

Health Consultation

Exposure Investigation Report

WEYERHAEUSER PULP AND PAPER MILL

PLYMOUTH, NORTH CAROLINA

EPA FACILITY ID: NCD991278540

MARCH 22, 2007

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Agency for Toxic Substances and Disease Registry
Division of Health Assessment and Consultation
Atlanta, Georgia 30333

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Prepared by:

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Executive Summary

In September 2003 the North Carolina Department of Health and Human Services (NCDHHS) notified ATSDR of public health concerns about air quality in Plymouth, Washington County, North Carolina. The concerns were based on 1) the estimated large quantities of hydrogen sulfide (H₂S) released by the Weyerhaeuser Pulp and Paper Mill in Plymouth, and 2) high asthma incidence rates in Washington County.

ATSDR evaluated Weyerhaeuser emissions data along with air modeling results provided by the NC Department of Environment and Natural Resources (NCDENR). After also evaluating emissions data from other kraft paper mills, ATSDR determined that air testing was needed in the Plymouth community [ATSDR 2003].

ATSDR proposed an Exposure Investigation (EI) to evaluate exposures to Plymouth's outdoor air. Air testing was performed from October 2004 to February 2005¹ and included:

- Real-time continuous H₂S monitoring at three separate locations
- Real-time continuous sulfur dioxide (SO₂) monitoring at two of these locations
- Grab samples collected with tedlar bags and tested for sulfides at a local lab (Research Triangle Park Labs, Inc.)
- Grab samples collected with canisters and tested for sulfides at an out-of-state lab (DataChem Laboratories, Inc.)

The H₂S levels found during the EI were usually below the ATSDR Minimal Risk Level (MRL). However, the recorded sulfur dioxide (SO₂) levels reached 200–400 ppb,² exceeding the lowest effect level of 100 ppb for respiratory effects in exercising asthmatics. Average SO₂ levels were well above the U.S. Environmental Protection Agency (EPA) 24-hr National Ambient Air Quality Standard (NAAQS) of 140 ppb. EPA categorizes air contaminants above a NAAQS level as “unhealthy.”³

In addition, carbonyl sulfide (COS), another respiratory irritant, was found in grab samples at levels averaging about 500 ppb. There are no established respiratory adverse effect levels (AELs) for COS, but there are data suggesting that exposure effects may be similar to those for H₂S.

Conclusions

1. SO₂ levels found in Plymouth can cause respiratory irritation and, thus, pose a public health hazard.
2. Elevated levels of other sulfur compounds, including COS, may contribute to respiratory irritation.

¹ EPA considers ambient monitoring for a period of less than one year to be a “short sampling period”, and ATSDR considers it to be sufficient for determining short-term and intermediate-term exposure.

² While the tapemeter (air monitoring instrument) met the data quality objectives for this EI, it is considered a screening instrument.

³ The air monitoring instrument is a screening instrument used for determining levels of a chemical expected to be present. It is not used as a federal reference method for collecting data to be compared with the NAAQS levels.

Recommendations

1. Children, asthmatics, or people with respiratory discomfort should avoid outdoor exertion if they smell sulfurous odors or sense respiratory irritation.
2. NCDENR should conduct sampling to ensure that the Weyerhaeuser facility emissions do not produce hazardous SO₂ levels in the ambient air near the facility.
3. NCDHHS should determine if there is a correlation between elevated SO₂ levels and respiratory and cardiovascular-related effects. Local emergency room and other medical-related statistics should be correlated with elevated SO₂ measurements to determine if there is an increase in respiratory and cardiovascular-related effects among Plymouth residents.
4. Sulfide emissions from kraft paper mills should be further characterized.
5. The Clean Air Act (CAA) Amendments of 1990 include carbonyl sulfide (COS) as a hazardous air pollutant (HAP). The U.S. Environmental Protection Agency (EPA) should formally evaluate exposure data in the toxicological literature and develop guidance levels for COS.

Outcomes

The National Council on Air Stream Improvement (NCASI) is currently conducting an air sampling investigation at the Plymouth facility. The results of this study will shed additional light on the emissions from this particular facility.

In addition, the EPA has initiated an evaluation of existing information on potential exposures to, and toxicological properties of, H₂S in order to assess the suitability of this chemical for addition to the CAA HAP list.

There is inadequate information to assess the toxicity of exposure to COS, which was detected in the ambient air in Plymouth. Therefore, ATSDR recommended to EPA that COS be considered as a candidate for inclusion in the Integrated Risk Information System (IRIS) assessment process.

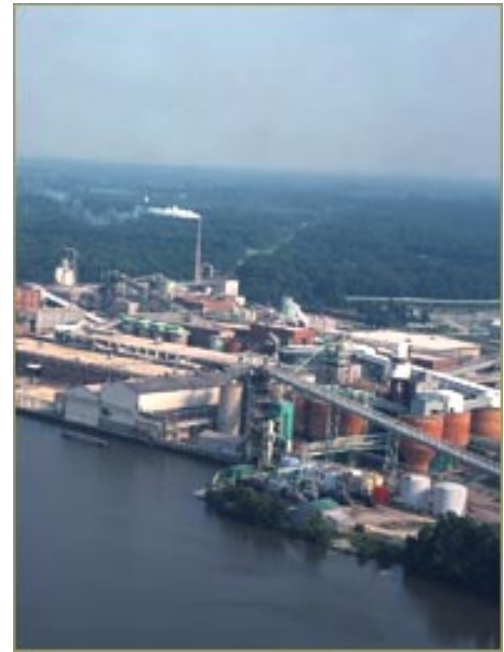
Finally, as a result of the findings in this EI, NCDENR is developing plans for a focused study of ambient SO₂ levels near the location where ATSDR investigators found ambient SO₂.

Background

The Weyerhaeuser Company operates a pulp and paper mill occupying an area of more than one square mile near Plymouth, Washington County, North Carolina [Weyerhaeuser 2005]. A total of 905 people live within one mile of the facility perimeter, and 4,403 people live within two miles [2000 U.S. Census]. The city of Plymouth (population 4,107), is located east-southeast of the facility.

Weyerhaeuser estimated that the Plymouth mill emits as much as 3,635,000 pounds per year of hydrogen sulfide (H₂S) — 99% of which comes from the waste water treatment plant (WWTP) [ATSDR 2003]. Using this total emissions rate, the North Carolina Department of Environment and Natural Resources (NCDENR) estimated ambient (outdoor) air concentrations of H₂S in the surrounding community.

Based on the Weyerhaeuser data, NCDENR estimated a maximum 1-hour H₂S concentration of 10,700 ppb and a maximum 24-hour concentration of 1,830 ppb at the facility property line. These air modeling estimates indicate that high concentrations of atmospheric H₂S may occur in neighboring communities. However, because of uncertainties associated with modeling atmospheric H₂S, ATSDR proposed an exposure investigation (EI) to better define community exposures by measuring actual ambient H₂S levels.



In addition to H₂S, many other sulfur compounds are produced during wood pulping operations. In particular, dimethyl sulfide (DMS), dimethyl disulfide (DMDS), and methyl mercaptan emissions occur and may actually exceed H₂S emissions. The sulfur compound emissions from the WWTP at another paper mill are shown in Table 1 below [NCASI 2002].

