

Analysis and Attribution of Hydrogen Sulfide (H₂S) Exceedances at the Liberty Monitoring Site from January 1, 2020 through March 1, 2022

Allegheny County Health Department Air Quality Program

March 3, 2022 Updated August 3, 2022

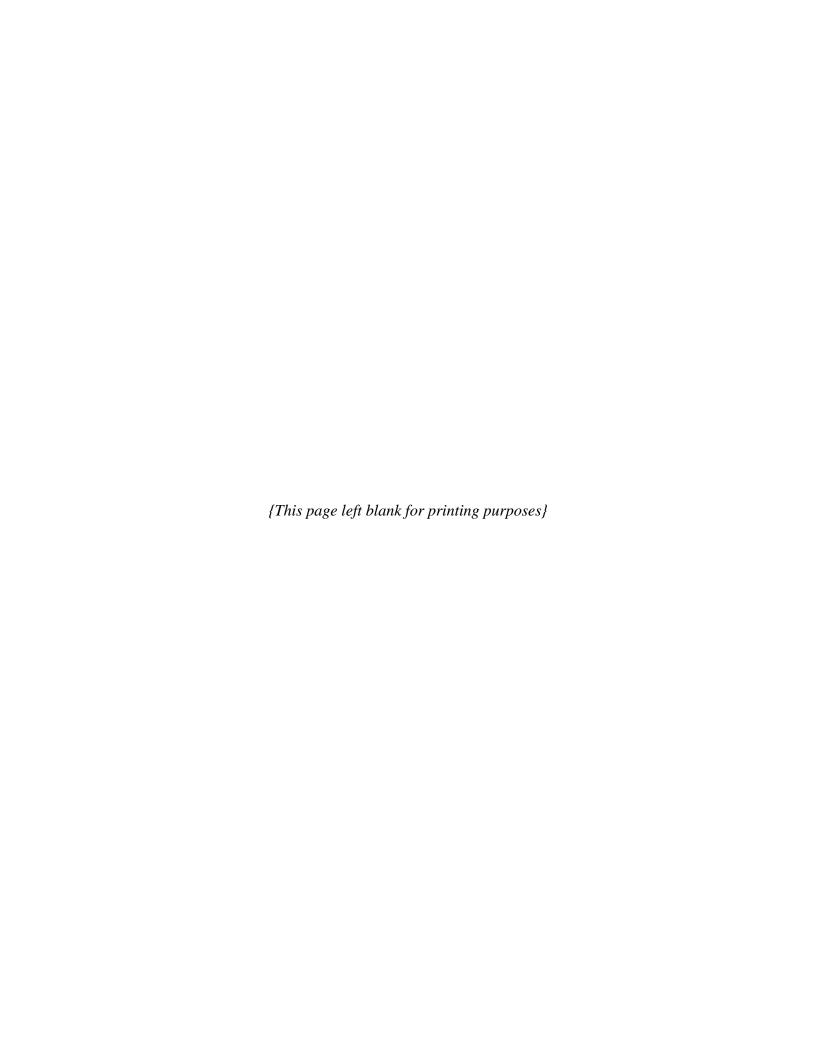


TABLE OF CONTENTS

1.	Overview	1
2.	Background	2
	Sources of H ₂ S in the Mon Valley and surrounding areas	3
3.	Analysis of Exceedances from January 1, 2020 through March 1, 2022	5
	3.1 Analysis of meteorology and H ₂ S concentration data at Liberty monitoring site	5
	3.2 Analysis of potential emissions from Clairton wastewater treatment facility	9
	3.3 Analysis of potential contribution from unknown fugitive sources of H ₂ S, including abandoned mines	15
4.	Summary and Conclusions	17
A	ppendix A: Additional data analysis and methodology	18
	Supporting information for analysis of exceedances from 2020 - 2022	18
	Additional analysis of Liberty monitor data from March 1, 2015 through March 1, 2022	18
	Methodology	22
R	eferences	23
A	ppendix B: August 5, 2022 Update	25

LIST OF TABLES

Table 3.1: Rolling 24-Hour H ₂ S Exceedance Days from January 1, 2020 to March 1, 202	5
Table A.1: Exceedances of the H ₂ S 24-hour rolling standard at the Liberty monitoring si	te from
March 2015 to March 2022	18

LIST OF FIGURES

Figure 2.1:	The H ₂ S Reference Concentration from EPA's IRIS database compared to the annual average concentrations measured at Liberty monitoring station
Figure 2.2:	Locations of Potential H ₂ S Sources and Monitor Sites
Figure 3.1:	Liberty monitoring site location and potential H ₂ S sources in the nearby region (left) and a wind rose for Liberty for January 2020 through February 2022 (right) showing prevailing winds from the south-southwest
Figure 3.2:	Example of H_2S concentrations (ppm) on an exceedance day (2/23/2020) at the Liberty Monitor.
Figure 3.3:	Daily, weekly, and monthly concentration trends for H ₂ S, SO ₂ , and PM _{2.5} at the Liberty Monitor from 1 January 2020 through February 2022
Figure 3.4:	Bivariate polar plots of H ₂ S concentrations (ppm, color scale) plotted against wind speed (concentric circles) and wind direction (0-359 degrees) for all days between January 2020 and February 2022
Figure 3.5	Bivariate polar plots of H ₂ S concentrations (ppm, color scale) plotted against wind speed (mph, concentric circles) and wind direction (0-359 degrees) for exceedance days listed in the April 1, 2021 Notice of Violation only between January 2020 and February 2021
Figure 3.6:	Polar plot of H ₂ S concentration (ppm) from January 2020 to February 2022 overlaid on a map of the region, with the center corresponding to the location of the Liberty monitoring station
Figure 3.7:	Location of Liberty monitor and two potential H ₂ S sources
Figure 3.8:	Location of known H ₂ S sources at the Clairton Wastewater Treatment Plant and the portable H ₂ S sensors installed by ACHD on the fence line of the property
Figure 3.9:	Comparison of H ₂ S concentrations (colored graphs series) with the concurrent measured wind speed (arrow length) and wind direction (arrow pointing with the wind flow) at the Liberty site (top) and the Clairton Wastewater Treatment Plant sensors (bottom six graphs).
Figure 3.10	9: H ₂ S polar plots from Liberty (top) and portable monitors deployed on the perimeter of the Clairton Wastewater Treatment Plant (bottom) plotted on the same concentration scale
Figure 3.11	: Map overlay of H ₂ S polar plots around the wastewater treatment plant and neighboring U.S. Steel Clairton Plant to the East
Figure 3.12	2: Comparison of H ₂ S concentrations (blue) with the concurrent measured wind speed (arrow length) and wind direction (arrow pointing with the wind flow) for one of the portable monitors at the wastewater treatment plant
Figure 3.13	3: Map of abandoned mines maintained by PADEP (white highlighted areas), ACHD's Liberty and Avalon H ₂ S monitoring sites, and ALCOSAN
Figure 3.14	4: Pollution rose for frequency of measured concentration of H ₂ S by wind direction for Avalon for 2019

