

**North Carolina Division of Air Quality (DAQ) Report on the
Study for Estimating Hydrogen Sulfide and Total Reduced Sulfur Compounds Emissions
from the Plymouth Paper Mill Wastewater Treatment System;
Submitted February 24, 2009 for March 11, 2009 NC Air Quality Committee Meeting**

Abstract

This abstract serves as a synopsis from the DAQ Director to the Environmental Management Commission (EMC) on three recent emission studies between 2007 and 2009 associated with the Plymouth paper mill wastewater treatment systems (WWTS).

After finding the 2005 paper industry emission study results for hydrogen sulfide (H₂S) and total reduced sulfur compounds unacceptable due to quality assurance (QA) issues, the paper industry re-conducted the emission study in 2006. DAQ approved the 2006 paper industry emission study per 15A NCAC 2Q .0714 (1) and the ensuing dispersion modeling results for the four NC paper mills, including the Plymouth paper mill. DAQ reported the results of the paper industry hydrogen sulfide (H₂S) studies for paper industry WWTS at the September 2006 Air Quality Committee meeting as required under 15 NCAC Rule 2Q .0714 (2).

The US EPA Office of Air Quality Planning and Standards (OAQPS) also had interest in the NC paper mill WWTS study and drew different conclusions than DAQ on the 2006 paper industry emission report for the Plymouth mill, due largely to a significant disparity in H₂S emissions between the EPA WWTS WATER9 model predictions (1,800 ton/yr) and the industry estimates (125 ton/yr). EPA presented their concerns at the same AQC meeting, and offered to conduct an emission study and report the results by Spring 2007. After consideration of the conflicting opinions from DAQ and EPA/OAQPS, the Environmental Management Commission (EMC) decided in its September 2006 meeting that:

- The emission study and dispersion modeling requirements under 2Q .0714 were met by all four paper mills,
- DAQ and paper industry shall collaborate with the EPA Plymouth mill WWTS study, and
- The DAQ Director shall report back to the EMC when EPA finished its study.

EPA OAQPS and the EPA Office of Research and Development (EPA/ORD) conducted their monitoring study at the Plymouth paper mill on June 19-20, 2007 with the mill and WWTS operating at near full production under typical conditions. However, the H₂S concentrations for many of the WWTS sources were too low for the EPA optical monitor to detect; therefore, most EPA data did not meet the stated minimum detection limit QA criteria. This prevented EPA from estimating H₂S emissions from many of the WWTS sources. Consequently, EPA produced an internal report to DAQ and paper industry collaborators in August 2008 that was not cleared for subsequent public distribution, thus inhibiting DAQ's ability to report EPA emission data from the study. The paper industry conducted parallel air monitoring using an electro-chemical based monitor, detected H₂S, and estimated emissions near 250 ton/yr. Industry H₂S WWTS emission estimates were comparable to the EPA unreleased emission estimates, and both were considerably lower than the EPA WATER9 predictions near 900 ton/yr.

A second study pertaining to Plymouth mill WWTS emissions was an ambient monitoring study conducted by DAQ and EPA Region 4 in 2007. This study monitored sulfur dioxide (SO₂) and H₂S

near Plymouth throughout 2007 in response to a 4-month study by the Agency for Toxic Substances and Disease Registry (ATSDR). Ambient H₂S levels reported from the ATSDR study were far below the NC Acceptable Ambient Level of 83 ppb 24-hr average, but SO₂ was observed in the 200–400 ppb range at one location, well above the US EPA National Ambient Air Quality 24-Hr Standard (NAAQS) of 140 ppb. However, a review by DAQ of this study concluded the SO₂ results were potentially flawed due to QA and tape meter operational consideration. The DAQ/EPA Region 4 monitoring results, in contrast, showed levels near the Plymouth mill were well below the concern levels for each pollutant (maximum 24-hr average concentrations of 10 ppb for SO₂ and 3.4 ppb for H₂S).

A third study was conducted to correlate actual measured H₂S concentrations during the 2007 Plymouth ambient monitoring study with the 2006 industry H₂S emission estimates. A source contribution analysis revealed that more than 99% of the maximum concentrations at the monitoring site were attributable to Settling Pond No. 1 emissions. The results of the study show a good correlation (within 20%) between the monitored and modeled 1-hr and 24-hr average concentrations. This tends to support the validity of the industry emission estimates as a baseline with one year of concentration data and meteorology at one location.

Collectively, the results from these three studies support DAQ conclusions that the 2006 industry emissions and dispersion modeling were valid, and the Plymouth paper mill appears to be in compliance with the SO₂ NAAQS and the H₂S AAL.

FULL REPORT

The Environmental Management Commission (EMC) decided in its September 2006 meeting that the DAQ Director was to give a report when the US Environmental Protection Agency (EPA) finished its emission monitoring study at the Plymouth paper mill¹ wastewater treatment system (see Section 3). Two other studies relevant to the extent of hydrogen sulfide (H₂S) emissions from the Plymouth paper mill wastewater treatment system (WWTS) have also been completed. One was an ambient monitoring study for H₂S and sulfur dioxide (SO₂) near Plymouth, NC (see Section 4) in response to a similar study by the federal Agency for Toxic Substances and Disease Registry (ATSDR). Another was a dispersion modeling analysis study using the Plymouth ambient monitoring study data performed by DAQ and EPA (see Section 5). The following report presents the findings of those three studies after giving background information in Sections 1 and 2 to provide context to the three study findings.