Table 1. Sulfur Compound Emissions from a Paper Mill Wastewater Treatment Plant

Sulfur Compound	Chemical Formula	Percentage of Sulfur Compound Emissions
Hydrogen Sulfide	H ₂ S	7.0
Methyl Mercaptan	CH ₃ SH	7.2
Dimethyl Sulfide (DMS)	(CH ₃) ₂ S	19.7
Dimethyl Disulfide (DMDS)	C ₂ H ₆ S ₂	66.2

These percentages are consistent with occupational exposures at kraft mills [Goyer 1990]. Sulfur dioxide (SO₂) is known to be produced from the mill boilers. However, the requisite scrubbers are expected to remove most of the SO₂ from the air and trap it into solution.

Community Concerns

The Weyerhaeuser facility straddles the Martin County and Washington County line, near the intersection of the borders of Washington, Martin, and Bertie Counties. For 2003, the North Carolina State Center for Health Statistics reported a statewide asthma hospitalization rate of 208 per 100,000 children (0–14 years). The following table shows the reported 2001 and 2003 rates for the entire state and the three counties potentially impacted by the Weyerhaeuser facility.

Table 2. Asthma Hospitalization Rates per 100,000 Children by Location

Location	2001	2003
Martin County	192	685
Washington County	319	184
Bertie County	268	202
North Carolina State Average	203	208

The impact of Weyerhaeuser emissions on the each of the county asthma rates is unknown. However, these emissions are a potential health concern because H₂S, SO₂, and other airborne sulfur compounds may trigger broncho-constriction in asthmatics or cause other respiratory effects [Jappinen et al. 1990, Jaakkola et al. 1990, ATSDR 1998, DOI & EPA 2005].

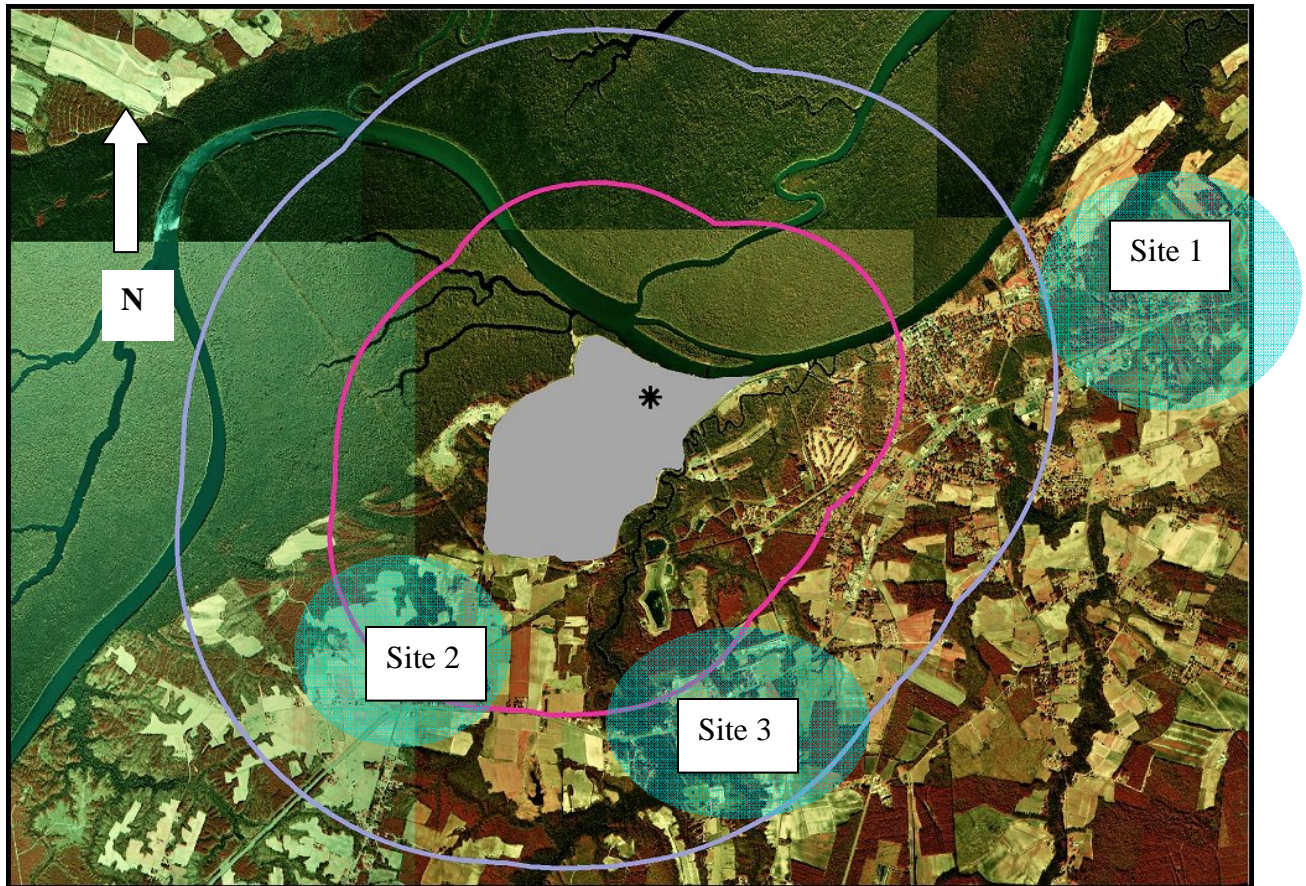
Rationale

ATSDR conducted this EI to better assess potential human exposure to H₂S, SO₂, and other sulfur-containing chemicals in ambient air near the Weyerhaeuser facility. During the EI, ATSDR monitored ambient air for H₂S and SO₂ at three separate locations for a 3-month period. In addition, ATSDR collected grab samples of ambient air at the same three locations. The samples were sent to two different laboratories to be tested for volatile sulfur compounds.

Target Population

The Washington County Health Department and the North Carolina Department of Health and Human Services (NCDHHS) recruited nearby residents to participate in the investigation. Three residential locations were selected for monitoring and sample collection sites. The approximate locations (Site 1, Site 2, and Site 3) are shown as shaded areas in Map 1. Site 1 is located about 3 miles northeast of the Weyerhaeuser waste water treatment plant (WWTP). Site 2 is less than one mile southwest of the WWTP, and Site 3 is approximately one mile south of the WWTP.

Map 1: Weyerhaeuser Plymouth Property with One and Two Mile Buffers



Methodology

Monitoring

Zellweger Single Point Monitors equipped with the ChemKey® and Chemcassette® detection system (also known as tapemeters) were used to monitor ambient air concentrations of H₂S and SO₂. H₂S was monitored continuously at all three locations (Sites 1–3) with measurements recorded once every minute. SO₂ was monitored continuously in 1-minute intervals at Sites 1 and 2. Duplicate measurements were collected at Site 1, with the locations noted as Site 1a and Site 1b.

A tapemeter (pictured at right) works by allowing a chemical in the air to react with a chemical impregnated on the tape.