Figure A.1:	Comparison of similarities in polar plots of H ₂ S and SO ₂ for very low wind speeds for 2020-2022 at Liberty.	18
Figure A.2:	Example of annual polar plots consistent with a single source of H ₂ S (top) and annual polar plots of SO ₂ (bottom) indicating a secondary source appearing in 2019 This new source corresponds to U. S. Steel Irvin Works' flaring of untreated coke oven gas after the December 2018 fire destroyed pollution controls at the Clairton coking facility.	
Figure A.3:	Polar plot of all H ₂ S hour data from March 2015 through February 2022 2	20
Figure A.4	Analysis of the 5 th (lower) and 95 th (upper) percentile confidence intervals in the smoothing of the concentration data on the polar plot for Liberty 2015-2022 H ₂ S. Bins with fewer than three datapoints were filtered out (greyed points)	21
Figure A.5:	Analysis of the 5 th (lower) and 95 th (upper) percentile confidence intervals in the smoothing of the concentration data on the polar plot for the H ₂ S portable sensor #3870.	21
Figure A.6:	Frequency of H ₂ S concentrations (ppm) at Liberty plotted by SO ₂ (ppm) concentration bins	22
Figure A.7:	Frequency of H ₂ S concentrations (ppm) at Liberty plotted by PM _{2.5} concentration bins	22
Figure B.1:	Bivariate polar plot of H_2S concentrations (ppm, color scale) plotted against wind speed (concentric circles) and wind direction (0-359 degrees) for all days between January 1, 2020 and August 1, 2022	25
Figure B.2:	Bivariate polar plots of H ₂ S concentrations (ppm, color scale) plotted against wind speed (mph, concentric circles) and wind direction (0-359 degrees) for exceedance days only between January 1, 2020 and August 1, 2022	26

1. Overview

The purpose of this expert report is to determine evidence of attribution of exceedances of the Pennsylvania Department of Environmental Protection (PA DEP) Hydrogen Sulfide (H₂S) ambient air quality standard of 0.005 parts per million (ppm), calculated as a 24-hour rolling average at the Liberty monitor. Analyses conducted by the Allegheny County Health Department (ACHD) have identified a single source, the U. S. Steel Mon Valley Works Clairton Plant ("U.S. Steel Clairton Plant"), as the cause of the exceedances at ACHD's Liberty monitoring site. ACHD did not identify evidence of any other source contributing to the exceedances. This conclusion is based on the following factors.

The ACHD compared H₂S concentrations measured at the Liberty monitor originating from all measured wind directions under different meteorological conditions including wind speeds, strong inversions, and stagnant air events. ACHD concludes that measurable concentrations of H₂S originate from one direction, south-southwest of the Liberty monitoring site; no sources from any other direction contributed to H₂S concentrations causing exceedances at ACHD's Liberty monitor.

The ACHD receives annual emissions inventory statements from larger permitted air emission sources within Allegheny County. These statements are a source submitted summary of emitted pollutants from their facilities. The only source which has submitted an air emissions inventory statement with H₂S and is located south-southwest of the Liberty monitor is U.S. Steel Clairton Plant's metallurgical coking facility. Another potential source of H₂S located south-southwest of the Liberty monitor is the Clairton Wastewater Treatment Plant ("Treatment Plant") which is owned by the Clairton Municipal Authority. To determine if this source contributed to measurable ambient air concentrations, portable gas sensors (Acrulog H₂S Parts Per Billion Monitor) were installed on multiple sides of the property line of the Treatment Plant to capture upwind and downwind concentrations. ACHD's analysis of the meteorological data combined with concentrations of H₂S at the fence line of the property indicates that the Treatment Plant did not contribute to H₂S exceedances at the Liberty monitor.

Finally, to determine if there are any unknown regional sources of H₂S that may contribute to high background concentrations of H₂S, ACHD analyzed data from a regulatory H₂S monitor that was located at the Avalon site to monitor emissions of H₂S from Shenango Coke Works prior to the plant's closure in 2016. The Avalon H₂S monitor was still operating during 15 of the H₂S exceedance days in 2020 at the Liberty site. This monitor was located downwind of a significant number of abandoned mine sites and wastewater treatment plants. This monitor is also located near ALCOSAN, the largest wastewater treatment facility in Allegheny County. The 24-hour averages for the 15 overlapping exceedance days with Liberty measured 0.000 ppm H₂S at Avalon.

There is no evidence that small, non-inventoried sources affect the Liberty H₂S monitor concentrations at any level, including exceedance levels. Therefore, based on all available data and resources, H₂S exceedances that occurred at the Liberty site during the period of January 1, 2020 through March 1, 2022 can be attributed entirely to emissions originating at US Steel's Clairton coking facility.

2. Background

Hydrogen sulfide (H₂S) is a flammable, colorless gas with a characteristic rotten egg smell. H₂S can occur naturally in volcanic gases and hot springs. It is also emitted by facilities such as wastewater treatment plants and landfills, livestock operations, and industrial activities including petroleum refineries, natural gas plants, petrochemical plants, and coke oven plants.

People can smell H₂S in the air at concentrations as low as 0.0005 ppm. Health outcomes from long-term exposure to lower concentrations of H₂S are uncertain, but evidence suggests that chronic exposure to lower concentrations of H₂S can cause eye irritation, headaches, and fatigue (ATSDR Hydrogen Sulfide Fact Sheet, 2017).