1. Summary of the Emission Monitoring and Dispersion Modeling Industry Study Results Presented by DAQ at the September 13, 2006 Air Quality Committee Meeting

In April 2005 Rule 15A NCAC 2D .1104 became effective to reduce the hydrogen sulfide Acceptable Ambient Level (AAL) from 2.1 to 0.12 milligrams per cubic meter (1,500 to 83 parts per billion) on a 24-hour average basis. Included in the rule were provisions to exempt paper mill wastewater treatment systems from the hydrogen sulfide AAL while requiring the paper industry to conduct a monitoring study to estimate their wastewater emissions. [Rule 2Q .0714 is included as an Attachment at the end of this report.]

¹ Weyerhaeuser sold its paper mill located in Plymouth, NC to Domtar Corp. in 2007; to avoid confusion without regard to its ownership, this paper mill is simply referred to as the Plymouth paper mill in this report.

The Division of Air Quality (DAQ) was assigned the responsibility and authority by the EMC to oversee and approve the paper mill wastewater emission monitoring study and dispersion modeling. DAQ formed a multidisciplinary review team of chemists, engineers, and dispersion modelers along with a national hydrogen sulfide expert and two NC State University professors. After beginning to review the industry monitoring plan in May 2004, DAQ required a few minor technical modifications and approved the plan in February 2005.

The paper industry research organization² conducted emissions studies that included measurements of reduced sulfur compounds³ concentrations and meteorological conditions in order to quantify emission rates of these compounds from two paper mill WWTSs. The protocol developed by Esplin^{4,5} was followed.⁶ The protocol provided the means by which pollutant concentrations were measured at several locations across the plume at four vertical elevations⁷ directly downwind of the source. Meteorological data were collected at 6- and 30-foot heights for wind speed, direction, and temperature.⁸ Also collected were key WWTS operational data and liquid sample analysis data that might provide information on WWTS sulfur emissions at both the Plymouth mill and the Roanoke Rapids mill.⁹

Industry conducted WWTS H₂S emission monitoring and reported the results to DAQ by November 2005. DAQ concluded that the analytical quality assurance (QA) data in the 2005 (Phase I) reports were unacceptable for the purpose of meeting 15A NCAC 2Q .0714. In response, industry improved their QA procedures and acquired more sensitive laboratory analytical equipment. The second attempt (Phase II) monitoring was completed in time to submit emission estimates and dispersion modeling analysis results by July 2006. A summary of the emission estimates and dispersion modeling results of the monitoring studies is presented in Table 1 for each paper mill. The results show three mills were below the AAL and the Plymouth mill was initially above the AAL.

² National Council for Air and Stream Improvement, NCASI.

³ Hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide.

⁴ G.J. Esplin, "Boundary Layer Emission Monitoring," Air Pollution Control Association Journal, Vol. 38, No.9, PP1158-1161, September 1988.

⁵ G.J. Esplin, "Total reduced sulfur (TRS) emissions from effluent lagoons," Pulp and Paper Canada, Vol. 90:10, PP. T398-400, 1989.

⁶ NCASI, "Spatial Ambient Air Sampling Methods for Quantifying Reduced Sulfur Compound and Methane Emissions from Kraft Mill Wastewater Treatment Plants, Technical Bulletin No. 957, November 2008.

⁷ DAQ requested that sampling be conducted at 4 elevations, not just 3 as industry proposed.

⁸ DAQ requested that meteorological towers be installed at each mill site, and not just use pre-existing towers located several miles away at nearby airports.

⁹ International Paper sold its paper mill located in Roanoke Rapids, NC to Kapstone Paper in 2006; to avoid confusion without regard to its ownership, this paper mill is simply referred to as the Roanoke Rapids paper mill in this report.

Table 1. Summary of Hydrogen Sulfide Emission Estimates and Dispersion Modeling Analysis

Paper Mill Location	Total Wastewater System Emission Estimate, ton/yr	Dispersion Modeling Results	
		Maximum Modeling Concentration, ug/m ³	Percent Acceptable Ambient Level*, %
Roanoke Rapids	220	85	71%
Riegelwood	45	76	63%
New Bern	38	36	30%
Plymouth	125	134	112% - initial
	125	108	90% - final**

* Acceptable Ambient Level, 120 ug/m³, 24-hr average

** Modeling under Uninhabitability Provisions in 15 NCAC 2Q .0709(a)(2).

Dispersion modeling was conducted by URS Corp for the Plymouth mill using Industrial Source Complex Model (ISC3) and emission estimates determined from industry measurements. The initial dispersion modeling results indicated expected concentrations at some receptors (in uninhabitable areas in the Roanoke River adjacent to the mill) were 112% of the H₂S AAL of 120 ug/m³ on a 24-hour average basis. As a result, the final dispersion modeling using an inhalation pathway exposure assessment under a provision for un-inhabitable areas¹⁰ [15 NCAC 2Q .0709(a)(2)(A)] demonstrated the modeled concentrations were less than the AAL (90% of AAL). DAQ reviewed and approved the initial and final (un-inhabitability provision) dispersion modeling resulting in an acceptable exposure level. After review of the Phase II study results, DAQ made the following conclusions and recommendations during the September 2006 Air Quality Commission (AQC) meeting:

Conclusions:

- Study produced valid emission estimates and modeling for all 4 mills in the study.
- Plymouth WWTS operated with H₂S emissions near normal during study.
- Plymouth H₂S AAL exceeded (112%) at property line beside uninhabitable area, but showed acceptable results allowed under Uninhabitability Provisions (90% of AAL).
- Rule calls for ambient monitoring study during 2007-2008 if results above AAL
- No major issues with H₂S AAL at other 3 mills

Recommendation

- Emission study and modeling meets 2Q. 0714 requirements for all NC paper mills

DAQ also reported at the AQC September 2006 meeting that the ATSDR released a May 2006 report on their separate ambient monitoring study. ATSDR monitored at three sites located 1-3 miles away from the Plymouth paper mill from November 2004 – February 2005.¹¹ Their report showed H₂S ambient levels at all three sites were below 2 ppb more than 99% of the time and below levels of concern. However, monitored SO₂ levels reached 200–400 ppb for several days at the site located 1-mile south-southwest of the paper mill property line, exceeding the 100 ppb adverse effect level for respiratory effects.

¹⁰ Un-inhabitable area means not inhabitable or occupied for the duration of the averaging time of the pollutant of concern.

¹¹ ATSDR, “Exposure Investigation Report - Weyerhaeuser Pulp and Paper Mill, Plymouth, North Carolina,” May 2006.

2. EPA Presentation on Industry Study for NC Paper Mills at September 2006 AQC Meeting

The US EPA had interest in the NC paper mill WWTS emission study because of an ongoing H₂S effort on nationwide characterization of emission sources, control technology, and health and exposure assessments. Staff from the EPA Office of Air Quality Planning and Standards (OAQPS) reviewed the Plymouth paper mill Phase 2 study report, drew different conclusions than DAQ, and presented their concerns at the September 13, 2006 AQC meeting. Those concerns included:

- Wastewater treatment liquid sample analytical data raised questions about testing during abnormal operating conditions and H₂S mass balance closure.
- Further questions were raised due to the disparity in overall hydrogen sulfide emissions between EPA's WATER9 wastewater model predictions (1,800 ton/year) and industry measured estimates (125 ton/year), and particularly in the difference between aerated pond WATER9 model predictions (1,170 ton/year) and industry-measured estimates (9 ton/year).
- EPA offered to conduct a measurement study at the Plymouth paper mill using a tunable diode laser (TDL) monitoring system and expected to report the study results by Spring 2007.

On September 14, 2006 the EMC decided that:

- The emission study and dispersion modeling requirements under 2Q .0714 were met by all four paper mills,
- DAQ and the paper industry shall collaborate with EPA in their study at the Plymouth paper mill WWTS, and
- The DAQ Director shall report back to the EMC when EPA finished its study.

3. EPA 2007 H₂S Emission Study at the Plymouth Paper Mill WWTS

The EPA staff from OAQPS and the Office of Research and Development (ORD) developed a plan to conduct a two-phase emission study in collaboration with DAQ and the paper industry. DAQ served as the 'project manager' for the project team in terms of organizing meetings and facilitating information exchange. EPA's Phase 1 objective was to determine whether the TDL would be sensitive enough to measure H₂S concentrations from the various WWTS sources. EPA also planned to use a conventional H₂S ambient air monitor to supplement their TDL measurements. If Phase 1 were successful, the Phase 2 objective would be to measure emission rates, wind conditions, and wastewater composition during normal operations. Phase 2 would be cancelled if Phase 1 H₂S were below TDL detection, or if levels were similar to those measured previously by industry.

EPA conducted their Phase 1 monitoring study with a TDL at the Plymouth paper mill on June 19-20, 2007 with 97 °F ambient air temperature. The mill and WWTS were operating at near full production and the WWTS characteristics as recorded from the routine monitoring systems were typical of normal and historical operations. The WWTS configuration for the settling ponds was normal yet different during the 2007 study (No. 2 Pond handled all water flow) than the industry 2006 study (No. 1 Pond handled nearly all water flow).

The H₂S concentrations were too low for the EPA TDL monitor to detect and to estimate WWTS emissions for many of the WWTS sources, as most of the monitoring data did not meet the stated minimum detection limit criteria in the EPA QA Project Plan. Given the insufficient data quality and its high level of uncertainty, EPA ORD produced an internal report to the working group

in August 2008 that was not cleared for public distribution. The EPA report included the statement 'do not cite or quote' on each page, so DAQ is inhibited in reporting any EPA emission data. There were no statements or data in the report on H₂S mass balance closure or on whether the WWTS operations were considered typical or not. EPA was unable to propose and implement acceptable EPA-approved WWTS liquid analytical method results for input to their WATER9 model. Because EPA alleged concerns with sample loss in the industry's procedures, DAQ videoed the paper industry's WWTS liquid sample collection and preservation. After reviewing the video, EPA had no further comment about their alleged concerns. Also note EPA indicated in the September 2006 AQC meeting the WATER9 model was validated for methanol in paper mill WWTS, but failed to clarify it was not validated for H₂S in paper mill WWTS. Given that EPA's criterion was not met for a Phase 2 study, there are no current plans to proceed with this phase of the study. [Note the EPA contractor performing the TDL monitoring did publish a paper on the TDL detection limit for this effort, and it likewise contains no H₂S emission estimates.¹²]

The paper industry staff conducted parallel ambient air monitoring using a Jerome H₂S meter during the EPA study. They monitored at several locations at ground level elevation across the full width of the plume directly downwind of the WWTS sources. Meteorological data were also collected at 6- and 30-foot heights for wind speed, direction, and temperature. Paper industry collected and analyzed WWTS samples. The paper industry staff also estimated H₂S emissions results using the protocol in their 2006 study. Emissions were estimated from estimated vertical concentration profile based on measured wind conditions. Three important results emerged from industry measurements:

- The effluents from the 2 settling ponds are combined and flow to the aerated basin through an open canal containing a Parshall flume for water flow monitoring. The open canal is < 0.02 acre, a small area in comparison to the 443 acres of the remaining WWTS. Three prior occasions showed the canal area was an insignificant H₂S emission source (< 2 ppb), as the sample recovery area was set up next to it for the industry studies. However, on arrival for the EPA study, noticeable emissions were being released from the canal area. Industry measurements indicated concentrations up to 3 parts per million (ppm) with a H₂S emission estimate of 27 ton/yr (0.77 gram/sec).
- Industry-produced overall WWTS H₂S emission estimates for the period during the EPA study in June 2007 (253 ton/yr, 6.5 g/s) were twice those from the industry study in March 2006 (125 ton/yr, 3.6 g/s). This was probably due to combination of higher liquid total sulfide, lower pH, and higher liquid temperature.¹³
- The measured data for the aerated basins at Plymouth, and other mills studied by the paper industry, continues to show that aerated stabilization basins (ASBs) are typically not highly emissive H₂S sources, as explained by the paper industry: "Minimal aeration in ASBs may result in relatively high H₂S emissions, especially with high sulfide input, and lower in-basin pH level will exacerbate the problem. However, with neutral or higher pH and adequate aeration, relatively low emissions can be expected from ASBs, regardless of the sulfide

¹² R. A. Hashmonay and M. T. Modrak, "Assessment of Hydrogen Sulfide Minimum Detection Limits of an Open Path Tunable Diode Laser," Paper No. 495, presented at 101st Annual Air and Waste Management Conference, Portland, OR, June 24-27, 2008.

¹³ NCASI, "Emissions of Reduced Sulfur Compounds and Methane from Kraft Mill Wastewater Treatment Plants," Technical Bulletin 956, September 2008, p. 82.

input.¹⁴ Relatively low H₂S emissions from ASBs are due to biological activity from sulfur-consuming microorganisms and chemical activity from the aerators oxidizing sulfides to sulfates.

Table 2 presents a comparison of the industry measured H₂S emissions for March 2006 and June 2007 along with the WATER9 model H₂S predictions for the same two WWTS conditions. It shows the industry measured H₂S emissions for the total WWTS were 125 ton/yr for the 2006 industry study and 253 ton/yr for the 2007 EPA study. Table 2 also shows the WATER9 predicted levels were 1,800 ton/yr for the total WWTS for the 2006 industry study and 892 ton/yr for the 2007 EPA study. The 2006 emission estimates are sometimes comparable between the industry measured and the WATER9 predictions for the No. 1 Settling Pond and both retention ponds. However, they are particularly dissimilar for the aerated basin for each of the 2006 and 2007 studies (9 and 44 ton/yr by industry estimates versus 1,170 and 517 ton/yr by WATER9 predictions, respectively).

While the 2007 study was unable to produce any EPA reportable results, it did provide several benefits:

1. It produced another combination of WWTS operating, meteorological, and H₂S emission conditions for the Plymouth paper mill different than what was previously available.
2. It showed the Canal and Flume area of the Plymouth WWTS can be a significant H₂S emission source.
3. It demonstrated the aerated basin H₂S emissions were low enough that the TDL was unable to detect them during the study, even though industry detected them with a Jerome H₂S meter and estimated the emissions to be 2-times higher than in the March 2006 study. Had the aerated basin emissions been close to WATER9 predicted levels, the TDL monitor would have detected them.
4. It demonstrated the measurement methodology adopted by industry, and approved by DAQ, was more appropriate for the paper industry WWTS emission estimates than EPA's selected TDL methodology.
5. It again demonstrated the WATER9 model may in some situations predict H₂S levels comparable to those measured for certain settling ponds, but WATER9 does not accurately predict H₂S emissions for aerated stabilization basins (as shown in Table 2), which are used in most pulp and paper mills.

¹⁴ NCASI, "Emissions of Reduced Sulfur Compounds and Methane from Kraft Mill Wastewater Treatment Plants," Technical Bulletin 956, September 2008, p.138.

Table 2. Summary of Paper Industry and EPA WATER9 Estimates¹⁵

Source	Paper Industry Measurement		EPA WATER9 Model	
	2006	2007	2006 ¹⁶	2007 ¹⁷
	H ₂ S Emissions, ton/yr		H ₂ S Emissions, ton/yr	
No. 1 Settling pond	102	108	150	3
No. 2 Settling pond	13	75	460	298
Canal and Flume	Insignificant ¹⁸	27	Not included	65
Aerated basin	9	44	1170	517
No. 1 Retention pond	Insignificant	Insignificant	5	9
No. 2 Retention pond	Insignificant	Insignificant	9	
All Sources	125	253	1800	892

4. Plymouth Ambient Monitoring Studies by ATSDR and DAQ/EPA Region 4

A. Agency of Toxics Substances and Disease Registry (ATSDR) Exposure Investigation¹⁹

After the start of the process to consider changing the H₂S AAL, DAQ asked the paper industry to provide a preliminary estimate of their WWTS H₂S emissions. Given a paucity of emission measurement data and liquid sample analysis data, industry performed a sulfur mass balance on their WWTS. Based on a mass balance, company engineers for the Plymouth paper mill provided a preliminary estimate of 1,760 ton/yr in 2002. Subsequent dispersion modeling of this emission estimate showed a large area around Plymouth would have public health concerns if this preliminary H₂S emission estimate were correct.