The tapemeter measures intensity (which is proportional to concentration) by scanning the tape with an optical sensor that is sensitive to a specific color. For example, H₂S in the air reacts with lead acetate in the tape to form lead sulfide. [The sulfide replaces the acetate ion.] H₂S, which creates the most efficient reaction, produces a specific color (grey to the human eye). However, any other sulfide present in the air can interfere with the instrument reading by producing a similar color on the tape.

Instrument calibration is done by the manufacturer at the factory. In addition, two single-point checks occur automatically each time the instrument is activated. Instrument challenges (i.e., response tests using known concentrations of the monitored chemical) were also conducted before, during, and after the EI.

By recording a sample result once every minute, each instrument provided virtually real-time monitoring for either H₂S or SO₂. The detection range for H₂S is 1–90 ppb with a linear response above 2 ppb. The detection range for SO₂ is 50–6000 ppb with a linear response above 200 ppb. ATSDR and its contractor placed the monitors in a sheltered area at each location. At Site 1, duplicate tapemeters were used to monitor both H₂S and SO₂, requiring a total of four instruments. Ambient air was drawn into each instrument through a collection tube. After installation, the tapemeters were maintained in place during the 3-month investigation.⁴ Meteorological data were simultaneously recorded at Site 1.

Sampling

Because pulp and paper mills emit a number of sulfur compounds, ATSDR collected ambient air samples to identify the specific sulfur compounds present. Ambient air grab samples were collected immediately adjacent to each of the three monitoring locations. A total of 14 air samples were collected. Seven samples were collected using evacuated silica-lined SUMMA® canisters. The remaining seven were collected in tedlar bags using a manual pump. Each of the concurrent SUMMA® canister and tedlar bag samples was collected only when a field investigator noted an elevated reading on the adjacent tapemeter. However, a sampling delay of at least ten seconds occurred to allow for the collection process.

Since atmospheric sulfur compounds are reactive and decay quickly, arrangements were made to have the tedlar bag samples analyzed expeditiously at a nearby lab. Because no local labs had the capability to analyze SUMMA® canister samples, ATSDR used an out-of-state lab for those analyses.

Laboratory Analysis

Local Laboratory

The tedlar samples were hand-delivered to the Research Triangle Park Labs, Inc. (RTP) in Raleigh, North Carolina. These samples were analyzed using a gas chromatograph with a flame photometric detector (GC/FPD) two to three hours after they were collected.

⁴ EPA considers ambient monitoring for a period of less than one year to be a “short sampling period”, and ATSDR considers it to be sufficient for determining short-term and intermediate-term exposure.

Out-of-State Laboratory

The canister samples were express-mailed to DataChem Laboratories in Salt Lake City, Utah for sulfur gas analysis using a gas chromatograph (GC) equipped with a sulfur chemiluminescence detector (GC/SCD) and pulsed-flame photometric detection. The lab used a modified ASTM method supplemented with cryo-focused identification. For method preparation, the instrument is calibrated by injecting five milliliters (mL) each of various standard gas mixtures prepared in one liter bulbs from a neat (undiluted) solution.

Using this methodology, the laboratory is capable of detecting methyl mercaptan, dimethyl sulfide, dimethyl disulfide, and other volatile sulfur compounds at a detection limit of 50 ppb or less. The ATSDR protocol required that all samples be analyzed by the laboratory within 24 hours of receipt to minimize reactive losses of sulfur compounds in the sample.

Investigators/Collaborators

ATSDR developed the protocol, selected the laboratories, coordinated equipment purchases, and provided funding for the Eastern Research Group (ERG) contract as well as the Interagency Agreement with the Division of Federal Occupational Health (DFOH). DFOH assisted with equipment purchases and laboratory contracts. ERG contractors maintained the field equipment throughout the project, collected samples, transported samples to the local lab for analysis, and performed statistical analyses on the data.

ATSDR worked with the Washington County Health Department and the NCDHHS to recruit community participants for this investigation. In addition, the ATSDR Regional Representative kept the USEPA regional office informed of the progress in investigation activities.

Results

The monitoring data show low H₂S levels, but elevated SO₂ levels near the facility. Sampling data show that carbonyl sulfide (COS) levels in Plymouth are higher than typical U.S. background levels and that there were isolated peaks of moderately high levels of H₂S. No other sulfur compounds were detected.

Hydrogen Sulfide

During the 3-month monitoring period, the overall H₂S levels recorded at all three sites were below 2 ppb more than 99% of the time, with H₂S most frequently detected near the Weyerhaeuser facility.

The Site 3 tapemeter (located about 1 mile southeast of the Weyerhaeuser facility) detected some (usually less than 2 ppb) H₂S 99% of the time. The Site 2 tapemeter (located less than one mile southwest of Weyerhaeuser) detected H₂S 30% of the time. The Site 1 tapemeter,

located farthest from Weyerhaeuser (about 3 miles northeast), detected H₂S with the lowest frequency (13%).

Overall, the recorded H₂S peaks were infrequent and low-level, with these measurements occurring most frequently at Site 2 (nearest to Weyerhaeuser). The peak H₂S tapemeter levels (based on 1-minute readings) exceeded 20 ppb on only one occasion. This particular Site 2 peak lasted for a total of ten minutes.

There were conflicting H₂S results for two odor events that occurred on November 23, 2004. During each of these two odor events, a field investigator smelled the sulfurous odor, and noted elevated tapemeter readings. When tapemeter readings exceeded 5 ppb, the investigator collected a Tedlar bag sample and then collected a co-located SUMMA® canister sample.

For each odor event, the time-averaged tapemeter readings were below 16 ppb⁵. The results for one Tedlar sample showed H₂S at 1800 ppb; the other Tedlar results showed H₂S at 1200 ppb. No H₂S was detected in either of the concurrent, co-located SUMMA® canister samples; however, those samples were analyzed by DataChem several days after collection. This delay likely resulted in reactive losses of H₂S and thus impacted the data quality of the results. This data quality impact is discussed further in Appendix B.

Because of the difference between the tapemeter readings and the Tedlar sample results, ATSDR requested information about the investigator's perception of the odor intensity. Based on previous experience, the investigator reported that the odors were stronger than usual, but were not likely to exceed a level of 1000 ppb. ATSDR noted that H₂S was not detected in Tedlar samples collected during subsequent odor events. In addition, quality assurance data do not suggest that the tapemeters provided false negative readings. Taking all this into consideration, ATSDR determined that H₂S levels were typically closer to levels recorded by the tapemeters.

The peak tapemeter measurements were most often recorded during calm wind conditions. As a result, there were too few data to correlate H₂S levels with wind direction from the Weyerhaeuser facility or any other source. One occasion in which peaks were associated with calm conditions occurred on November 23, 2004, as illustrated in Figure 1.

⁵ The tape meter recorded H₂S levels every 2-minutes. As a result, each data point recorded is a 2-minute average that tends to reduce peak measurements. However, we do not know why there was such a large difference between the high Tedlar sample result and the much lower tapemeter reading.