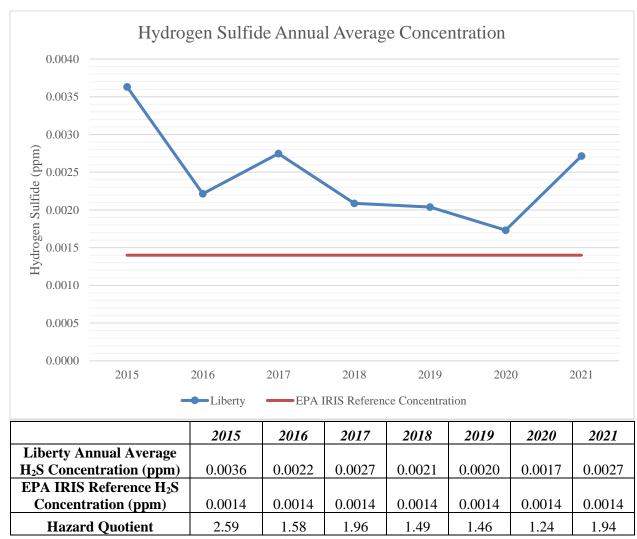


Figure 2.1: The H₂S Reference Concentration from EPA's IRIS database compared to the annual average concentrations measured at Liberty monitoring station

The EPA IRIS database identifies and describes the health hazards of chemicals found in the environment. The EPA Reference Concentration (RfC)¹ for H₂S is 0.0014 ppm of continuous lifetime inhalation exposure. The EPA defines the hazard quotient (HQ) as the ratio of the potential exposure to a substance and the level at which no adverse effects are expected. A HQ greater than 1 indicates that the potential for adverse health effects increases, but it is unknown by how much. Average annual concentrations of H₂S at the Liberty monitor have exceeded the EPA IRIS Reference Concentration for all of the last seven years, resulting in Hazard Quotients between 1.24 (2020) and 2.59 (2015) (Figure 2.1).

Allegheny County does not have a specific regulation on ambient hydrogen sulfide concentrations. Allegheny County incorporates the Pennsylvania Department of Environmental Protection (PA DEP) regulations by reference in Article XXI. The ambient air quality standards for H₂S are set forth in Title 25 of the Pennsylvania Code, § 131.3 (relating to ambient air quality standards). There are two ambient air H₂S standards:

24-hour average concentration threshold of 0.005 ppm 1-hour concentration threshold of 0.1 ppm.

Sources of H₂S in the Mon Valley and surrounding areas

Emissions of H₂S in Allegheny County are dominated by the largest industrial sources – steel and coke manufacturing facilities. The only other inventoried source of H₂S in Allegheny County is the Allegheny County Sanitary Authority (ALCOSAN), the largest wastewater treatment facility in the county, located north of the City of Pittsburgh and not a contributing source to the Liberty monitoring site.

Potential sources of H₂S in the Mon Valley include three U.S. Steel facilities as well as numerous wastewater treatment facilities and landfills (Figure 2.2). ArcelorMittal Monessen, a coke making facility in Westmoreland County, is the largest source outside of Allegheny County near the Liberty monitor. Previous analysis done by the ACHD indicates that ArcelorMittal, when in operation, does not impact the monitor at higher than background levels. Impacts from distant sources from the N or NW directions would also be measured at the Avalon and North Braddock monitoring sites (analysis of Avalon monitor is detailed in section 4.3).

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¹ RfC - An estimate (with uncertainty spanning perhaps an order of magnitude) of a continuous inhalation exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime.

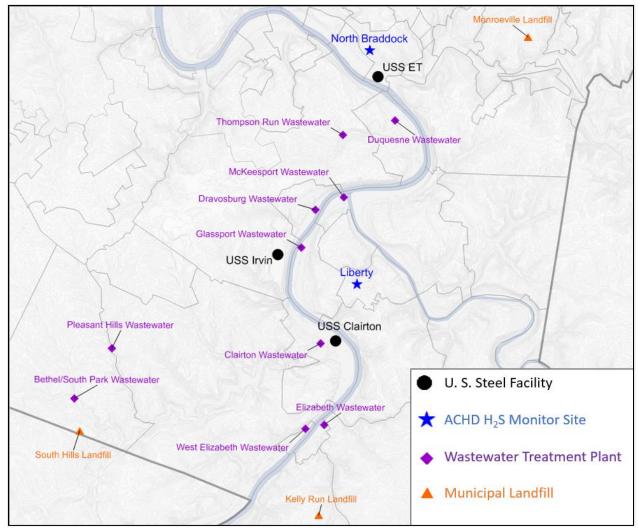


Figure 2.2: Locations of Potential H₂S Sources and Monitor Sites

There may be other sources of H_2S that are not inventoried with any source sector, such as municipal wastewater treatment plants or landfills. A study of potential impacts of a wastewater treatment plant on the Liberty monitoring data is detailed in section 3.2. Evidence shows that emissions from these sources are trace amounts compared to those from large point sources.

3. Analysis of Exceedances from January 1, 2020 through March 1, 2022

The short-term exceedances that are the focus of this report are given below in Table 1.

Table 3.1: Rolling 24-Hour H₂S Exceedance Days from January 1, 2020 to March 1, 2022

Year	Calendar Days on Which there were H ₂ S Exceedances
2020	46
2021	94
January 1, 2022 – March 1, 2022	13

This section provides analysis of monitored data at the Liberty site during the exceedances in 2020 and 2021, data from portable H₂S monitors deployed around the Clairton Wastewater Treatment Plant, and data from the Avalon H₂S monitor prior to its removal in November 2020.

Monitored concentrations at the Liberty and Avalon sites are based on official measurements performed by ACHD. Meteorological data are from the ACHD monitors at Liberty and the meteorological station located at the U.S. Steel Clairton Plant for in-valley wind speeds and directions.