The North Carolina Department of Health and Human Services (DHHS) notified ATSDR of potential public health concerns regarding air quality in Plymouth, NC. The concerns were based on what DHHS believed to be large quantities of H₂S released by the Plymouth paper mill; which had, in turn, been based on the preliminary mass balance estimate mentioned above performed as a first approximation of the potential emissions. ATSDR’s monitoring study was performed from October 2004 to February 2005 with semi-continuous H₂S tape meters at three locations and semi-continuous SO₂ tape meters at two locations. However, the protocols ATSDR employed did not meet EPA Federal Equivalent Method requirements nor use state-of-the-art monitoring technologies and protocols. In addition, a review by DAQ of this study concluded the SO₂ results were potentially flawed due to QA and tape meter operational consideration. The tape meters ATSDR employed:

- Are commonly used in situations where less rigorous performance and QA standards than those meeting US EPA performance standards are acceptable,

¹⁵ Insufficient data quality prevented EPA from reporting emission estimates in 2007 EPA study.

¹⁶ Presented by EPA/OAQPS at the September 2006 AQC Meeting.

¹⁷ Provided by EPA/OAQPS to DAQ on February 18, 2009.

¹⁸ Previous measurements in 2005 and 2006 indicated this area had insignificant emissions, as the laboratory trailer used for sample preparation and recovery was located in this area.

¹⁹ ATSDR, “Exposure Investigation Report - Weyerhaeuser Pulp and Paper Mill, Plymouth, North Carolina,” May 2006.

- Do not use primary standards (e.g., US National Institute of Standards and Technology (NIST) traceable standards) for daily calibration and quarterly audits.

Ambient H₂S levels reported from the ATSDR study were far below levels of concern (see Table 4 below). However, the SO₂ tape meter monitored SO₂ levels that were observed to be 200–400 ppb continuously for several days at the site located 1 mile south-southwest of the Plymouth paper mill property line. The 200–400 ppb SO₂ observed levels were also well above the US EPA’s National Ambient Air Quality 24-Hr Standard (NAAQS) of 140 ppb.

B. DAQ and EPA Region 4 Ambient Monitoring Study In Plymouth

As a result of the ATSDR study, ATSDR and EPA Region 4 initially requested DAQ to perform ambient SO₂ monitoring in Plymouth. Later EPA Region 4 offered their H₂S monitor to be co-located alongside of the DAQ SO₂ monitor. ATSDR, EPA Region 4, and DAQ agreed to set the monitor site at the same location where ATSDR observed high SO₂ levels. The DAQ’s Ambient Monitoring Section conducted a robust study utilizing Federal Equivalent Method (FEM) monitors and collected meteorological data. For SO₂, DAQ staff had responsibility for (installed, maintained, calibrated, and audited) the FEM monitor. For H₂S, EPA Region 4 staff had responsibility for their state-of-the-art H₂S monitor. The DAQ staff only checked the H₂S data for notifying EPA when data quality issues occurred. Noteworthy differences between the ATSDR study from October 2004 to February 2005 and the DAQ study throughout 2007 are presented in Table 3 in terms of equipment quality, data quality, methodology review, and study time. Table 3 shows a superior study in terms of attributes (overall data quality, traceability, and time period) was conducted by DAQ / EPA Region 4 compared to the short-term ATSDR study.

Table 3. Comparison of Attributes Between ATSDR and DAQ Studies in Plymouth

Attribute	ATSDR Monitoring	DAQ and EPA Region 4 Monitoring
Quality of instrumentation	Non-FEM for SO ₂ and non state-of-the-art for H ₂ S	FEM for SO ₂ and state-of-the-art for H ₂ S
Data quality procedures	Not NIST traceable*	NIST traceable*
Time period of study	4 months	12 months

* NIST traceable means standards are traceable to primary standards maintained by the US National Institute of Standards and Technology.

During the DAQ/EPA Region 4 study, SO₂ and H₂S data were collected for a 1-year period from December 31, 2006 to December 31, 2007. All DAQ and EPA Region 4 reported data were quality-assured to meet FEM requirements. For SO₂, the highest 24-hr average observed level by the FEM monitor was only 10 ppb relative to the NAAQS 24-hr Standard of 140 ppb. Similarly for H₂S, the highest 24-hr average observed level by the EPA monitor was only 3.4 ppb relative to the DAQ 24-Hr Acceptable Ambient Level of 83 ppb for H₂S. Both highest single 24-hour SO₂ and H₂S concentrations for the year were recorded on December 15, 2007. Ambient concentration data collected during 2007 were well below the levels of concern for both SO₂ and H₂S as shown in Table 4. The H₂S data in the DAQ/EPA Region 4 study are in general agreement with the ATSDR H₂S data, but the SO₂ data in the DAQ/EPA Region 4 study are lower than ATSDR SO₂ data.

In summary, the results of the DAQ/EPA Region 4 ambient monitoring study throughout 2007 shows SO₂ and H₂S monitored levels in the vicinity of the Plymouth paper mill were well below the levels of concern for each pollutant. Given these results, DAQ concludes the monitoring performed by DAQ and EPA Region 4 addresses the concerns associated with the SO₂ monitoring data collected in the ASTDR study.