Figure 1: Hydrogen Sulfide Monitoring: November 23, 2004 at Site 2, Plymouth, NC

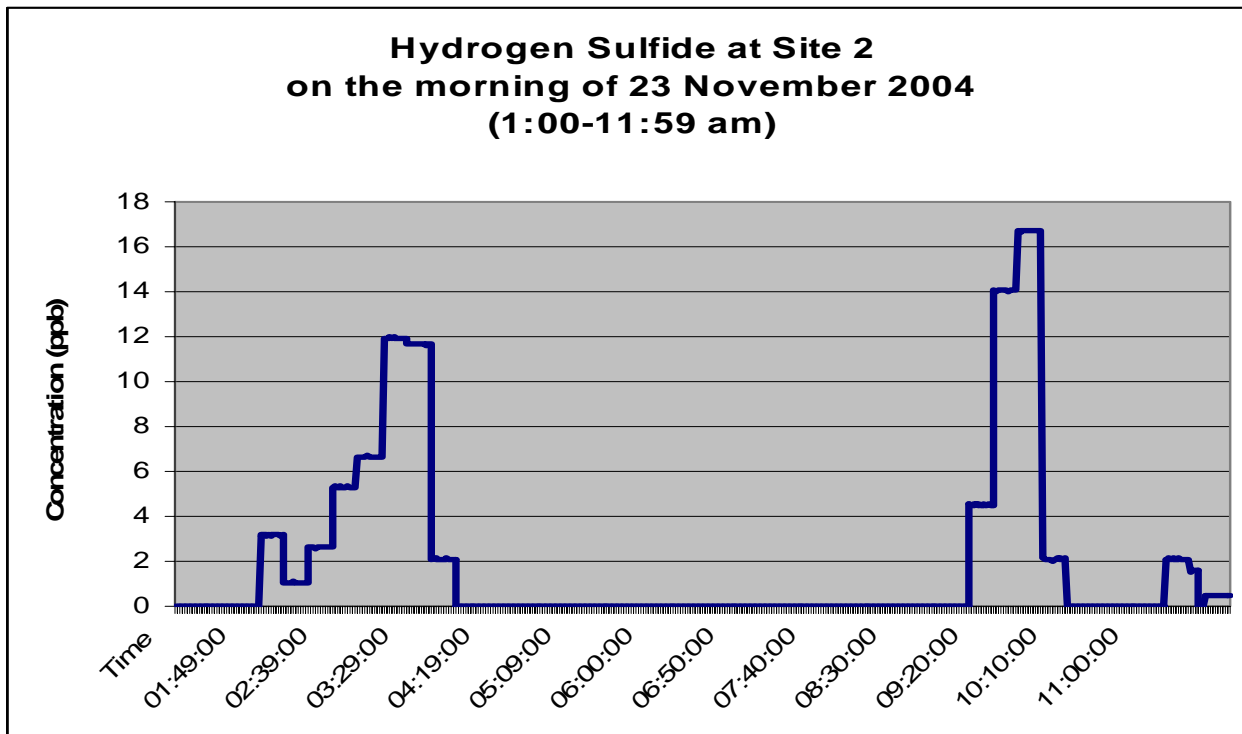


Figure 1 illustrates the two elevated H₂S concentrations found at Site 2 on the morning of November 23, 2004. [This pattern of two H₂S peaks occurred on several other days during the investigation.] On November 23, 2004 winds were generally calm, but each peak ended when there was a slight increase in wind speed. These bimodal results may reflect a source that is either:

- periodic
- constant, but with dispersion reducing levels to below the detection level
- near Site 2, with odors decreasing as winds increase

Sulfur Dioxide Monitoring

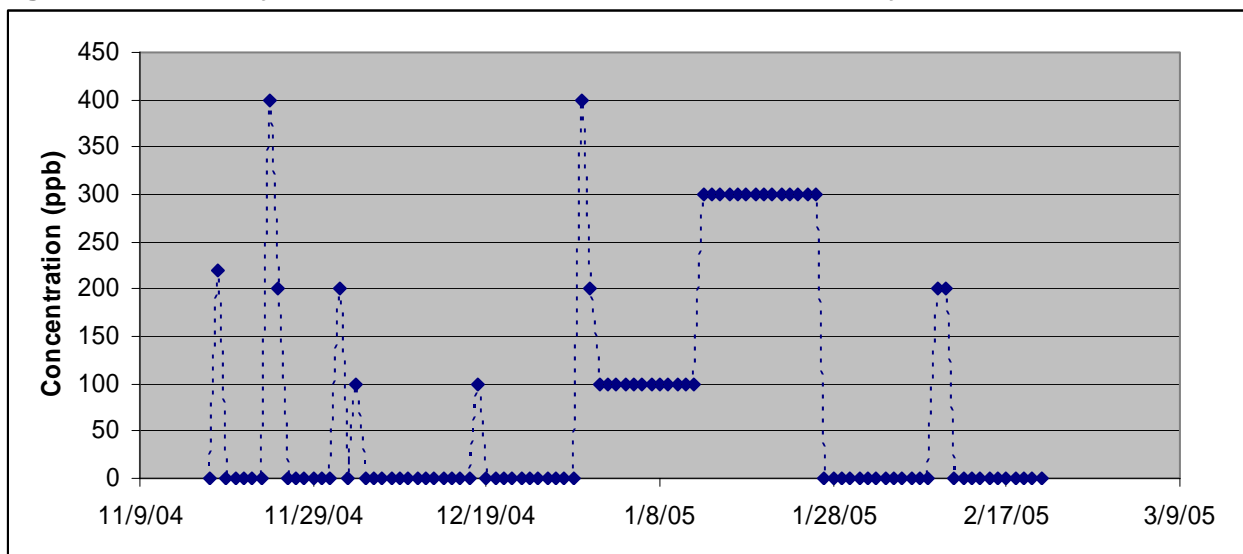
Although SO₂ was seldom detected at Site 1, it was detected 28% of the time at Site 2. The following is a summary of SO₂ levels measured at Site 2:

- ≥ 100 ppb 27.6% of the time
- ≥ 200 ppb 14.5% of the time
- ≥ 300 ppb 4.8% of the time

The peak SO₂ levels exceeded 300 ppb on four separate occasions and exceeded 400 ppb once (for about 10 minutes).

Figure 2 illustrates the Site 2 daily peak measurements. It shows that most of these peaks occurred during January, and that SO₂ was not detected every day.

Figure 2: Peak Daily Sulfur Dioxide Measurements at Site 2 in Plymouth, NC



The graph reveals the single (one minute) peak for each day of sampling. These peak SO₂ measurements were 300 ppb on several days starting on January 13, 2005.

From January 13–20, the mean 24-hr average SO₂ level was 237 ppb. In some cases during this time span, the 24-hr average level approached 300 ppb. This event also coincided with elevated H₂S measurements.

Wind speeds were very low during the entire 3-month monitoring period. Because low wind speeds are typically associated with variable and uncertain wind direction, it is difficult to correlate odor events and wind direction in this scenario. Furthermore the SO₂ measurements were within a small range⁶, which limits the statistical significance of data comparisons. Generally, calm conditions and westerly winds were associated with low SO₂ measurements.

On a few occasions, when winds were sufficiently strong to determine wind direction, peak SO₂ measurements corresponded to specific events. These events included periods when Weyerhaeuser emission controls did not operate properly or when farmers burned vegetation in nearby fields.⁷ However, there were also peak SO₂ occurrences that did not correspond to any known event. Furthermore, measured SO₂ levels were highest at Site 2 when winds were from the northwest. Weyerhaeuser is located northeast of Site 2 and was not likely to be a primary source of SO₂ during those peak events. Several of the peak SO₂ measurements occurred on days when H₂S peaks were also recorded (See Appendix C).