3.1 Analysis of meteorology and H₂S concentration data at Liberty monitoring site

This section will present analysis of the H₂S concentrations and concurrent wind speed and wind direction measured at the Liberty site. The wind measured at Liberty most frequently comes from the southwest (Figure 3.1), but all wind directions were experienced at the site and are included in this analysis to determine which nearby sources could contribute to the exceedances.

The ACHD compared H₂S concentrations measured at the Liberty monitor originating from all measured wind directions under different meteorological conditions including wind speeds, strong inversions, and stagnant air events. ACHD concludes that measurable concentrations of H₂S originate from one direction, south-southwest of the Liberty monitoring site; no sources from any other direction contributed to H₂S concentrations causing exceedances at ACHD's Liberty monitor.

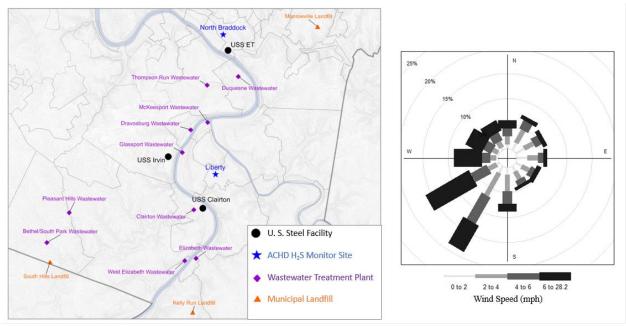


Figure 3.1: Liberty monitoring site location and potential H₂S sources in the nearby region (left) and a wind rose for Liberty for January 2020 through February 2022 (right) showing prevailing winds from the south-southwest.

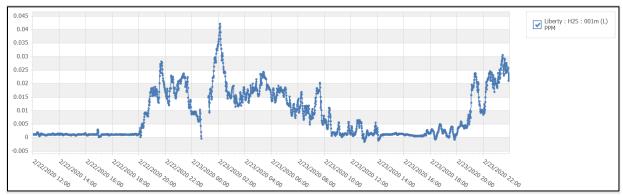


Figure 3.2: Example of H₂S concentrations (ppm) on an exceedance day (2/23/2020) at the Liberty Monitor.

An analysis of the daily, weekly, and monthly trends of different pollutants can help to identify a source. The average concentrations of H_2S , sulfur dioxide (SO_2), and fine particulate matter ($PM_{2.5}$) were all correlated, and consistently elevated during nighttime hours (Figure 3.3). This suggests a source of all three pollutants that has emissions overnight.

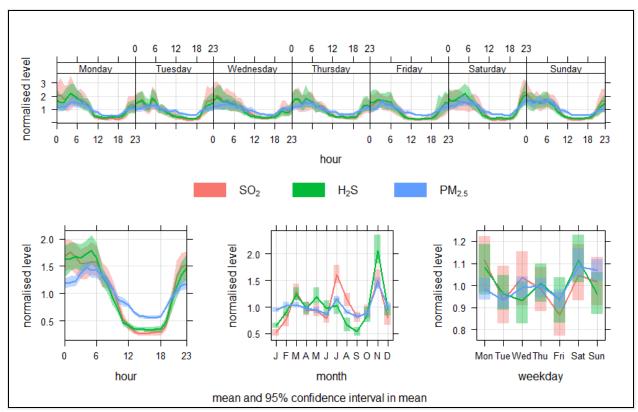


Figure 3.3: Daily, weekly, and monthly concentration trends for H₂S, SO₂, and PM_{2.5} at the Liberty Monitor from 1 January 2020 through February 2022.

Using wind speed and wind direction, ACHD identified the direction of the source of the H_2S at the Liberty monitor. Polar plots are used to visualize and assess the mean pollutant concentrations for a pollutant – in this case H_2S – graphically displayed by concurrent wind speed and wind direction data. The concentrations are plotted as a 'heatmap' with cooler colors reflecting lower concentrations and hotter colors reflecting higher concentrations. A scale bar for the concentrations is included to the right of each plot. The measured concentrations are plotted

with their wind direction (0 - 359°, labelled on plot as N, S, E, and W) and their corresponding wind speed (concentric circles in miles-per-hour).

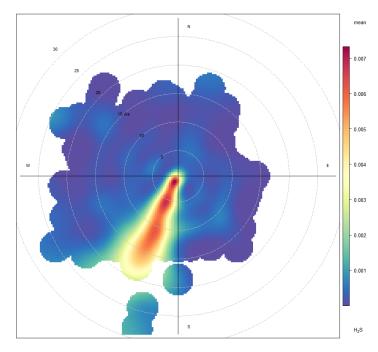


Figure 3.4: Bivariate polar plots of H₂S concentrations (ppm, color scale) plotted against wind speed (concentric circles) and wind direction (0-359 degrees) for all days between January 2020 and February 2022.

These results (Fig. 3.4) are consistent with a single source of H₂S, at both high and low wind speeds. The same analysis was performed on the exceedance days only (Figure 3.5). The variability of concentrations and wind direction seen at very low wind speeds (closest to the center of the plot) is an expected result of air stagnation. A polar plot of SO₂ concentrations for the same time period demonstrates the same source direction and variability at low wind speeds (Appendix, Figure A.1), implicating a common source for both H₂S and SO₂. As SO₂ is a byproduct of combustion, the nearby wastewater treatment facilities are not sources of SO₂ – the only source of both H₂S and SO₂ south-southwest of the monitor is the U.S. Steel Clairton Plant. An example of a polar plot for multiple sources contributing to high SO₂ concentrations at the Liberty monitor in 2019 can be found in the Appendix (Figure A.2).

Despite potential sources to the west and the north of the Liberty site, ACHD did not identify a separate H₂S source a contributing to the monitor (Figure 3.6). There is no known evidence that small, non-inventoried sources affect the Liberty H₂S monitor concentrations at any level, including exceedance levels.

Additionally, analysis of Liberty H₂S data from March 1, 2015 through March 1, 2022 shows a persistent single source that has not changed during this time period (Appendix, Figure A.2).