Table 4. Summary of 2007 Plymouth SO₂ and H₂S Ambient Concentration Monitoring Data

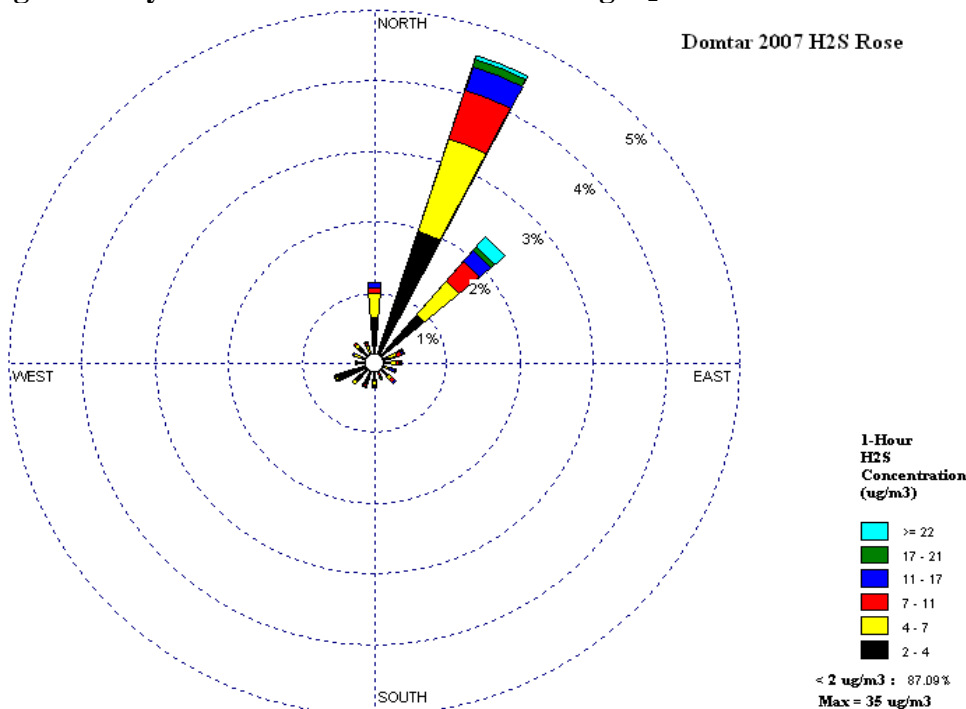
SO₂		
Parameter	Concentration (ppb)	2007 Date
Single Highest Measured 24-hr Average	10	Dec 15
NAAQS 24-hr Average	140	
H₂S		
Single Highest Measured 24-hr Average	3.4	Dec 15
NC AAL 24-hr Average	83	

One common approach to presenting long-term ambient monitoring data is with a pollutant rose. A pollution rose consists of selective averages of concentrations of an air pollutant for all sectors of the wind rose. Generally the sectors are 10 or 20 degrees wide and one-hour averages of concentrations and wind directions are used. Figure 1 shows the H₂S rose for selective averages of H₂S concentrations from the 2007 study and indicates the majority of the H₂S recorded at the monitor were when winds were from the north through the northeast (direction of the Plymouth paper mill). Table 5 tabulates the time periods corresponding to the H₂S monitored concentrations, illustrating the relatively small amount of time with elevated H₂S observations coming from the direction of the Plymouth paper mill WWTS at one monitoring location.

Table 5. Tabulated H₂S Pollutant Rose from the North through the Northeast

H₂S Airborne Concentration		Percentage of Time (%)
ppb	ug/m³	
< 1.4	< 2	87.1
1.4 – 2.9	2-4	3.4
2.9 – 5.0	4-7	2.0
5.0 – 7.8	7-11	1.1
7.8 – 12.1	11-17	0.7
12.1 – 15	17-21	0.4
> 15	>22	0.4
Observations from all other directions		4.9

Figure 1: Plymouth 2007 Ambient Monitoring H₂S Rose



Note: 1-hr concentration ranges in the Figure 1 legend are presented in micrograms per cubic meter (ug/m³). Values presented in Table 5 are presented in units of ppb and ug/m³. The conversion factor is 1.4 to convert from ppb to ug/m³ (1 ppb = 1.4 ug/m³)

5. Dispersion Modeling Analysis with Plymouth Ambient Monitoring Data²⁰

The purpose of the dispersion modeling study was to attempt to correlate actual measured H₂S concentrations during the 2007 Plymouth Ambient Monitoring Study with the industry-developed H₂S emission estimates from the 2006 measurements obtained by industry. The dispersion modeling study was not a requirement under 2Q .0714, but voluntarily performed by Domtar and DAQ to see what additional value could be derived from the 2007 Plymouth Ambient Monitoring Study. Generally speaking, a weak point with emission data collected over a short-term period is it only represents a ‘snapshot’ in time, and does not necessarily represent variation over diverse emission source conditions and seasons. This dispersion modeling study provided a unique opportunity to get an indication of the extent and frequency of emission variation over one year.

A source contribution analysis, performed as a key part of the modeling with the paper industry measured emission estimates in Table 2 from all WWTS sources, revealed that more than 99% of the maximum concentrations at the monitoring site were attributable to Settling Pond No. 1 emissions. This pond is the WWTS source with the highest H₂S emissions as shown in Table 2. Given the source contribution results, the other WWTS sources’ emission rates were assumed not to significantly impact the measured concentrations at the monitoring site for the purpose of this study. The study was designed to determine whether a H₂S emission rate(s) from only the largest contributing WWTS source could be shown to correlate with the maximum (worst-case) ambient H₂S concentrations.

