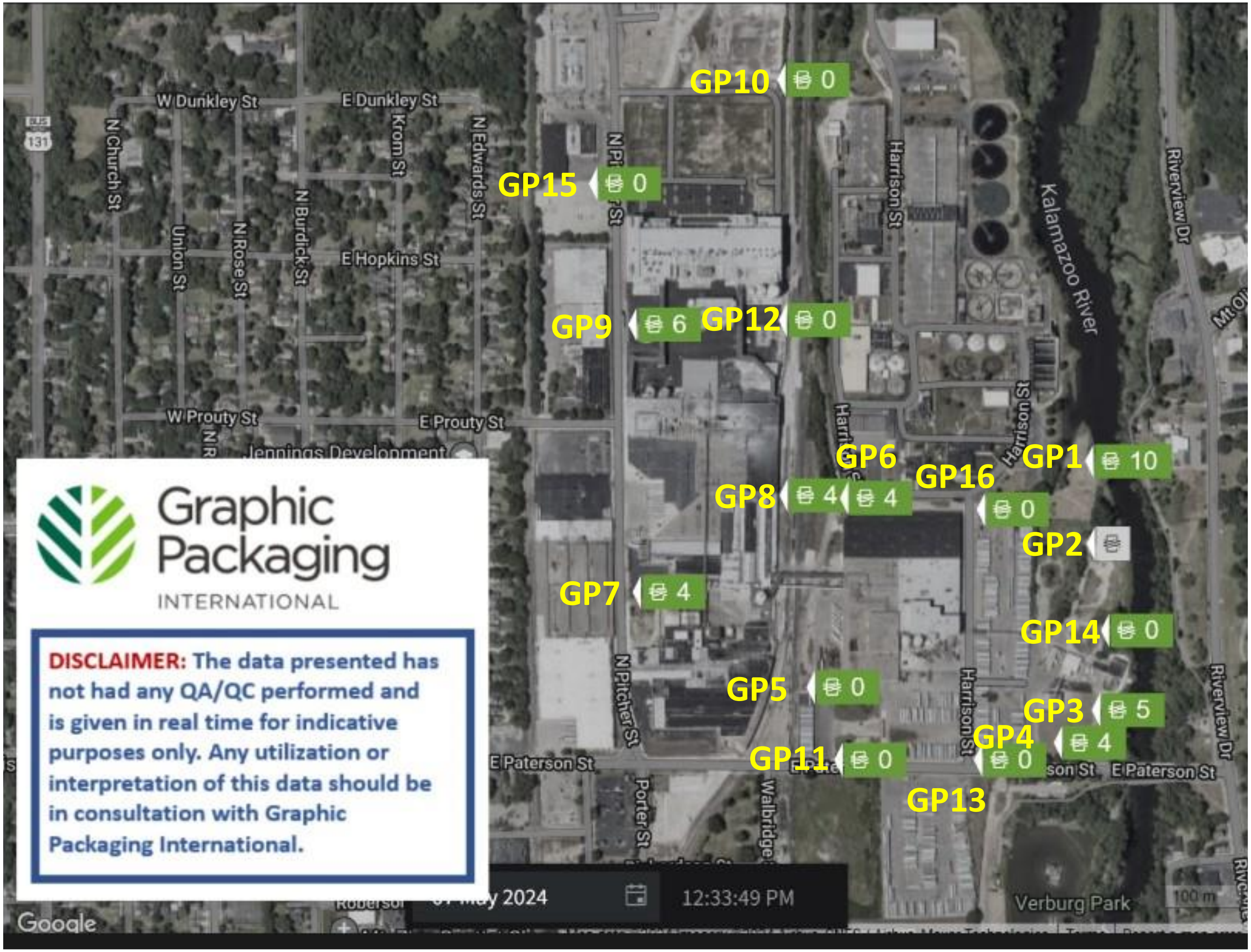


Graphic Packaging International H_2S Sensor Network

Study Motivation

- Direct measurement of long-term, spatially variable, low-ppb concentrations of H_2S is currently impractical.
- It is much easier to estimate emissions from measured short-term H_2S concentrations close to sources under favorable meteorological conditions (stronger signals).
- Estimated emissions can be used in an air dispersion model such as AERMOD to generate long-term concentrations over a wider area with more general meteorology.
- This assumes the inferred emissions are steady and much less influenced by variable weather than concentrations.