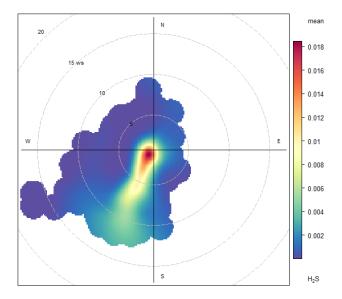


Figure 3.5 Bivariate polar plots of H₂S concentrations (ppm, color scale) plotted against wind speed (mph, concentric circles) and wind direction (0-359 degrees) for exceedance days listed in the April 1, 2021 Notice of Violation only between January 2020 and February 2021.

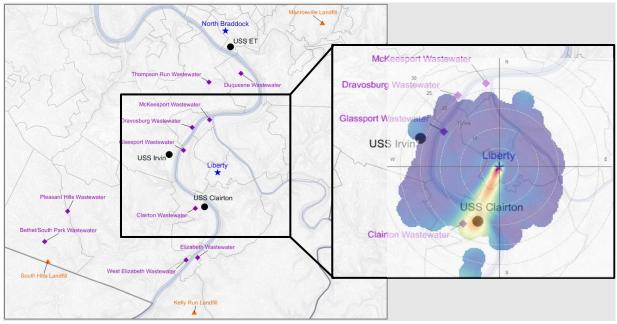


Figure 3.6: Polar plot of H₂S concentration (ppm) from January 2020 to February 2022 overlaid on a map of the region, with the center corresponding to the location of the Liberty monitoring station.

3.2 Analysis of potential emissions from Clairton wastewater treatment facility

From the analysis in the previous section, ACHD has concluded that the only source of H₂S contributing to the Liberty monitor is located south-southwest of Liberty. There are two facilities

in this source region - U.S. Steel's Clairton Plant and the Clairton Wastewater Treatment Plant (Figure 3.7).

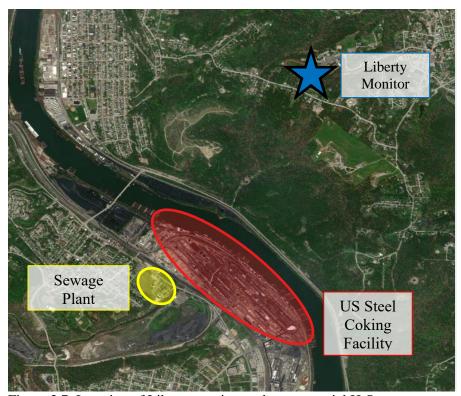


Figure 3.7: Location of Liberty monitor and two potential H₂S sources

To determine if the Treatment Plant is a source contributing to measurable ambient air concentrations of H_2S , portable H_2S gas sensors were installed on multiple sides of the property line of the facility to capture concentrations from all wind directions (Figure 3.8). Working with Treatment Plant employees, ACHD identified known sources of H_2S within the facility and compared the H_2S concentrations measured in enclosed spaces at the facility and concentrations at the fence line of the property.



Figure 3.8: Location of known H_2S sources at the Clairton Wastewater Treatment Plant and the portable H_2S sensors installed by ACHD on the fence line of the property.

The portable sensors measured significantly lower concentrations of H₂S at the property line of the wastewater treatment facility than were measured at the Liberty monitor during the same time period. Figure 3.9 below shows concentrations of H₂S measured at the Liberty monitor (top) and at the Treatment Plant's fence line (bottom six graphs). Note the significantly higher concentration range on the scale bar for the Liberty monitor (top). Overlaid on the graphs are

arrows representing the wind speed (length of arrow) and wind direction (arrow pointing with the flow of the wind).

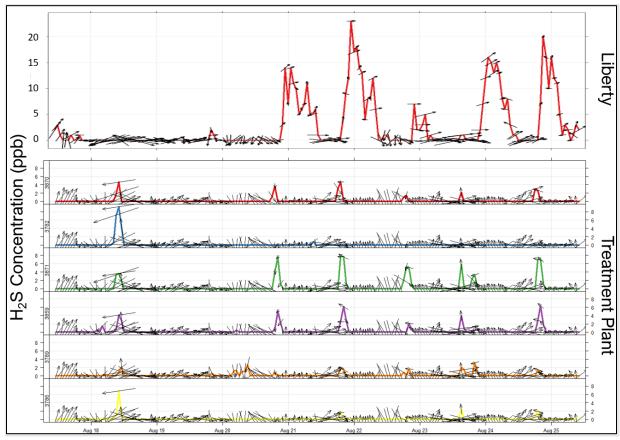


Figure 3.9: Comparison of H₂S concentrations (colored graphs series) with the concurrent measured wind speed (arrow length) and wind direction (arrow pointing with the wind flow) at the Liberty site (top) and the Clairton Wastewater Treatment Plant sensors (bottom six graphs).

The peaks measured by the fence line monitors corresponded with wind coming from the east (or under variable wind directions and low wind speeds) and not H₂S generated from known sources on site. Polar plots (described in section 3.1) were also generated for the portable sensors and compared to the results from the Liberty site (Figure 3.10). When these plots are overlaid on a map, they point to a source east of the Treatment Plant (Figure 3.11).

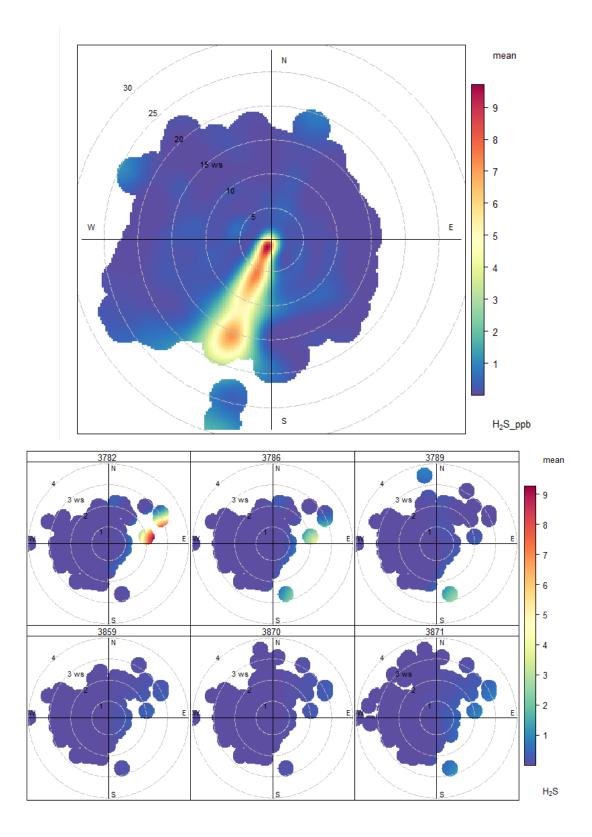


Figure 3.10: H₂S polar plots from Liberty (top) and portable monitors deployed on the perimeter of the Clairton Wastewater Treatment Plant (bottom) plotted on the same concentration scale.