Other Sulfur Compounds

The atmospheric carbonyl sulfide (COS) levels measured in grab samples were much higher than expected. Overall, COS levels ranged from non-detect (ND) –1300 ppb. COS was

⁶ The range is small relative to the instrument reporting range (100–400 ppb). The small variations in measured values cannot be effectively modeled.

⁷ Although the elevated SO₂ measurements occasionally corresponded to the timing of Weyerhaeuser emission control malfunctions, the durations of the SO₂ measurements and the malfunctions did not match.

detected in all samples analyzed locally by RTP, within 2–3 hours of collection. These locally analyzed samples showed COS levels ranging from 70–1300 ppb, with an average of 520 ppb. COS was also detected in the three samples analyzed within 24 hours of receipt by DataChem⁸. Therefore, the lab results for samples analyzed within 2 days of collection, showed an average COS level of 346 ppb. For *all* lab results (including those from DataChem considered to be unreliable¹), the average COS level was 277 ppb (assuming ND = 0).⁹ Table 3 shows the results of the co-located grab samples (excluding the QA samples).

Table 3. Co-located Ambient Sulfide Levels in Grab Samples

Collection Date	Location	Compound	Tedlar Results [†] (ppb)	Canister Results (ppb)
25 Oct	Site 1	H ₂ S	1800	ND *
25 Oct	Site 2	H ₂ S	1200	ND *
25 Oct	Site 1	COS	1300	ND *
25 Oct	Site 2	COS	900	ND *
17 Nov	Site 1	COS	70	43 **
17 Nov	Site 2	COS	180	90 **
17 Nov	Site 3	COS	150	38 **

* analyzed on Oct 29, 2004; ND = not detected

** analyzed on Nov 18, 2004

† analyzed within 5 hours

Although the following sulfur compounds have been found at other kraft paper mills [NCASI 2002], none was detected during this EI.

Methyl mercaptan	Thiophene
Dimethyl disulfide	Tetrahydrothiophene
n-Butyl mercaptan	Isopropyl mercaptan
Dimethyl sulfide	n-Propyl mercaptan
Carbon disulfide	Ethyl mercaptan
Diethyl sulfide	t-Butyl mercaptan

Quality Assurance Data

As described below, the SO₂ and H₂S tapemeter results for this EI are considered reliable. The RTP lab results reported for H₂S and COS are within acceptable tolerance and, therefore, considered to be of good quality. However, neither the COS and H₂S results from DataChem, nor the methyl mercaptan and dimethyl disulfide results from either RTP or DataChem meet quality assurance requirements.

⁸ To ensure an acceptable quality of laboratory results, ATSDR requested sample analysis within 24 hours of sample receipt. However, DataChem analyses for four of the seven samples occurred approximately 72 hours after receipt.

⁹ Although the quality for each method was evaluated for this investigation, the methods have never been evaluated for comparability. Since method detection levels differed widely, we chose not to average data across methods.

Tapemeters

EI field investigators periodically tested the precision of tape meter readings using a known quantity of H₂S. This testing utilized the automatic electronic check mechanism that runs internally upon equipment start-up. The standard deviation of these readings ranged from 0.57%–2.98%, which is well within an acceptable tolerance of ±15%.

To ensure tapemeter data reliability (accuracy and precision), field investigators also “challenged” the instruments with known quantities of different sulfur compounds. These compounds included H₂S and SO₂ as well as others (e.g., COS) that might produce a biased response, i.e., a false positive or false negative response. The largest average biases were negative: -8.70% for SO₂ and -2.49% for H₂S. Although these negative biases indicate that detected levels were lower than the levels used to challenge the instrument, they are within an acceptable ±15% tolerance. In most cases during testing, the tapemeters showed a negative bias. This negative bias increased slightly in magnitude toward the end of the investigation. Overall, the testing results indicate that false positives of any significant magnitude were unlikely.

The H₂S tapemeter also responded to the presence of COS; however, the response ratio was greater than 50 to 1. This means that COS present at more than 50 ppb produced a 1 ppb (or lower) response on a H₂S tapemeter. Such a response ratio is well within acceptable tolerance.¹⁰ Additional details are provided in the Exposure Investigation Report: Kraft Pulp and Paper Mill, Plymouth, NC [ERG 2006].

Laboratory samples

Each laboratory (RTP and DataChem) analyzed seven samples for atmospheric sulfides. Both labs followed standard quality assurance protocols to ensure that lab instruments could identify and quantify the specific sulfides of interest. RTP had higher method detection limits (MDLs) (200–500 ppb) for these compounds than did DataChem (5 ppb). However, the RTP instrument detection level (IDL) was as low as 70 ppb.¹¹ Documentation provided with the analytical results indicates that both labs either met or surpassed their respective MDLs.

Because it was locally available, RTP could analyze samples more quickly, thus limiting any reactive losses generated by longer sample holding times. Delays in DataChem analyses for several samples led to unacceptably long holding times, likely causing the generally lower levels found in DataChem results.

Multiple samples with known quantities of sulfur compounds (i.e., spiked samples or spikes) were sent to each lab to ascertain the data quality of reported results. This procedure checked whether lab results accurately represented the sample contents. RTP results indicated good recovery of the spikes, but DataChem results did not. DataChem detected COS in the spikes, but the reported levels were significantly less than actual levels [ERG 2006].

¹⁰ Although the manufacturer (Zellweger) has not reported a false positive H₂S response in the presence of COS, they have not refuted the slightly false positive findings from this investigation [Zelweger 2004].

¹¹ The instrument detection limit (IDL) was lower than the MDL.

For co-located samples, the DataChem results were consistently lower than the corresponding RTP results. The DataChem results show COS levels of about one-half those found by RTP (Table 1). Higher detection levels of the RTP method could account for three of the higher measurements because methods tend to overestimate concentrations near or below the detection level. However, the DataChem quality assurance data suggest that, for each day the sample analysis was delayed, DataChem results were reduced by one-half. The results from both the co-located samples and spiked samples indicate that COS levels in a sample container had a half-life of about one day.^{12,13} Therefore, the data from DataChem show a bias toward lower-than-actual levels. In comparison, the RTP measurements more nearly approximate the range of atmospheric COS (70–1300 ppb) in Plymouth during the investigation.

The spiked sample results from both labs show unreliable recovery of dimethyl disulfide and methyl mercaptan. DataChem detected dimethyl disulfide, but with recoveries that were outside acceptable tolerance, and did not detect any of the methyl mercaptan. RTP detected neither the dimethyl disulfide nor the methyl mercaptan.

Dimethyl disulfide and methyl mercaptan were not found in any of the EI field samples. These compounds were, however, expected to be present in the Plymouth area.

Discussion

This EI was designed to measure levels of atmospheric sulfur compounds thought to be associated with releases from the Weyerhaeuser mill in Plymouth. The EI results differ from the results of previous air modeling as well as data collected near other kraft mills.

Modeling calculations predicted a peak H₂S level of 10,700 ppb and a peak 24-hr level of 1830 ppb at the facility perimeter [NCDNER 2002, ATSDR 2003]. However, the peak H₂S level found during the investigation was an unconfirmed 1800 ppb, and the peak 24-hr level was <2 ppb.

