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This memo documents the approach and results used to estimate emissions of hydrogen sulfide from the wastewater treatment system at the Georgia-Pacific Toledo operations; this serves as an update on the earlier results from March 28, 2022. Emission estimates were generated using the large amount of ground level monitoring data collected by the facility. The average emission rate was estimated to be 9.3 lb/day using data collected from October 13, 2021 to May 9, 2022.

Background

NCASI has executed multiple rounds of direct emission measurements of hydrogen sulfide and other TRS compounds from industry wastewater treatment plant units. These studies are presented in the following reports:

- NCASI Technical Bulletin No. 956, **Emissions of Reduced Sulfur Compounds and Methane from Kraft Mill Wastewater Treatment Plants**, presents the results of direct emission measurements from primary clarifiers, primary settling basins, aerated stabilization basins (ASBs), activated sludge treatment plants, tertiary settling ponds and wastewater transport systems. Emission measurements are based upon measured downwind concentrations at several elevations and contemporaneous meteorological data.

- NCASI Technical Bulletin No. 957, **Spatial Ambient Air Sampling and Analysis Methods for Quantifying Reduced Sulfur Compounds and Methane Emissions from Kraft Mill Wastewater Treatment Plants**, describes the sampling and analytical procedures and includes detailed descriptions of the calculation methods.

The overall procedure involved collecting a vertical concentration profile downwind of a process unit along a fixed downwind path length, typically over the course of one to two hours. The wind speed and other meteorological information were also measured. The emission rate is then calculated by integrating the concentration and mass air rate through a virtual crosswind plane with a width equal to the path length and height equal to the pollutant boundary layer height. Details of this calculation procedure can be found in Chapter 2 of NCASI TB No. 957.

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Vertical Concentration Profiles

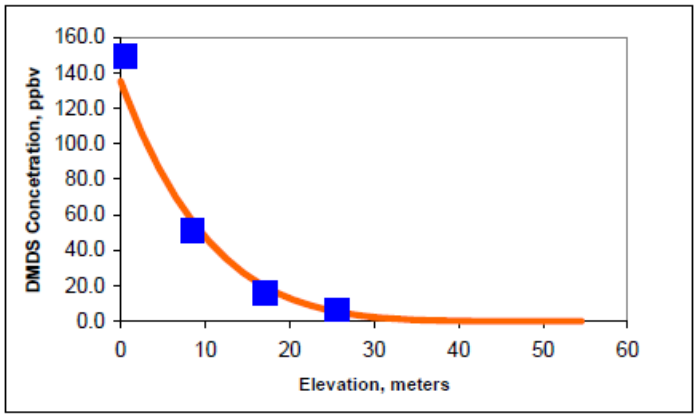
One key result from these studies was the development of vertical concentration profiles for hydrogen sulfide downwind of a WWTP unit. This value, represented as ***b***, is an exponential factor representing the shape of the concentration curve in which the pollutant concentration goes from the ground level concentration to zero, when tracking in the vertical direction:

$$C(z) = C_0 \cdot \left(1 - \frac{z}{z_B}\right)^b$$

where ***C(z)*** and ***C_0*** are the concentration at height z and ground level, respectively, and ***Z_B*** is the boundary layer height.

An illustration of the concentration profile curve fitting procedure is presented in the following figure.

Figure 1: An example vertical concentration profile, used to estimate *b* for Dimethyl Disulfide



Forty-one individual sampling runs at five facilities were combined to develop an average concentration profile exponent value for hydrogen sulfide of 3.9. This analysis is presented in Sections 5.2 and 5.3 of TB No. 957. The concentration profile has been demonstrated to apply to a wide range of ambient hydrogen sulfide concentrations.