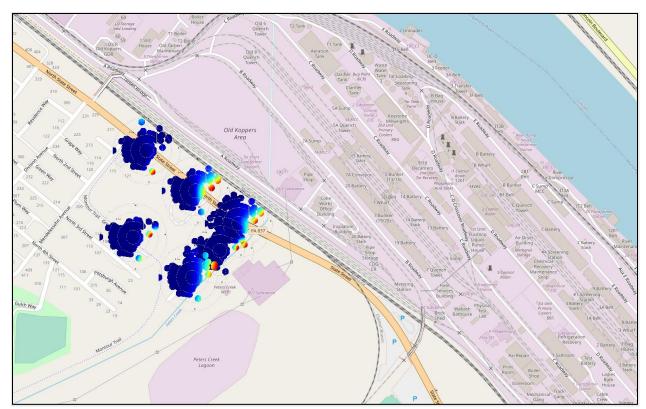


Figure 3.11: Map overlay of H₂S polar plots around the wastewater treatment plant and neighboring U.S. Steel Clairton Plant to the East.

The results of this study demonstrate that the Clairton Wastewater Treatment Plant is not a contributing source of H₂S to the Liberty monitor. Indeed, the highest concentrations of H₂S seen at the property line of the wastewater facility corresponded to winds coming from the east, indicating the neighboring U.S Steel Clairton Plant as the source (Figure 3.9-12).

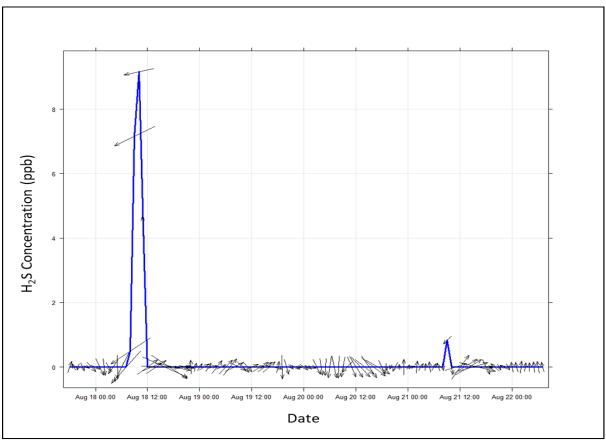


Figure 3.12: Comparison of H₂S concentrations (blue) with the concurrent measured wind speed (arrow length) and wind direction (arrow pointing with the wind flow) for one of the portable monitors at the wastewater treatment plant.

3.3 Analysis of potential contribution from unknown fugitive sources of H₂S, including abandoned mines

ACHD measured H₂S at the Avalon site from January 2006 until November 2020. The site was initially installed to monitor emissions from Shenango Coke Works ("Shenango"), which subsequently closed in January 2016. After the closing of Shenango, the monitor functioned as an urban background site for potential sources of H₂S (e.g. abandoned mines, wastewater treatment plants) because of the absence of a combustion-related H₂S point source.

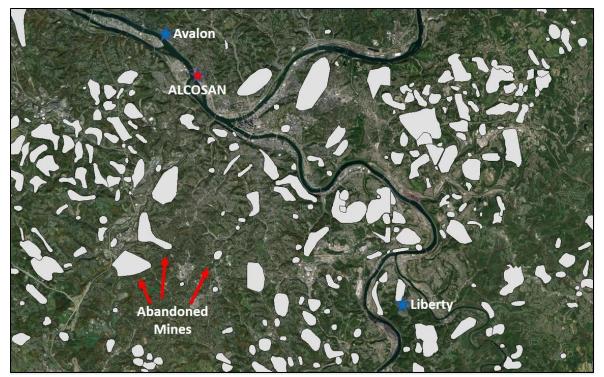


Figure 3.13: Map of abandoned mines maintained by PADEP (white highlighted areas), ACHD's Liberty and Avalon H₂S monitoring sites, and ALCOSAN.

The Pennsylvania Department of Environmental Protection (PA DEP) maintains an Abandoned Mine Land Inventory GIS database (Figure 3.13). Both the Liberty and the Avalon monitoring sites have nearby abandoned mines in areas upwind of the monitors. In addition, the Avalon monitor is located approximately 2 miles from ALCOSAN, the largest wastewater treatment facility in Allegheny County. The Avalon monitor measured a daily average concentration of 0.000 ppm of H₂S on 257 of the 258 days that the monitor was operating in 2020 and 361 out of 363 days in 2019. Despite ALCOSAN processing an average of 185 million gallons of wastewater a day, there was only a small contribution of H₂S to the Avalon monitor from ALCOSAN (Figure 3.14). For comparison, the Clairton Municipal Treatment Plant processes an average of approximately 3 million gallons of wastewater per day. There is no evidence that fugitive emissions from any of the abandoned mines impact either of the monitoring sites.

The Avalon H₂S site was operating during 15 of the exceedance days at the Liberty site in 2020. During those overlapping days, the 24-hour averages of H2S at Avalon were 0.000 ppm, indicating no evidence of a contribution of small distributed fugitive sources that might build up in concentration during stagnant air events. After the shutdown of Shenango in 2016, there have been no exceedances of the H₂S standard at the Avalon site.