Modeling results might not reflect actual field conditions that are directly measured using air monitoring and sampling techniques. Other atmospheric sulfur studies revealed differences between modeling and sampling outcomes [van Aardenne 2002]. Because H₂S is a highly reactive gas, levels are likely to degrade over a relatively short period of time. Nevertheless, the H₂S levels found during the EI were lower than expected. Based on the results found during other EIs, the half-life of H₂S in a sampling container is approximately one day [ATSDR 1997, ATSDR 2006]. However, the reactivity of H₂S alone may not account for the low levels found in Plymouth, because a half-life of one day does not account for the differences in the predicted and measured values (at Weyerhaeuser).

¹² At their in-house laboratory, ERG spiked SUMMA® samples with 100 ppb COS and shipped them to DataChem for analysis. The results for aliquots analyzed after holding times of 1, 2, and 3 days were 42 ppb, 25 ppb, and ND respectively.

¹³ The DataChem results reported for a “blank” quality assurance sample appear to have been switched with the results from a sample spiked with COS (and other sulfur compounds). Based on this assumption, ATSDR includes the DataChem COS results in the estimation of COS half-life. If those sample results were not switched, then DataChem detected a compound that was not present in one sample and did not detect compounds that were present in another sample.

Kraft mills are known to produce high levels of methyl mercaptan, dimethyl disulfide, and dimethyl sulfide [NCASI 2002]. No trace of these compounds was detected during this EI. On the other hand, kraft mills typically produce significantly more H₂S than either SO₂ or COS; however, the COS and SO₂ levels found in Plymouth exceeded H₂S levels. This result might have occurred because most of the atmospheric sulfur released by the facility is either in the form of SO₂ and COS, or once emitted as H₂S, is largely converted to SO₂ and COS. The available data do not indicate which of these possibilities is true. The EI findings, combined with modeling predictions and data from other kraft paper mill studies indicate uncertainty about the fate and transport of airborne sulfides. The EI results suggest that further characterization of airborne sulfur compounds is needed in communities near kraft mills.

Summary of Atmospheric Sulfur Compounds

The sulfur compounds detected during this EI include respiratory system toxicants. The compounds that proved most difficult to measure (methyl mercaptan, dimethyl disulfide, etc.) are odorous at low levels. However, they are much less toxic than the compounds that were actually detected (SO₂, H₂S, COS). SO₂, a very stable atmospheric compound, is likely to be the most toxic [NIOSH 2005]. Table 4 summarizes the noteworthy EI results along with corresponding comparison values for each chemical. Relative toxicities can be determined based on the comparison values for each chemical.

Table 4. Summary of Maximum Levels, Comparison Values (ppb), and Health Effect Levels, Exposure Investigation, Plymouth, NC

Chemical	Duration	Maximum Level (ppb)	Health-Based Comparison Value (ppb)	Health Effect Level (ppb)
SO ₂	7 min	400	10 ⁽¹⁾	250 ⁽⁵⁾
	24 hr	237	10 ⁽¹⁾ and 140 ⁽²⁾	100 ⁽⁶⁾ , 250 ⁽⁵⁾ , and 120 ⁽⁷⁾
H ₂ S	1 min peak	1800	200 ⁽¹⁾	2000 ⁽⁸⁾
	>24 hr	<2	20 ⁽¹⁾	30 ⁽⁹⁾
COS	1 min peak	1300	53.3 ⁽³⁾	NA ⁽¹⁰⁾
	Average	500	16.4 ⁽⁴⁾	10,000 ⁽¹¹⁾

Measurements noted in **Bold** text are higher than the corresponding comparison value

- (1) ATSDR Minimum Risk Level (MRL) based on a 10-minute exposure study [ATSDR 1998; ATSDR 2005]
- (2) EPA 24-hr National Ambient Air Quality Standard [EPA and DOI 2005]
- (3) Arizona 1-hr Ambient Air Quality Standard [Arizona 1999]
- (4) Arizona 24-hr Ambient Air Quality Standard [Arizona 1999]
- (5) Lowest level associated with respiratory effects for 5-min exposure [Bethel 1985]
- (6) Lowest level associated with respiratory effects for 10-min exposure [Sheppard 1981]
- (7) Daily exposures associated with an increase in respiratory and cardiovascular mortality [Venner 2003].
- (8) Lowest level associated with respiratory effects for 30-min exposure [Jappinen 1990]
- (9) Lowest level associated with respiratory effects for 24-hr exposure [Campagna 2004]
- (10) No low effect levels studies are available for COS
- (11) Levels shown to produce reproductive effects in mice 6 hrs/day, 5 days/week for 13 weeks [Monsanto n.d.]

The findings for each sulfur compound are discussed below.

SO₂: Sulfur Dioxide

SO₂ is internationally recognized as an air pollutant because it is associated with urbanization and adverse health effects. SO₂ is a relatively stable compound compared to most other atmospheric sulfur compounds. However, even dispersion of this frequently monitored and relatively stable sulfur compound is not fully understood [van Aardenne 2004].

The Clean Air Act “requires that EPA set National Ambient Air Quality Standards (NAAQS) for SO₂ and five other pollutants considered harmful to public health and the environment. The law also requires EPA to periodically review the standards to ensure that they provide adequate health and environmental protection and to update those standards as necessary” [EPA 2005]. The EPA sets primary and secondary air standards. Primary standards provide limits to protect public health, including the health of “sensitive” populations such as asthmatics, children, and the elderly. Secondary standards set limits to protect public welfare, including protection against decreased visibility or damage to animals, crops, vegetation, and buildings. The NAAQS primary standards for SO₂ are 140 ppb for 24 hours and an average of 30 ppb for 1 year. The 24-hr standard should not be exceeded more than once per year and the annual standard should never be exceeded. The secondary SO₂ standard is 500 ppb for 3 hours and should not be exceeded more than once per year.