Source Attribution of H_2S

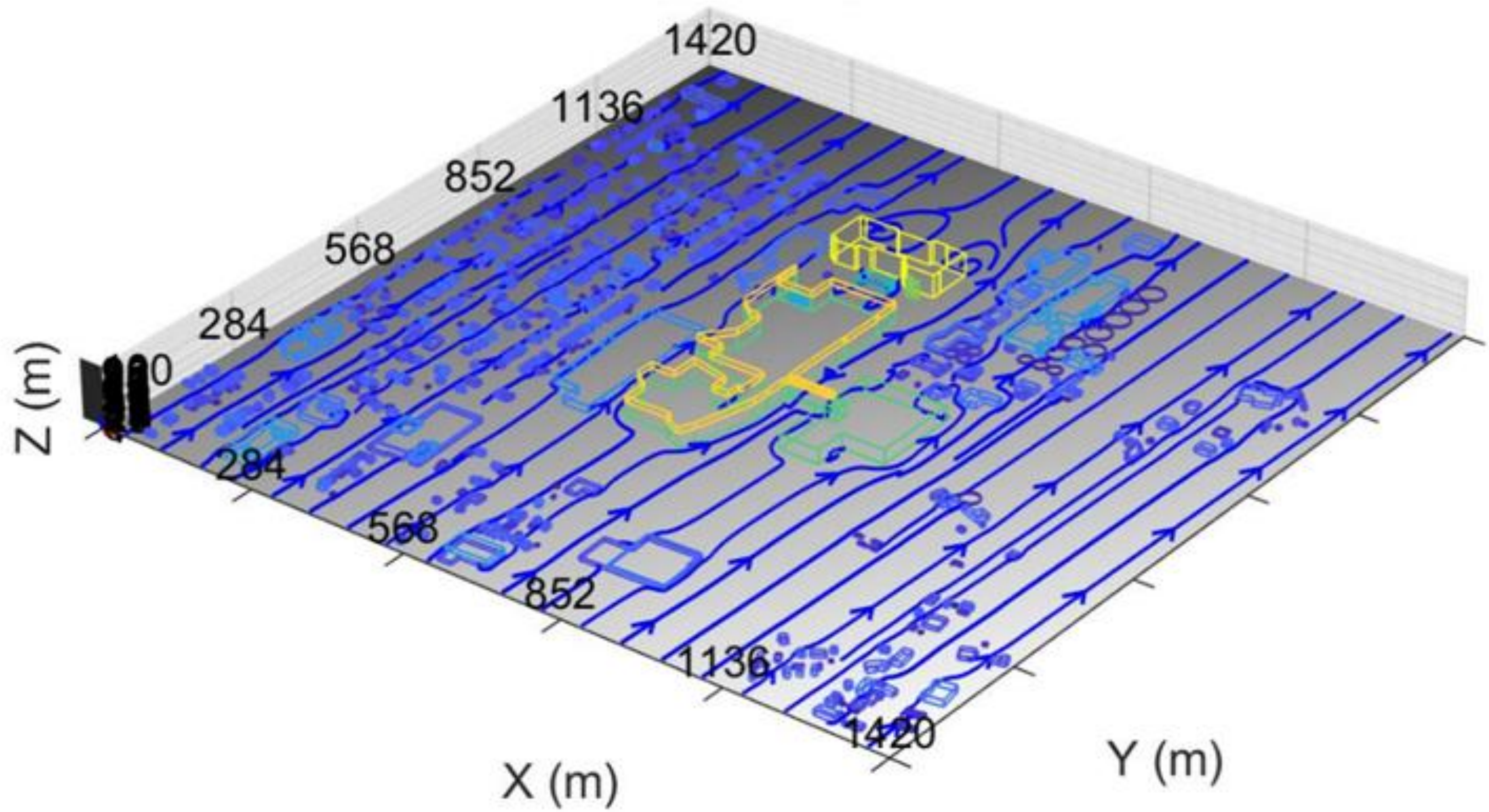
- **Possible emission sources:**
  - Fugitive and/or stack emissions (GPI, KWRP)
  - Diesel engines (trucks, rail, off-road equipment)
  - Anaerobic bacterial decomposition of sewer waste
  - Kalamazoo River water and sediments
- **Inverse modeling:**
  - 3D Eulerian transport model (H_2S as a passive tracer)
  - 4D variational data assimilation (4Dvar) of sensor measurements to quantify emissions from sources
  - Assume stable atmospheric conditions during May 2023 to limit dilution by vertical mixing

Microscale Forward and Adjoint Chemical Transport Model (MicroFACT)

- Fine-scale, 3-D Eulerian grid model with forward and inverse (adjoint method, 4Dvar data assimilation) modes
- Building-sensitive winds derived from QUIC model
- Transport by mean wind (advection) and air turbulence (diffusion)
- Chemistry is simulated by 116 gas-phase, 7 heterogeneous reactions (ground and aerosol surfaces)
- Simulates cumulative ambient exposure to multiple reactive chemicals
- Chemistry turned off for simulations of passive tracers
- Can infer emissions from ambient air measurements
- Previously used to estimate formaldehyde emissions from industrial and mobile sources based on Aerodyne mobile lab measurements in the 2021 Michigan-Ontario Ozone Source Experiment (MOOSE)

Olaguer, E.P., 2023. *Atmosphere, 14,* 931. https://doi.org/10.3390/atmos14060931

QUIC Model Wind Simulation



Layer Number	1	2	3	4	5	6	7	8	9	10
Mid-Point Height (m)	1	3	5	7	9	12.6	21	35.8	57	84.6
Layer Thickness (m)	2	2	2	2	2	5.2	11.6	18	24.4	30.8

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Meteorological Data for May 2023

Parameter	0 deg	45 deg	90 deg	135 deg	180 deg	225 deg	270 deg	315 deg
Friction Velocity (m/s)	0.12	0.15	0.10	0.14	0.14	0.10	0.20	0.33
Lapse Rate (K/m)	0.009	0.009	0.009	0.009	0.009	0.009	0.009	0.009
Mixing Height (m)	113.9	149.4	83.7	128.2	136.5	80.7	251.0	509.0
Monin-Obukhov Length (m)	35.4	32.2	22.1	32.8	28.4	19.5	93.3	191.5
Surface Roughness (m)	0.029	0.029	0.033	0.030	0.031	0.043	0.033	0.037
Wind Speed (m/s)	1.8	2.3	1.5	2.1	2.2	1.4	3.0	4.9
Air Temperature (K)	286.5	286.3	288.1	287.6	286.0	284.9	280.6	282.5
Relative Humidity (%)	69.1	55.1	58.5	71.5	64.4	59.2	76.2	71.2
Surface Pressure (atm)	0.988	0.990	0.990	0.987	0.986	0.986	0.976	0.978

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Avg 1-Hr H_2S Data (ppb) for May 2023