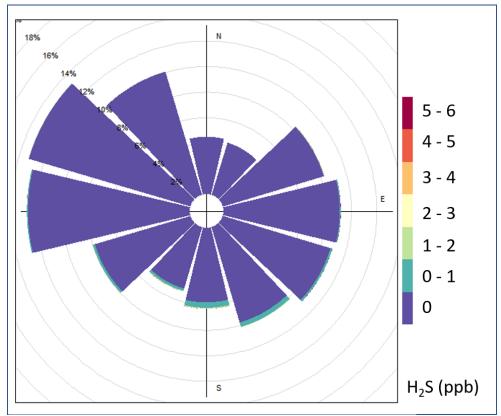


Figure 3.14: Pollution rose for frequency of measured concentration of H₂S by wind direction for Avalon for 2019.

4. Summary and Conclusions

Between January 1, 2020 and March 1, 2022 ACHD identified 153 days in which concentrations of H₂S exceeded the PA DEP ambient air quality standard of 0.005 parts per million (ppm), calculated as a 24-hour rolling average, at the Liberty monitor.

The monitoring data from Liberty points to a single source south-southwest of the monitor. Special studies conducted by ACHD along with the analysis of the monitored data concluded that there is no evidence that fugitive emissions from wastewater treatment plants, landfills, or abandoned mines contributed to the H₂S exceedances measured at the Liberty monitoring site.

Based on all available data and resources, H₂S exceedances that occurred at the Liberty site during the period of January 1, 2020 through March 1, 2022 can be attributed entirely to emissions originating at U. S. Steel's Clairton Plant.

Appendix A: Additional data analysis and methodology

Supporting information for analysis of exceedances from 2020 - 2022

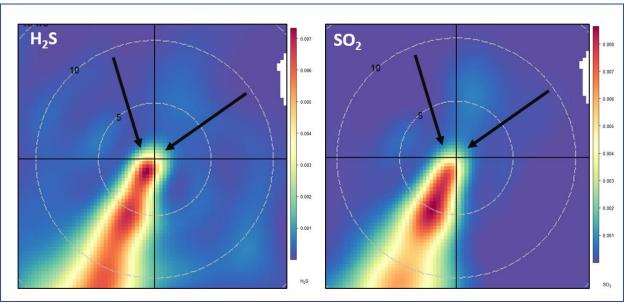


Figure A.1: Comparison of similarities in polar plots of H₂S and SO₂ for very low wind speeds for 2020-2022 at Liberty.

Additional analysis of Liberty monitor data from March 1, 2015 through March 1, 2022

There were additional exceedances of the H_2S standard at the Liberty monitor going back at least until 2015 (Table A.1).

Table A.1: Exceedances of the H₂S 24-hour rolling standard at the Liberty monitoring site from March 2015 to March 2022

Year	Rolling 24-hr
	H ₂ S Exceedances
March 1 - December 31, 2015	1,879
2016	1,083
2017	1,456
2018	868
2019	865
2020	618
2021	1,287
January 1 – March 1, 2022	164

Additional data analysis and figures generated from the 2015 – 2022 dataset are included below.

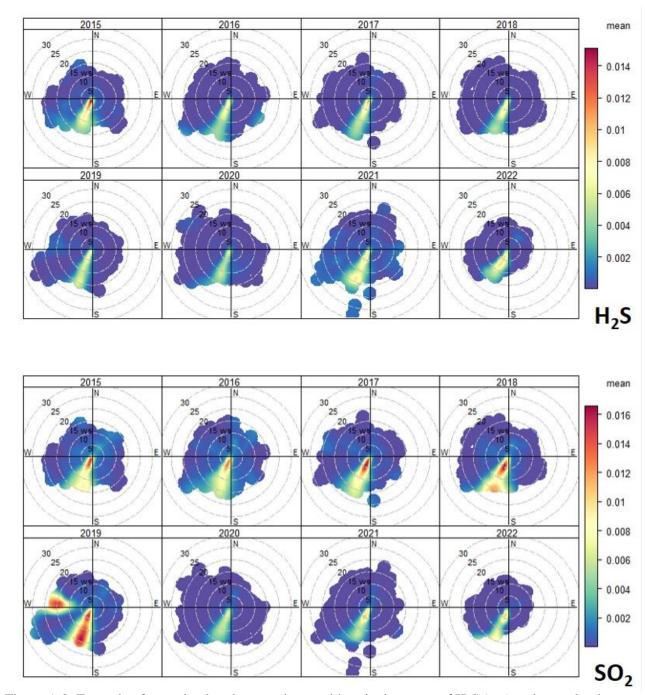


Figure A.2: Example of annual polar plots consistent with a single source of H₂S (top) and annual polar plots of SO₂ (bottom) indicating a secondary source appearing in 2019. This new source corresponds to U. S. Steel Irvin Works' flaring of untreated coke oven gas after the December 2018 fire destroyed pollution controls at the Clairton coking facility.

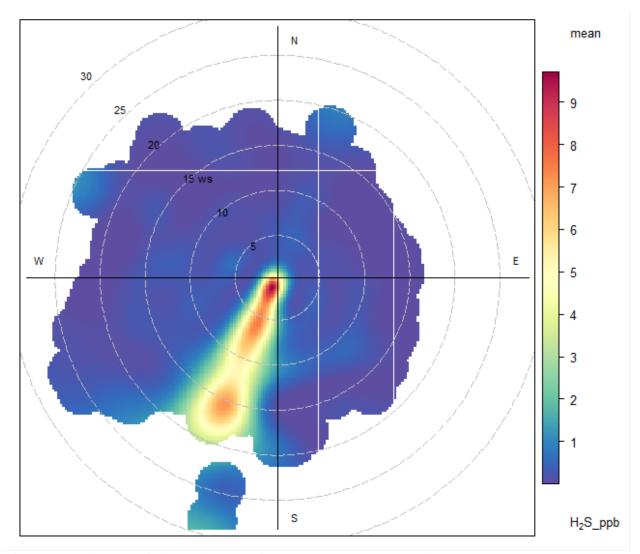


Figure A.3: Polar plot of all H₂S hour data from March 2015 through February 2022.