²⁰ URS Corp, “Domtar Plymouth Hydrogen Sulfide Modeling Study, February 2009.

Model selection

The CALPUFF dispersion model was selected to use in the attempt to verify the validity of the H₂S emission estimates. CALPUFF was selected because it incorporates several features not available in previous and current EPA guideline dispersion models such as ISC3 and AERMOD. Some of CALPUFF features pertinent to the study are described as follows:

- 1) CALPUFF is a “puff” model that allows compound accumulation from one hour to the next while ISC3 and AERMOD assumes the compound is immediately transported to a receptor.
- 2) CALPUFF allows for a better representation of changes in hourly emissions when modeling a moist plume.
- 3) CALPUFF allows for plume processing during calm and low-wind periods, whereas ISC3 and AERMOD ignores periods with wind speeds less than 1.0 m/s.
- 4) CALPUFF can be applied using ISC3 formatted meteorological data. This mode of operation uses a simplistic method of handling terrain variation similar to ISC3. This was important since no CALMET processing would be required.

For this study, CALPUFF was executed using surface meteorological data collected during the 2007 Plymouth Ambient Monitoring Study combined with upper air data from the Newport, NC National Weather Service station. DAQ quality assured and processed the meteorological data.

Modeling methodology

The modeling methodology used followed a several step process. To help establish baseline concentrations for comparison, initial model runs were made using the ISCST3 and CALPUFF models with the 2007 on-site collected meteorological data and assumed a constant H₂S emission rate. The ISC3 model was selected since this model was used to demonstrate compliance with the AAL during the 2006 modeling study. Subsequent model runs were then made using the AERMOD and CALPUFF models assuming hourly-varying emission rates. For CALPUFF modeling two methodologies were used: 1) the CALPUFF “FOG” module which primarily accounts for temperature and moisture effects on emissions, and 2) the “Lake” evaporation factor method that accounts mainly for wind effects on emission rates. These two methodologies are discussed in more detail in Sect. 2.2 of the report. For AERMOD modeling only the “Lake” evaporation factor method could be used.

Model performance evaluation and summary

Following guidance provided by EPA²¹ and the measured H₂S concentrations, each model performance was evaluated. Because AERMOD meteorological data became available late in the modeling process, the AERMOD model was not included in this performance review. If it were, the model would have been the worst performing model with respect to modeling area sources. However, AERMOD is considered the superior model for evaluating elevated point sources. The evaluation showed poor correlation between the maximum measured and predicted concentrations for the ISC3, CALPUFF (constant emission rate), and CALPUFF (FOG) model runs, but very good correlation using the CALPUFF “Lake” evaporation factor method. These suggested emissions could be influenced by changes in atmospheric moisture and temperature with a significant contribution from changes in wind speed. The poor correlation using ISC3 and CALPUFF is not surprising, since both these models assumed a constant emission rate that would be inconsistent given the type of emission

²¹ EPA, “Protocol for Determining the Best Performing Model,” 1992, Report No. EPA-454/R-92-025.

source (open pond) and winds that vary over time. The CALPUFF (FOG) model, primarily designed for cooling tower evaporation, also does not factor in wind speed.

Table 6 presents the results for each of the six modeling approaches comparing modeled (predicted) and monitored (measured) for the 1-hr and 24-hr maximum concentrations. Note the *monitor* concentration for the 1-hr and 24-hr maximums, respectively, remains the same and that the *model* concentrations change for each modeling approach. Using the 24-hour averaging period as an indicator, the correlation between the modeled and measured concentrations are not close (almost 10 times too high) for the AERMOD (Approach 1), but progressively improve for Approaches 2-6 as the correlations get within 20% for the CALPUFF Lake approach predictions. The correlation within 20% between the measured levels and the model predictions with CALPUFF Lake tends to support the validity of the industry emission estimates as a baseline when modeled with one year of measured ambient concentrations and wind conditions at one location.

Table 6. H₂S Maximum Model Predicted and Monitor Concentrations (ppb)

Dispersion Model Approach	Emission Rate	Modeled	Monitored	Modeled	Monitored
		1-Hr		24-Hr	
1. AERMOD	Constant	490	25	36	3.6
2. AERMOD	Variable	126	25	19	3.6
3. ISC3	Constant	181	25	14	3.6
4. CALPUFF	Constant	68	25	10	3.6
5. CALPUFF Fog	Variable	71	25	8.6	3.6
6. CALPUFF Lake	Variable	28	25	4.3	3.6

6. Conclusions and Recommendations From Three New Studies Since September 2006

Conclusions

A. EPA Study in June 2007

While the EPA did not report results, several important points can be gleaned from the study, including:

1. EPA selected a measurement methodology intended to be sufficiently sensitive to the levels predicted by WATER9. However, actual airborne concentrations were not sufficiently high to meet the EPA’s QA criteria for reportable results. This in itself would indicate that the aerated basin emissions were significantly lower than the WATER9 predicted values.
2. It demonstrated the WATER9 model does not accurately predict emissions for aerated stabilization basins, which are used in most paper mills. However, this study does not provide any information that would suggest WATER9 would not accurately predict methanol emissions, which behaves in manner different than H₂S due to its chemical structure.
3. The paper industry conducted concurrent measurements during the 2007 EPA study that showed H₂S air emissions were twice those found in the industry’s March 2006 study. This finding, in relationship to Number 1 above, demonstrated the methodology developed by industry and approved by DAQ was more appropriate and accurate for estimating paper mill H₂S WWTS emissions than EPA’s monitoring methodology and EPA WATER9 model predictions.