Sensor ID	0 deg	45 deg	90 deg	135 deg	180 deg	225 deg	270 deg	315 deg
GP1	3.04	1.59	2.73	2.35	2.07	2.25	2.67	2.37
GP2	1.87	0.59	1.14	2.14	1.31	1.04	1.25	0.91
GP3	2.53	1.36	2.08	1.79	0.99	2.37	1.88	2.14
GP4	3.16	1.56	2.38	2.43	1.33	2.79	3.73	2.98
GP5	4.61	1.60	2.54	2.52	2.86	2.80	2.26	1.31
GP6	9.30	4.29	6.69	5.42	3.05	10.43	4.07	2.25
GP7	3.10	2.20	3.20	2.89	3.08	3.48	3.43	3.69
GP8	4.69	2.89	4.66	2.78	2.35	6.41	3.62	2.10
GP9	0.17	0.45	0.40	0.13	0.30	0.07	0.10	0.13
GP10	0.50	0.10	0.07	0.20	2.43	0.07	0.33	0.62
GP12	0.00	0.09	0.00	0.17	5.06	0.00	0.01	0.46
GP14	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.21
GP16	0.22	0.00	0.00	0.01	1.64	0.00	0.00	0.00
Building 21	6.57	3.60	4.92	5.75	3.40	8.47	4.53	4.44
Fine Screen	1.28	0.33	0.66	0.80	2.24	0.54	0.60	0.54
Gull and Riverview	2.28	0.89	0.98	1.39	1.64	1.32	1.41	1.24
Industrial Chamber	0.52	0.07	0.25	0.30	0.32	0.00	0.32	0.07
Krom & Prouty Park	5.02	3.07	3.93	3.73	4.16	5.03	4.69	4.19
Raw Pumping Station	1.95	0.89	1.09	1.75	1.03	1.00	0.40	0.50
Secondary Clarifier 2	5.81	4.43	6.15	4.42	4.90	9.08	6.22	3.61
Secondary Clarifier 8	0.43	0.20	0.20	0.31	0.27	0.07	0.00	0.65
Sludge Storage Facility	14.04	12.84	10.52	9.93	7.68	8.19	7.22	5.71
Verberg Park	5.83	3.80	4.13	3.53	4.38	5.55	4.71	3.87
Hospital	5.32	2.57	4.42	3.39	2.90	5.11	3.93	4.13
Measurement Error	1.96	1.67	2.89	2.01	2.99	4.38	2.73	1.91
Boundary Condition	0.32	0.20	0.45	0.47	0.27	0.17	0.135	0.135

Measurement Error = Average Site Uncertainty; Site Uncertainty = (10 ppb)/sqrt(N)

N = # of hours in wind scenario for which $0 < H_2S < 800$ ppb

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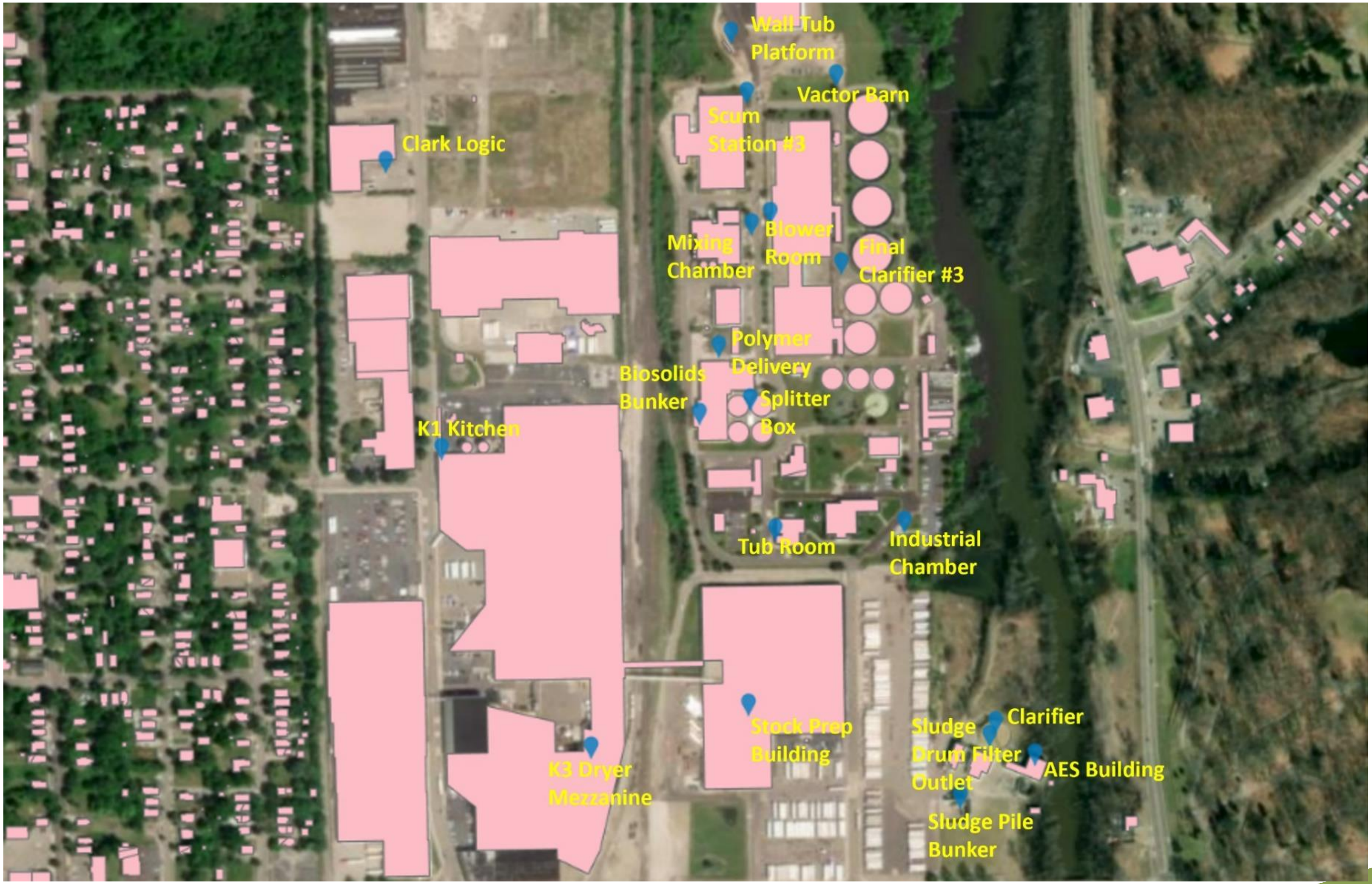
Fugitive Emission Sources



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Model-Inferred Fugitive Emissions