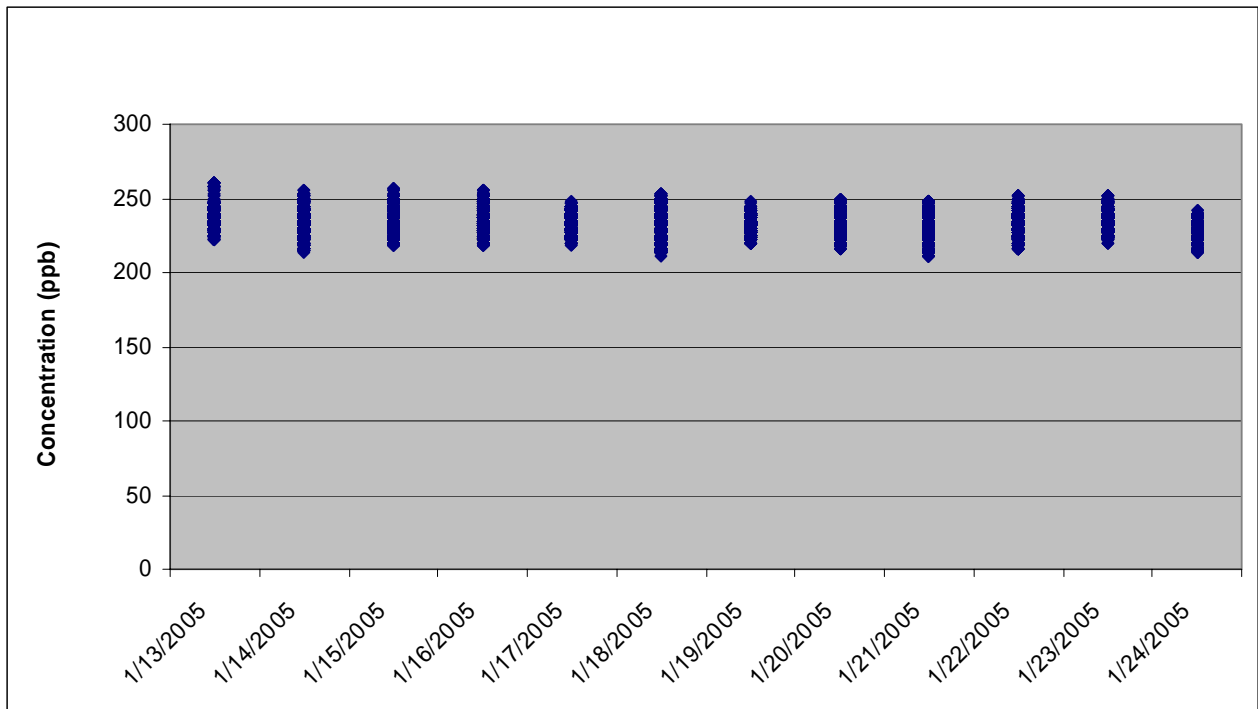
In January 1997, EPA proposed a new program to address the potential health risks posed to asthmatics by short-term peak levels of SO₂ in some regions of the US. Although there is a significant health concern about these exposures, no short-term peak standard has been established [EPA 2005]. However, California has set a 1-hr SO₂ standard of 250 ppb and their contracted review found that this value will “not protect all members of the community” [CAAQS 1984, Koenig 2000]. State and local environmental agencies typically measure the levels of a variety of pollutants at monitoring locations throughout each state and post the results on an Internet-accessible computer database called the Air Quality System (AQS; see <http://www.epa.gov/air/data/index.html>). Through the Air Quality Index (AQI), EPA communicates with the public about daily air quality using the collected monitoring data. The AQI is an index that indicates how clean or polluted outdoor air is, and what associated health effects might be a concern for the population in a given area. The AQI focuses on health effects that may be experienced within a few hours or days after breathing polluted air. EPA calculates the AQI for five major air pollutants regulated by the CAA — ground-level ozone, particle pollution (also known as particulate matter), carbon monoxide, sulfur dioxide, and nitrogen dioxide. The AQI for sulfur dioxide is provided in Appendix A (Table A4) [EPA 2005].

Based on current scientific information, ATSDR sets guidance levels called minimal risk levels (MRLs). An MRL is an estimate of the daily human exposure to a hazardous substance that is likely to be without appreciable risk of adverse non-cancer health effects over a specified duration of exposure (e.g., acute, up to a two week duration). In particular, an MRL is below a level expected to cause adverse health effects in the most sensitive population. It is important to note that an MRL is not designed to be an exposure limit. The ATSDR MRL for acute SO₂ exposures is 10 ppb and based on an exposure study involving a 10-minute exposure [ATSDR 1998].

The SO₂ tapemeters used in this EI were configured to detect short-term peak SO₂ levels of 200–6000 ppb. EPA air quality monitors are typically configured to detect hourly averages of 5–500 ppb. As a result, the EI tapemeter data should be compared to acute effect levels rather than to the EPA 24-hr average NAAQS level. The SO₂ tapemeter results demonstrated relatively good precision at 4600 ppb and 5250 ppb (but with a -3.24 to -8.70% bias); however, the precision at lower levels (near 200 ppb) likely approached the limits of acceptability ($\pm 15\%$).

Because the SO₂ readings near or above 200 ppb met the ATSDR data quality objectives, they were interpreted based on short-term human exposure studies [ATSDR 1998]. In addition, since the results show that on many occasions SO₂ levels remained above 200 ppb for 24 hours, the data may also be compared to the 24-hr SO₂ NAAQS. Levels remained above 200 ppb for several days in January. The Site 2 SO₂ average hourly measurements from January 13–25 are illustrated in Figure 3.

Figure 3: Range of Site 2 SO₂ Hourly Average Concentrations (ppb) January 13–26, 2005, Plymouth, NC.



The continuous measurements throughout this period averaged more than 230 ppb for each day. Measurements were higher than 281 for several 24-hr periods.¹⁴

¹⁴ Consistently elevated levels of SO₂ measured over several days, are uncommon nowadays in the US. However, since the presence of SO₂ was confirmed during other periods, these results cannot be disqualified on the basis of instrument error. Therefore, ATSDR considers that SO₂ was present, but at uncertain concentrations because the recorded levels were near the detection limit.

Since atmospheric concentrations seldom remain stable for long periods, it is uncertain whether the air concentrations were elevated for this extended length of time. However, comparison of the co-located tapemeter results, indicate that there were H₂S peaks during the SO₂ peaks, thus, implying the presence of a contaminant plume (See Appendix C).

Although the instrument used in this EI (a tapemeter) is different than the instrument used to show compliance with the SO₂ NAAQS, the tape meter levels recorded at Plymouth are much higher than those typically recorded around the US from 1994–2005 [EPA 2005]. Most cities reported levels <100 ppb for the highest 24-hr average during the year. In addition, the highest 24-hr average level measured in 1995 in Chongqing China (considered remarkably polluted) was 218 ppb [Venner 2005].

Using the EPA AQI, the SO₂ levels recorded in January 2005 would be considered **“unhealthy”** [DOI and EPA 2005]. EPA recommends that children, asthmatics, and people with heart or lung diseases reduce their outdoor exertion during these conditions.¹⁵

The SO₂ data collected from the two monitoring sites cannot be conclusively correlated with specific sources. Site 1 instruments never detected SO₂, and the majority of the SO₂ detected at Site 2 were during calm events. Therefore, we can not triangulate between the two measurement sites or with Site 2 and wind direction. Some SO₂ sources¹⁶ at Weyerhaeuser could theoretically produce the SO₂ levels measured. However, as would be expected in that case, we did not observe elevated measurements when the wind originated from the northeast.¹⁷

The highest sustained SO₂ levels occurred during January 2005 (Figure 3). These sustained levels were measured at approximately the same time that numerous odor-causing events occurred. These events included prescribed (permitted) agricultural burns (on January 13 and 14) as well as several un-prescribed agricultural burns. Weyerhaeuser reported flow problems into the scrubbers on January 23 and a scrubber-shutdown on January 25. These were minor problems expected to last <24 hours rather than several days. Another SO₂ peak on November 18, 2004 (from 3:00–10:00 AM) correlates to a period when two of the 18 Weyerhaeuser scrubbers were shut down. An event occurring on 24 and 25 November 2004 did not correlate with Weyerhaeuser events or agricultural burns, but may loosely correlate with other (distant and smaller) industrial SO₂ sources. In one case, SO₂ measurements returned to non-detect after a new tape was installed in the tapemeter. Similar observations¹⁸ have been made during other EIs when the tape media became discolored, affecting the instrument’s ability to correctly measure airborne contaminants [ATSDR 1998].