The concentration profile exponent can be used to develop an estimate of the vertical distribution using only ground level measurements. The emission measurements for the third phase of testing at Mill E and the testing at Mill T were developed using this approach (see TB No. 956). In this manner, ground level concentrations around the WWTP at a facility can be combined with site-specific met data to generate emission estimates. The concentration profile exponent was developed for wastewater treatment units and may not be applicable to other area sources.

Site- Specific Emission Estimates

The GP Toledo facility has implemented extensive ground level monitoring for hydrogen sulfide. A map of the monitor locations is presented in Figure 2.

Figure 2: Hydrogen Sulfide Monitor Locations for the GP Toledo WWTP

Concentrations were measured at five locations at roughly 10-minute intervals. A meteorological station is also located on site and reported information hourly. The compiled concentration measurements and meteorological data were provided to NCASI for the October 2021 to January 2022 time period.

These data were used to generate site-specific estimates for the hydrogen sulfide emission rate using the procedures described in TB No. 956. A large amount of data pre-treatment was needed, as the time stamps for the five monitors and for the met station were not in sync. The following pre-treatment steps were performed:

1. Compilation of all monitor and met station data
2. Conversion of text to relevant standardized inputs (for example, SSW for wind direction becomes 203°)
3. Unit conversions
4. Determination of a single reference time (i.e. t=0) and time step, in this case 10 minutes
5. Assignment of concentration values and met data for each time step. Periods of monitor downtime were recorded as blank values. Periods of calm wind speed were recorded as 0 m/s.
6. Solar radiation was estimated as HIGH, LOW or NIGHT based upon the time of day as compared to the times for dawn and sunset
7. Monitor 2, 4 or 5 was selected as the downwind monitor, depending on the wind direction

The data compilation resulted in ~12,000 discrete time blocks. An attempt to calculate an estimated emission rate was generated for each time block, using the following screening procedure:

1. Periods of rain were flagged. An emission estimate was not generated for these periods.
2. Periods of unstable wind conditions were flagged. An emission estimate was not generated for these periods.
3. Periods of calm were flagged. An emission estimate was not generated for these periods.
4. Periods for which there was no monitored concentration data were flagged. An emission estimate was not generated for these periods.

Approximately half of the 10-minute time blocks were screened out by the criteria above.

A key decision was the selection of the appropriate monitor to use to represent the ground level concentration. Several approaches were executed, including using

a) The downwind monitor among Locations 2, 4 and 5, based on wind direction. This approach resulted in a large number of discarded time blocks due to monitor downtime or due to periods were the wind direction fell between monitors.
b) The maximum monitor concentration among Locations 2, 4 and 5 for a given time block.
c) The average monitor concentration among Locations 2, 4 and 5 for all time blocks.
d) Monitor Location Number 3 for all time blocks. Monitor three is located in the middle of the WWTP and generally recorded the highest concentrations.

The final estimates were generated using option b.) above. The average downwind monitor concentration ranged from 3 to 109 ppb for this time period. This conservative approach generated the highest emission estimates among the options but resulted in a lower amount of discarded time blocks from the screening process and is less calculation intensive. The selected concentration can be interpreted as the ground level concentration for a virtual plane downwind from the WWTP, irrespective of the wind direction. Estimates using this approach are representative of the total WWTP emission rate; it is not possible to decouple emission rates for individual WWTP unit operations from these results.

The calculation results in emission rates (units of g/s) associated with each 10-minute time block. The blocks were then used to generate hourly and daily emission estimates. Time blocks with an estimated emission rate of zero (due to all monitors reading zero) were not included. Note that this approach is conservative; periods of calm and rain likely have lower emission rates than other periods but are excluded from the average. Results are presented in the table below.

Table 1: Emission Estimate Results

Number of 10-minute blocks included	9741
H2S Concentration at the Downwind Monitor (Maximum of Location 2, 4 or 5)	Range: 3-865 ppb Average: 19 ppb
Number of Valid Daily Blocks	174
Average Daily Emission Rate	9.3 lb/day
Maximum Daily Emission Rate	25.4 lb/day