Emission Source	Average (lbs/yr)	Maximum (lbs/yr)
Biosolids Bunker	634.2	1126.9
Tub Room	7.1	8.0
Splitter Box	346.0	953.6
Polymer Delivery	17.2	25.2
Mixing Chamber	11.3	24.8
Blower Room	11.3	24.8
Scum Station #3	7.2	8.0
Wall Tub Platform	7.0	7.6
Back Pad Mailbox	7.1	7.8
Final Clarifier #3	1066.6	1578.7
Industrial Chamber	7.1	7.5
Vactor Barn	7.0	7.1
Clarifier	13.0	43.1
Sludge Drum Filter Outlet	8.7	14.1
AES Building	8.1	11.5
Sludge Pile Bunker	35.5	162.6
Stock Prep Building	21.1	55.1
K1 Kitchen	11.6	18.5
K3 Dryer Mezzanine	66.5	183.0
Clark Logic	8.1	11.6
KWRP TOTAL	**2129.2**	**3144.1**
GPI TOTAL	**164.5**	**277.2**

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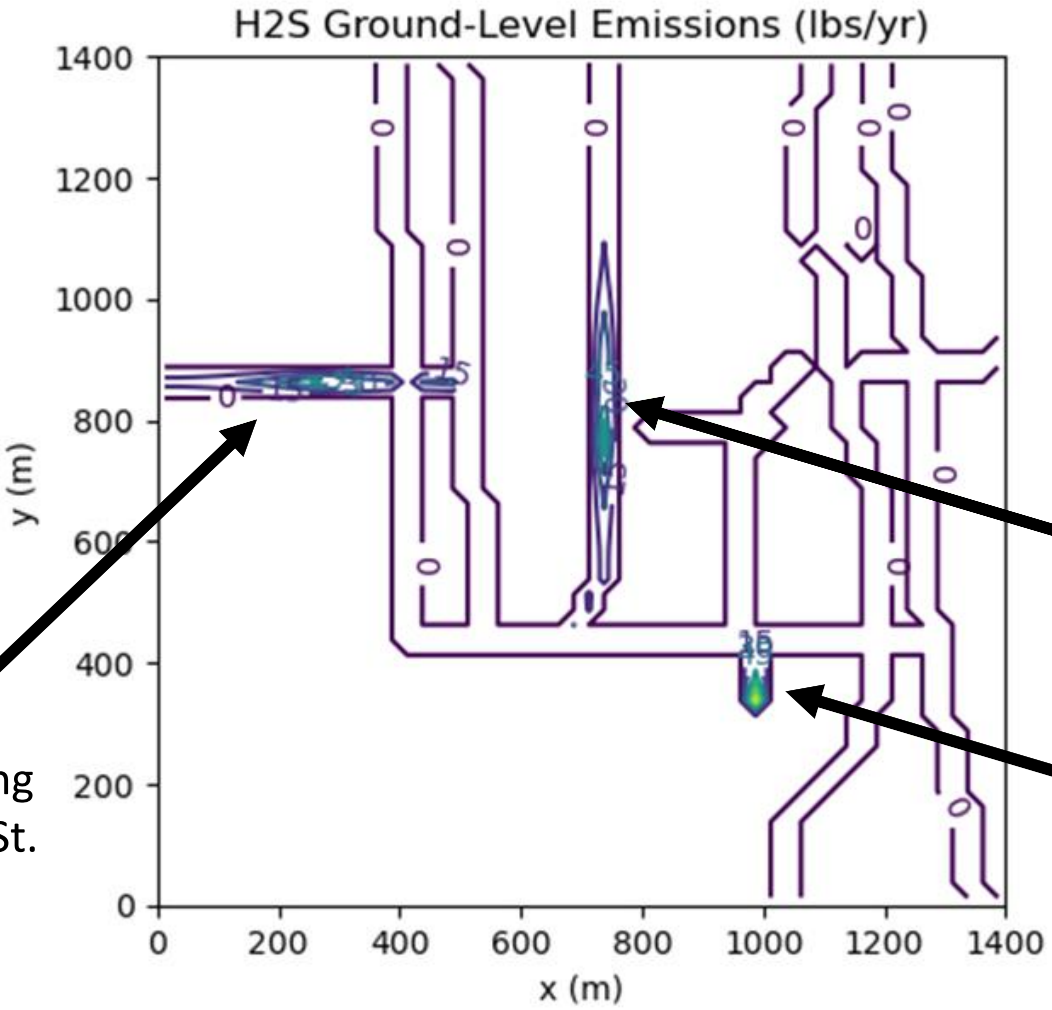
Road, Rail, River, and Sewer Emissions

Emission Source	Average (lbs/yr)	Maximum (lbs/yr)
E Prouty St	1431.5	5384.6
N Pitcher St	345.0	461.6
E Paterson St	272.0	319.4
Harrison St	128.1	179.6
Kalamazoo River Valley Trail	323.5	487.8
Riverview Drive	448.6	557.4
Railroad West	284.7	303.5
Railroad East	376.3	963.9
Kalamazoo River	80.4	134.1
Sewer Line	53.1	85.2

Unusual Activity Emissions



SW Wind Scenario

Railroad activities

Traffic re-routing at East Prouty St.