4. The 2006 emission estimates and dispersion modeling results produced by industry, and approved by DAQ, addresses the concerns EPA expressed concerning industry emission estimate validity at the September 2006 AQC meeting.

B. Plymouth Ambient Monitoring Studies

The results of the study throughout 2007 show ambient monitoring was performed with an EPA FEM for SO₂ by DAQ and with a state-of-the-art monitor for H₂S by EPA Region 4. Based on quality assured data, monitored levels near the Plymouth paper mill were well below the EPA 24-Hr Standard of 140 ppb for SO₂ and the DAQ 24-Hr Acceptable Ambient Level of 83 ppb for H₂S. Monitoring performed by DAQ and EPA Region 4 alleviates the public health concerns associated with the SO₂ monitoring data collected in the 2004/2005 ASTDR study.

C. Dispersion Modeling Analysis with Plymouth Ambient Monitoring Study Data

A conclusion from the dispersion modeling analysis was reached that the paper industry emission estimate as a baseline provided a reasonable H₂S emission rate estimate from Settling Pond No. 1. The results suggest higher emissions induced by high wind speeds produce comparable ambient concentrations. Since high winds normally occur under helpful atmospheric mixing and are associated with better dilution (dispersion), the modeling tends to confirm the higher rates are offset by better dispersion conditions. The results of this study alleviates EPA concerns, expressed at the September 2006 AQC meeting, that higher emissions, induced by high wind speeds may have an adverse impact on off-site concentrations.

In summary, the three studies performed since September 2006 indicate that:

- The emission estimates produced by the paper industry are reasonably accurate,
- The dispersion modeling submitted by industry, which were based on those emission estimates, are reasonably accurate, and
- The Plymouth paper mill appears to be in compliance with the SO₂ NAAQS and the H₂S AAL.

Recommendations

Collectively, the data from the three studies conducted since September 2006 summarized above provide an unquestionably clear basis to conclude the requirements in 15A NCAC 2Q .0714 have been satisfactorily met by the paper industry and DAQ. On this basis, DAQ recommends the AQC find these requirements completely satisfied.

ATTACHMENT

15A NCAC 2Q .0714 Wastewater Treatment Systems at Pulp and Paper Mills

(a) This Rule applies to wastewater collection and treatment systems at pulp and paper mills that are exempted under Rule .0702 of this Section.

(b) Except for facilities that employ activated sludge type wastewater treatment systems, the owner or operator of a wastewater collection and treatment system covered under this Rule (2Q .0714) shall:

- (1) submit to the Director estimates of hydrogen sulfide, total reduced sulfur, and methyl mercaptan emissions from wastewater collection and treatment systems and components using estimation methods or factors developed through industry testing and analytical studies and approved by the Director by November 1, 2005. In deciding approval of the estimation methods and factors, the Director shall consider field validation procedures including the number of valid samples taken, when measurements are made, laboratory and field measurement quality assurance procedures, and other information necessary in producing accurate and precise measurements. The Director shall report to the Environmental Management Commission the information submitted under this Subparagraph by January 1, 2006;
- (2) using the emission estimates developed under Subparagraph (b)(1), perform air dispersion modeling of all hydrogen sulfide emission sources, including all emissions associated with the wastewater collection and treatment system, as described in 15A NCAC 2D .1106 (a) through (i). If the modeling analysis demonstrates that predicted concentrations of hydrogen sulfide are below the acceptable ambient levels outlined in 15A NCAC 2D .1104, no further plan development, measurement or monitoring action is required to maintain the exemption provided by this Rule. The results of the favorable modeling demonstration must be submitted to the Director by July 1, 2006. The Director shall report to the Environmental Management Commission the information submitted under this Subparagraph by September 1, 2006;
- (3) if the dispersion modeling performed under Subparagraph (b)(2) of this rule shows that the acceptable ambient level for hydrogen sulfide is exceeded, submit to the Director, on or before September 30, 2006, for approval by the Director, an ambient air quality monitoring plan designed to assess actual ambient levels of hydrogen sulfide typical of pulp and paper mill operations. The monitoring plan may be undertaken at each of the individual mill sites or, at the option of the affected mill sites, it may be undertaken at a single North Carolina mill site that the Director determines to be representative of the industry. The Director shall complete review and make the decision regarding approval of the monitoring plan by December 31, 2006;
- (4) by June 30, 2007, implement the ambient monitoring study plan required in Subparagraph (b)(3) to determine the actual ambient levels of hydrogen sulfide near pulp and paper mills;
- (5) complete the ambient hydrogen sulfide monitoring plan and report the results to the Director and to the Chairperson of the Environmental Management Commission by December 31, 2008 and the Director shall report to the Environmental Management Commission the information submitted under this Subparagraph by February 28, 2009 for further consideration.

(c) To perform ambient monitoring for hydrogen sulfide under Subparagraph (b)(3) of this Rule, the owner or operator shall use monitoring methods and procedures approved by the Director. The Director shall approve the monitoring methods and procedures if he determines that they are an appropriate measure of ambient air concentrations of hydrogen sulfide. *Eff. . April 1, 2005.*