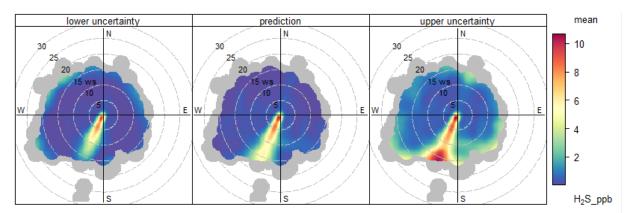


Figure A.4 Analysis of the 5^{th} (lower) and 95^{th} (upper) percentile confidence intervals in the smoothing of the concentration data on the polar plot for Liberty 2015-2022 H_2S . Bins with fewer than three datapoints were filtered out (greyed points)

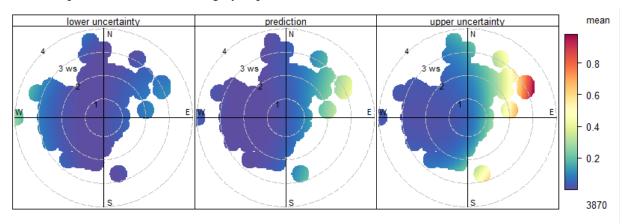
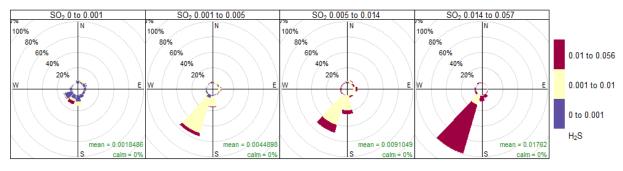
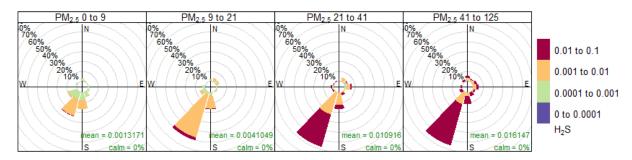


Figure A.5: Analysis of the 5th (lower) and 95th (upper) percentile confidence intervals in the smoothing of the concentration data on the polar plot for the H₂S portable sensor #3870.



Frequency of counts by wind direction (%)

Figure A.6: Frequency of H₂S concentrations (ppm) at Liberty plotted by SO₂ (ppm) concentration bins



Frequency of counts by wind direction (%)

Figure A.7: Frequency of H₂S concentrations (ppm) at Liberty plotted by PM_{2.5} concentration bins.

Methodology

The monitored data at the Liberty monitoring site have been fully validated and quality assured. At the Liberty monitoring site there are two (2) Teledyne T100 sulfur dioxide analyzers which are a United States Environmental Protection Agency (USEPA) approved Equivalent Method for the measurement of sulfur dioxide in the air through the principles of ultraviolet fluorescence. One of the analyzers has an upstream hydrogen sulfide converter (Ecotech H2S-1100) which converts hydrogen sulfide in the sample air to sulfur dioxide. To determine ambient concentrations of hydrogen sulfide, readings from the dedicated ambient sulfur dioxide analyzer (SO₂) are subtracted from those of the other sulfur dioxide analyzer (H₂S + SO₂) through a dedicated math channel on the data logger [(H₂S + SO₂) - (SO₂) = (H₂S)]. The analyzers are run in accordance with ACHD's standard operating procedures for hydrogen sulfide and sulfur dioxide, which involve quality assurance and operational practices to ensure reliable performance.

The monitored data from the Treatment Plant were obtained using Acrulog H₂S Parts Per Billion Monitors. These portable gas instruments utilize a built-in sample pump and electrochemical sensor to measure H₂S concentrations as low as 0.003 ppm. Sampling readings are stored through an internal data-logger on each device.

Datasets were analyzed in R and visualizations were prepared using the open-source package OpenAir (Carslaw and Ropkins, 2012). Map visualizations were prepared in R and ArcMAP.

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Information on the Author

This report was prepared by Dr. Aja Ellis, an Air Quality Administrator at the Allegheny County Health Department, Bureau of Environmental Health, Air Quality Program, Planning and Data Analysis Section. Dr. Ellis' experience and education are in the areas of atmospheric pollution and source attribution of fugitive emissions. Background: B.S. Physics, University of Nevada, Reno; Ph.D. Physics, Curtin University, Australia; Postdoctoral Researcher, Center for Atmospheric Particle Studies, Carnegie Mellon University.

Appendix B: August 5, 2022 Update

The section updates the report published online in March 2022 to include additional data and analysis and identifies an error that was found on Page 3 of the original report incorrectly stating that an H₂S monitor was located at Lawrenceville; this has been corrected to North Braddock. Additionally, errors in figure numbering in the original March 2022 report were identified and corrected in this update.

There have been additional exceedances of the PA DEP 24-Hour Average H₂S standard of 0.005 ppm since the initial data analysis was performed. This section includes updates of Figures 3.4 (updated version Figure B.1 below) and 3.5 (updated version Figure B.2 below) to include the additional data.

Results of the analysis of the additional data are consistent with the original dataset published in the report in March 2022, indicating that US Steel Clairton Plant continues to be the only detectable source of H₂S contributing to exceedances of the PA DEP H₂S 24-hour standard at the Liberty monitoring site.

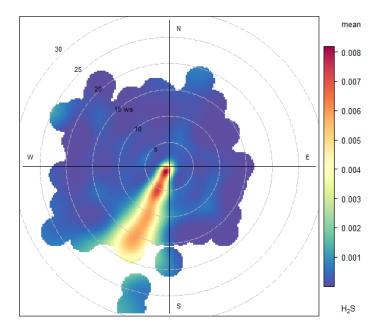


Figure B.1: Bivariate polar plot of H₂S concentrations (ppm, color scale) plotted against wind speed (concentric circles) and wind direction (0-359 degrees) for all days between January 1, 2020 and August 1, 2022.

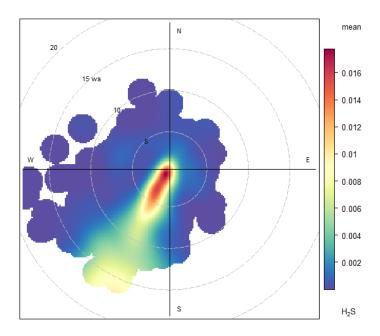


Figure B.2: Bivariate polar plots of H₂S concentrations (ppm, color scale) plotted against wind speed (mph, concentric circles) and wind direction (0-359 degrees) for **exceedance days only** between January 1, 2020 and August 1, 2022.