Dredging at Kalamazoo River Valley Trail

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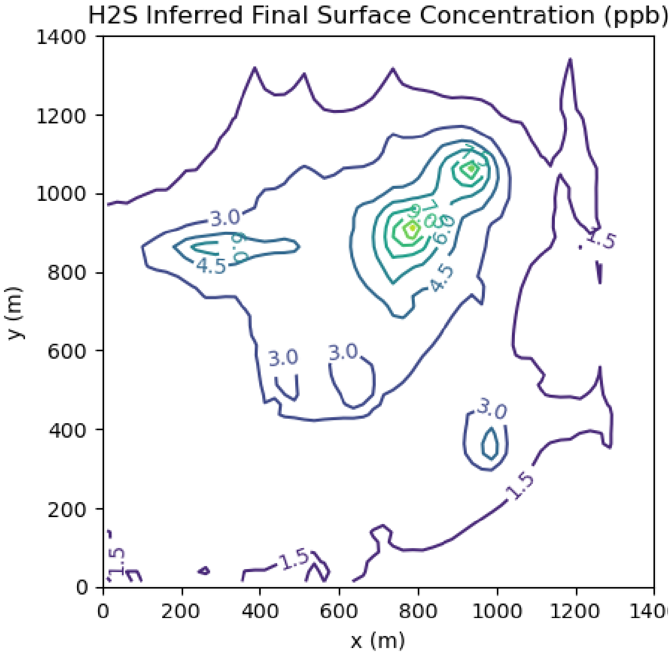
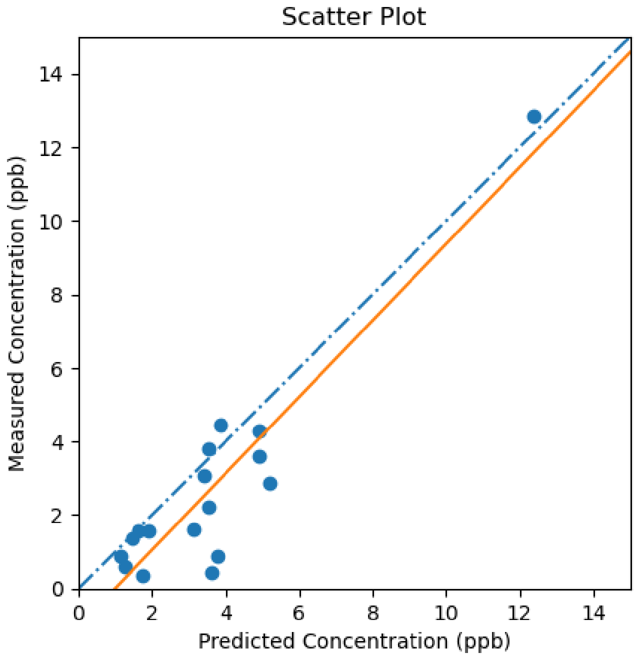
Performance Evaluation

NE Wind Scenario





All Wind Scenarios

Wind Scenario	Slope	Correlation Coefficient (R)	R^2
N	1.076	0.897	0.805
NE	1.040	0.927	0.858
E	1.026	0.853	0.728
SE	1.045	0.859	0.737
S	1.143	0.808	0.653
SW	1.111	0.832	0.692
W	0.972	0.862	0.744
NW	1.081	0.891	0.793

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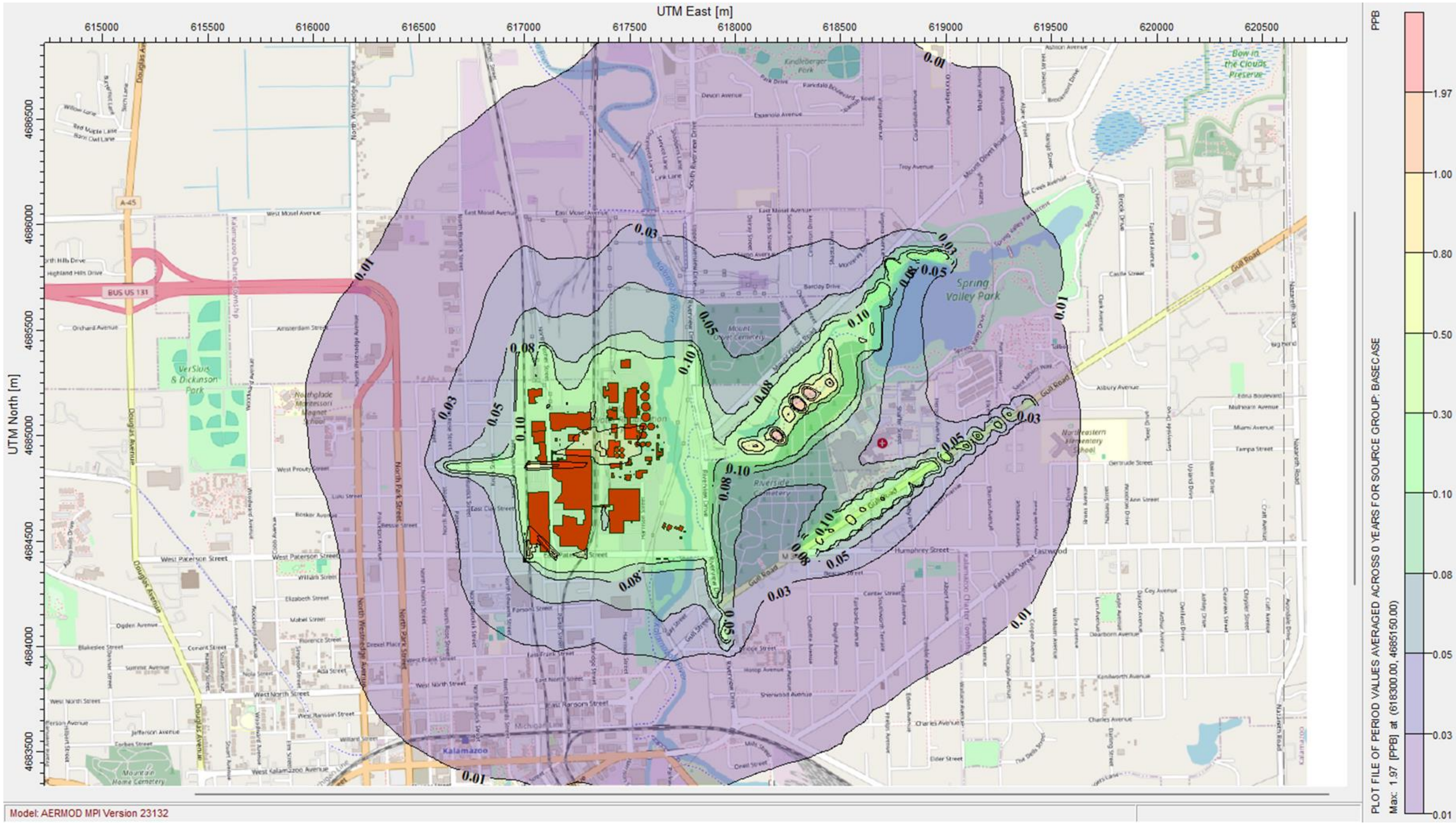
Base Case 5-Year Average Impacts



Note: Unusual or discontinued emissions removed or replaced by typical emissions.

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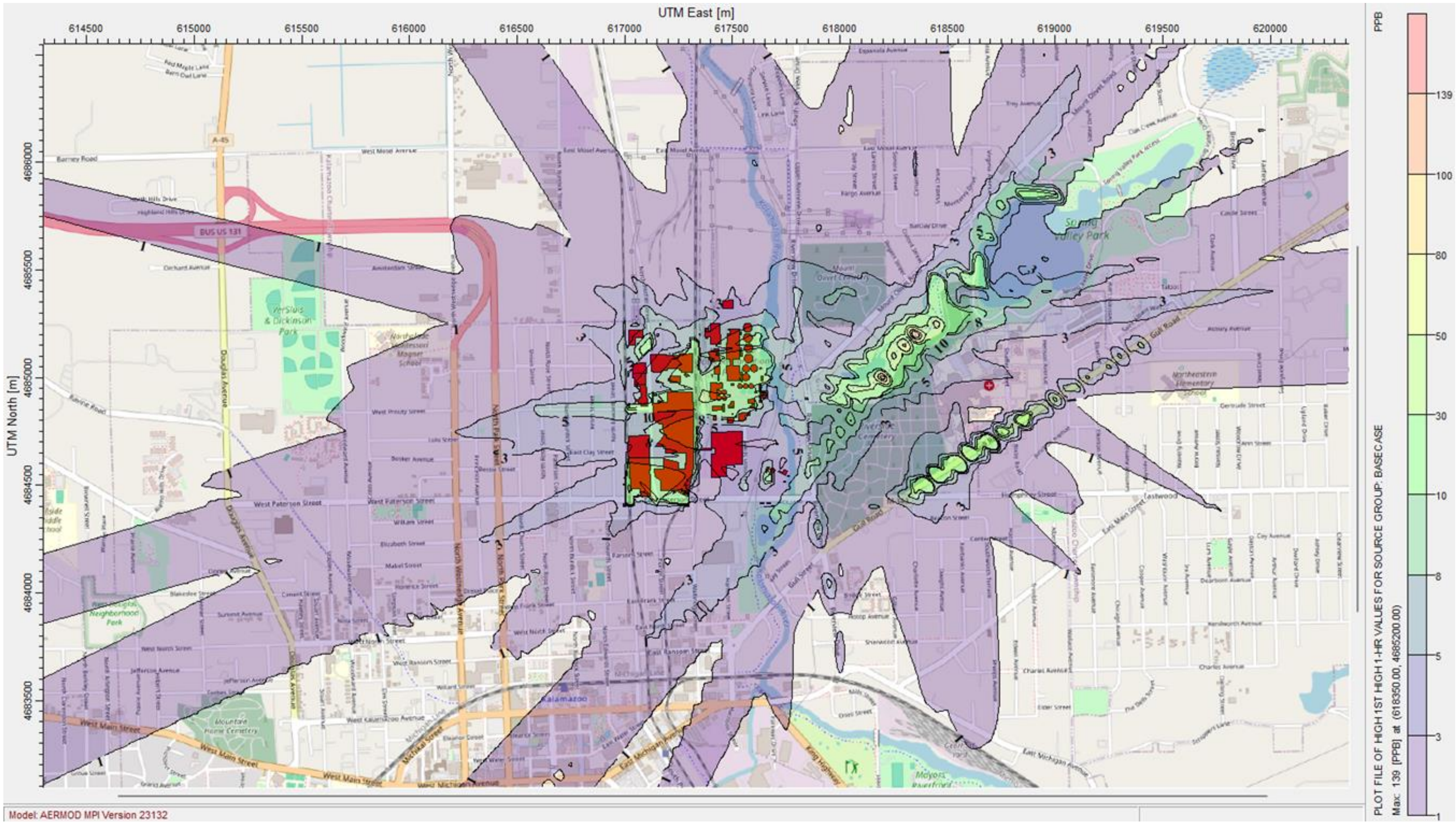
Base Case 1-h Maximum Impacts



Note: Unusual or discontinued emissions removed or replaced by typical emissions.

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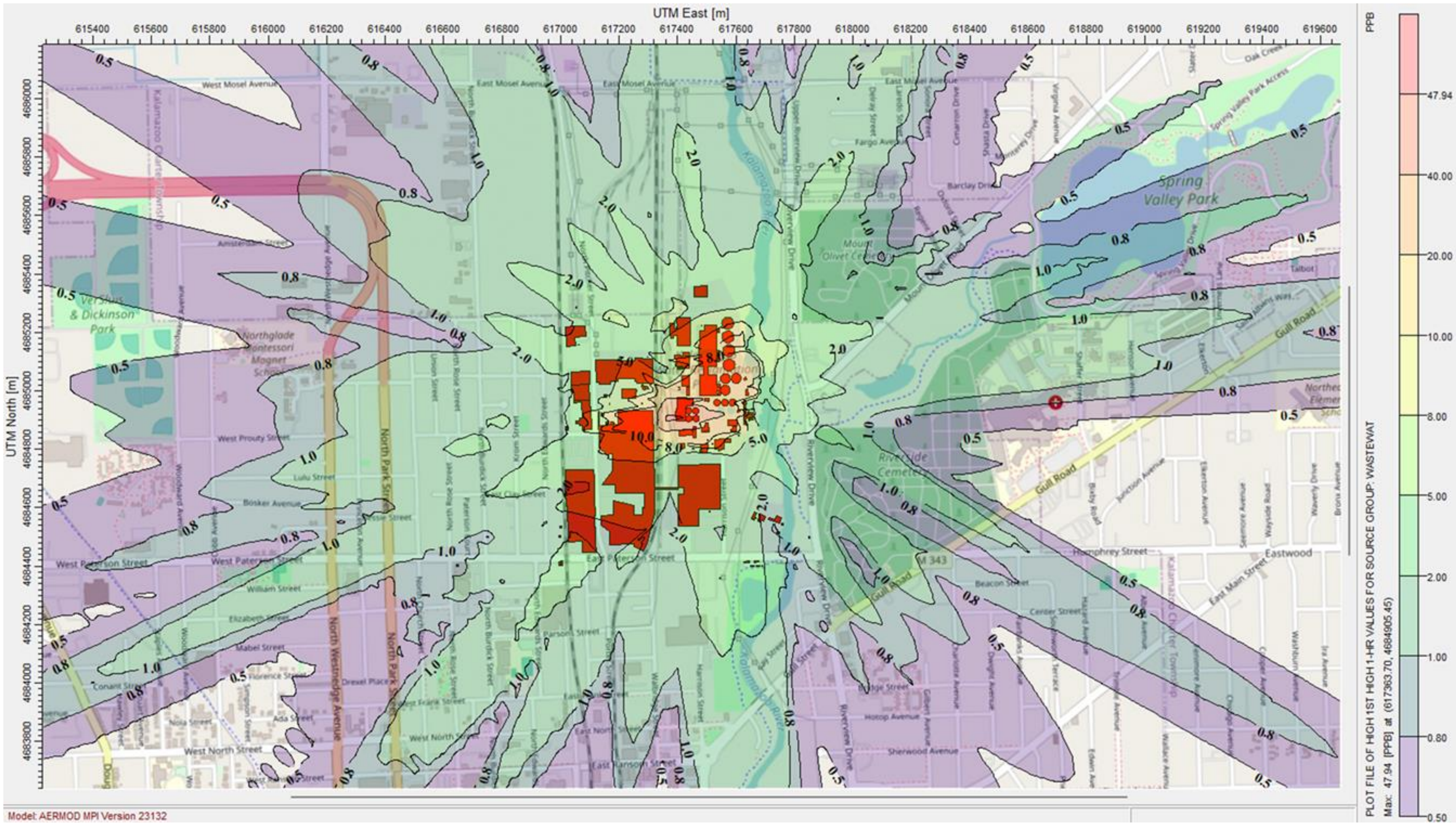
KWRP 1-h Maximum Impacts



Note: Only emissions from KWRP included.

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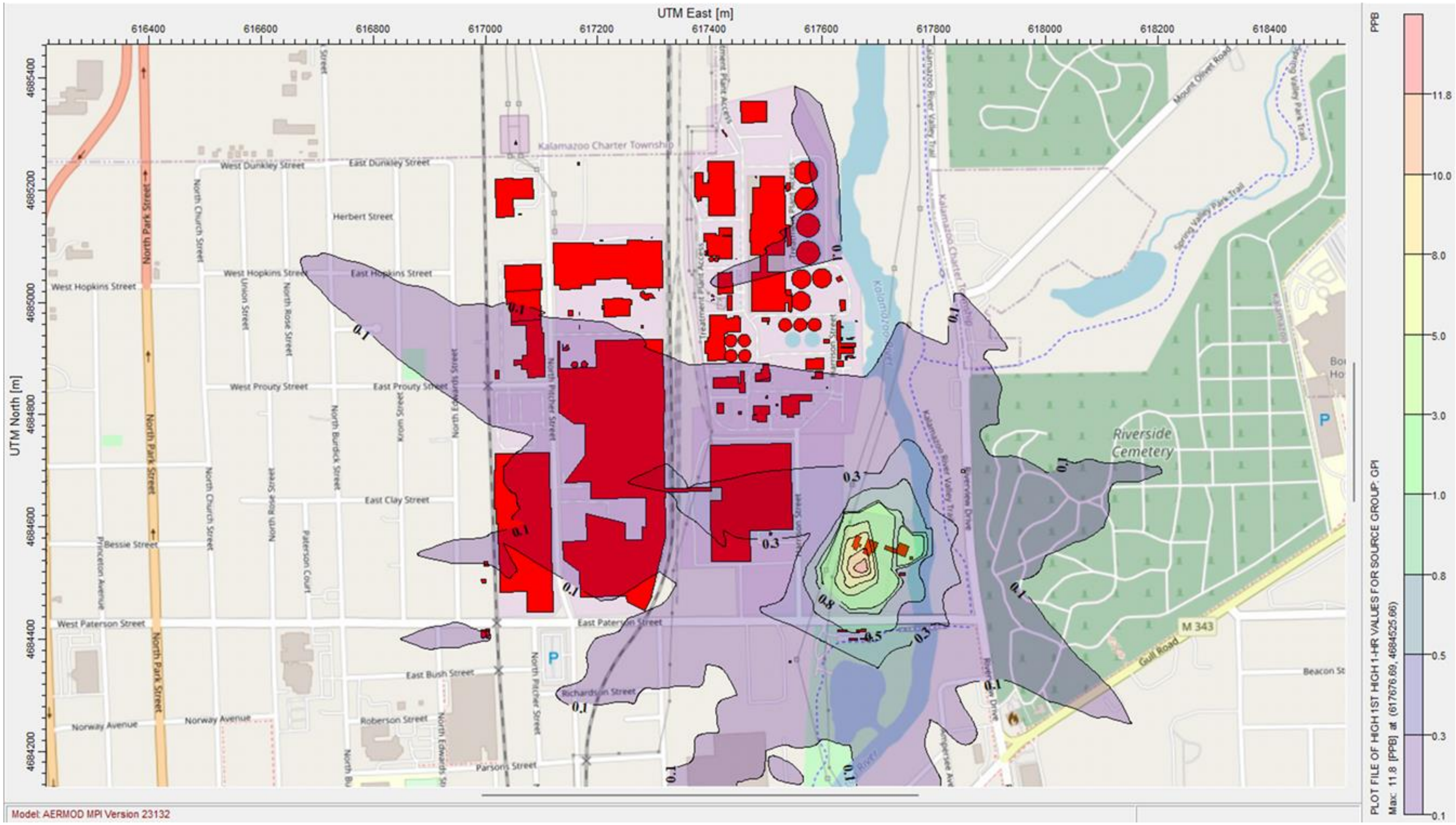
GPI 1-h Maximum Impacts



Note: Only emissions from GPI included, except for K3 Dryer Mezzanine.

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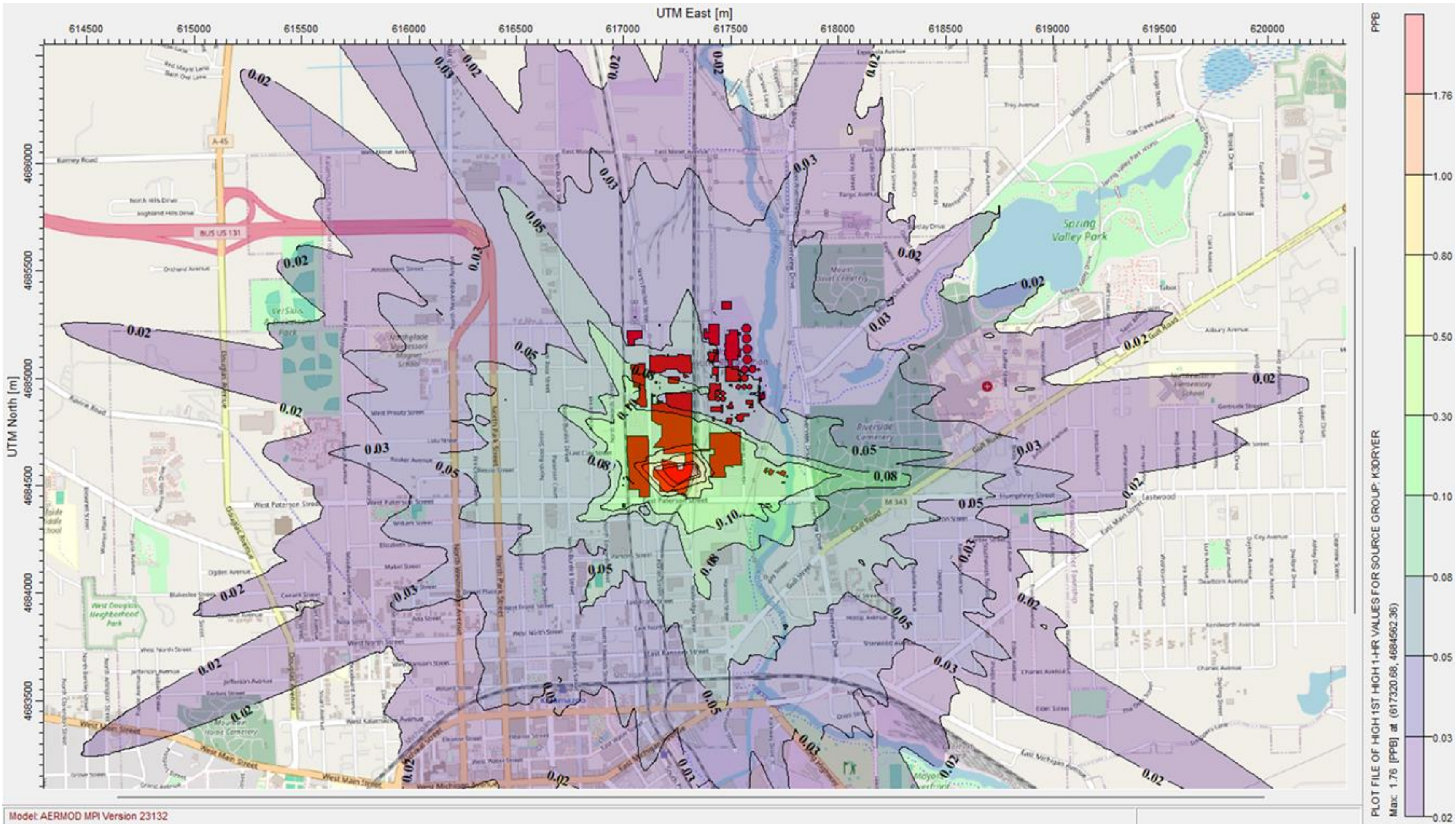
K3 Dryer 1-h Maximum Impacts



Note: Only emissions from K3 Dryer Mezzanine included.

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Conclusions

- Fugitive emissions of H_2S from individual sources at KWRP and GPI range from a few pounds to over a thousand pounds per year.
- Total emissions from stacks (12 lbs/yr) are minor compared to fugitives.
- Total emissions of H_2S from wastewater treatment exceed 1 US ton/yr, more than ten times greater than total emissions of H_2S from the paper mill.
- Diesel engine emissions of H_2S are competitive with fugitive emissions but are generally more diffuse, except where unusual activities such as local traffic re-routing or dredging occur.
- Emissions of H_2S associated with rail activities may also be important.
- Under stable conditions, maximum H_2S concentrations of 10-15 ppb may occur at the most intense local sources, while ambient H_2S concentrations above 1.4 ppb can persist up to ~1 km downwind of these sources.
- Unstable atmospheric conditions during the day mitigate long-term exposure to H_2S, such that $H_2S > 1.4$ ppb unlikely outside KWRP and GPI.
- Odors are likely due to a combination of H_2S emissions from all sources, with KWRP being the most important stationary source contributor.
- Regular H_2S emissions from GPI do not by themselves result in concentrations above the odor threshold outside GPI. This does not rule out odors from emission events (e.g., process upsets), which are not considered by this study.