Winds were typically low and variable throughout the monitoring period and the measured levels were narrowly distributed (0–400 ppb). As a result, we could not link the measured concentrations to a source. However, the tapemeter nearest Weyerhaeuser (Site 2) detected SO₂ 28% of the time, while Site 1 (a few miles away) detected SO₂ less than 1% of

¹⁵ The tapemeter that recorded these measurements is not the instrument specified by the federal reference method used to determine if the NAAQS has been exceeded.

¹⁶ The Weyerhaeuser Riley boilers emit 200 pounds of SO₂ per hour.

¹⁷ The average SO₂ measurement was the same (about 200 ppb) whether wind came from the northeast (the direction of Weyerhaeuser) or from the southeast (the opposite direction).

¹⁸ Based on the authors’ experience, tapemeter readings may show dampened peaks, but may also show a longer event duration.

the time. In addition, there was some indication of an occasional association between SO₂ and H₂S (discussed further in Appendix C).

Health Implications of SO₂ Exposures:

SO₂ was measured at 400 ppb for a 10-minute period and averaged more than 200 ppb on several different days during the EI. Ten human challenge studies were conducted to investigate whether an association exists between SO₂ at levels near 400 ppb and respiration health effects. Eight of these studies indicate an adverse effect, while two do not. In five of the studies, airway resistance and broncho-constriction were measured after 3–10 minutes of exposure to concentrations of 100–500 ppb [Sheppard, 1981, Bethel 1983, Linn 1983, Bethel 1984, Bethel 1985]. In three studies, the results showed an increase in airway resistance after 10–75 minutes of exposure to 400–500 ppb [Koenig 1985, Linn 1987, Roger 1985]. No effect was measured in two studies after 30–40 minutes of exposure to 500 ppb [Jorres and Magnussen 1985, Schachter 1984]. However, the 1984 Schachter study measured an increase in airway resistance and clinical effects from exposure to SO₂ at 750 ppb after 40 minutes of exercise.

In addition to the peak exposure levels discussed above, on one occasion, SO₂ levels in Plymouth remained high (above 200 ppb) for a period of several days. Although long term effects are not completely studied, epidemiologic research has shown an association with SO₂ and mortality. Daily exposure to SO₂ levels above 120 ppb posed an increase risk of respiratory and cardiovascular mortality [Venners 2003]. In addition, several epidemiologic studies show an increase of cardiovascular mortality with a daily increase of SO₂ of less than 38 ppb [Zmirou 1998, Koenig 2000, Sunyer 2002, Venners 2003]. While there is some uncertainty as to the duration of the longer peak events that occurred in Plymouth, the measurements indicate a need for further study.

H₂S: Hydrogen Sulfide

Throughout the EI, overall H₂S levels remained low with little fluctuation. On November 25, 2004, however, two peaks exceeding 1000 ppb occurred. We have no explanation for these peak measurements.

H₂S tapemeter readings may reflect the presence of other sulfur compounds, including some COS (as described in the “Quality Assurance Data” section of this report). However, H₂S tapemeter responses did not appear to be impacted by SO₂ levels. In other words, the presence of SO₂ did not appear to “blind” the monitors to the presence of H₂S. Alternatively, however, SO₂ may be reacting with, and reducing, the levels of H₂S in the atmosphere.

Health Implications of H₂S Exposures:

The H₂S levels found might cause respiratory irritation, possibly due to its irritating odor [Schiffman and Williams, 2005, van Gemert 2003, Campagna 2004]. However, the levels were below those known to produce any measurable health effects [ATSDR 2005]. Comparison values for H₂S are shown in Appendix A.

COS: Carbonyl Sulfide (and other sulfides)

EI sampling results showed persistently elevated levels of COS. The average level was 498 ppb.¹⁹ There are at least two major sources of COS in Plymouth. The first is the salt marsh and the second is the Weyerhaeuser kraft paper mill. Since both sources are large, a significant amount of data would be required to distinguish their relative contributions.

Globally, COS is the most abundant atmospheric sulfur compound, averaging less than 1 ppb [NASA 2002]. Volcanoes are the largest natural source. Airborne COS has been measured in salt marshes at levels as high as 74 ppb (180 $\mu\text{g}/\text{m}^3$) [Johnson and Bates 1993, Thornton 1998, NASA 2002], but no COS emissions data from the salt marshes surrounding Plymouth are available.

In addition, no published atmospheric COS data were found that address community exposures from paper mills. Although the EPA lists COS as a Hazardous Air Pollutant (HAP), there are no available health-based comparison values, and COS is not monitored near paper mills [EPA 1989]. COS is known to be emitted from kraft mills [Simons 1994, Whitford, 1999, NCASI 1999] and is a break-down product of carbon disulfide (CS_2) — which Weyerhaeuser emits.

Health Implications of COS Exposures:

COS, like H_2S , is an odorous respiratory irritant. It is immediately metabolized to H_2S in humans. Animal studies have shown that COS and H_2S have a similar dose-response for some health effects, but little is known about the COS dose-response relationship for respiratory exposures.

At levels $>50,000$ ppb, COS effects in humans are similar to those from H_2S [ITC 1983, HSDB 1994, Chengelis 1980, Monsanto n.d., Monsanto, 1985]. In the absence of low-level COS exposure studies, ATSDR cannot determine what COS levels are clearly safe. However, toxicological analogies are often drawn between similar chemicals. In reviewing the existing toxicological data, it is reasonable to expect that COS effects are qualitatively similar to the effects from H_2S exposures, since COS is metabolized to H_2S .

Respiratory irritation might occur from exposures to the COS levels found during this investigation, i.e., an average level of 520 ppb as well as 1-minute peaks of 900 ppb and 1300 ppb. Respiratory effects could also reasonably be expected to exacerbate any concurrent effects associated with exposures to SO_2 and H_2S . The highest short-term COS level measured (1300 ppb) is less than the lowest human effect level (2000 ppb) for H_2S (for a small population of 10), and data suggest that COS is slightly less of a respiratory irritant than H_2S .²⁰ As a result, we would not expect COS to pose a public health hazard. Available comparison values for COS are provided in Table A1 in Appendix A.

¹⁹ The average of all samples analyzed by RTP within 24 hours of collection was 498 ppb. The results from DataChem analyses after a 24-hour or more delay were much lower.

²⁰ COS is not as acidic as H_2S ; is expected to be less reactive; is less soluble; and is expected to have a higher olfactory detection level [Pulgar et al. 1975, ATSDR 2005]. Anecdotal data suggest that people tolerate longer COS exposures compared to H_2S exposures.

Conclusions

Some of the measured atmospheric SO₂ levels are known to cause, in sensitive humans, broncho-constriction over short periods as well as other respiratory and cardiovascular effects over longer periods. As a result, some of the SO₂ levels detected in the ambient air closest to the Weyerhaeuser facility in Plymouth pose a public health hazard. Although the highest SO₂ levels were detected near Weyerhaeuser, the wind direction data do not strongly suggest that the facility was the source of the SO₂ measured. The impact of facility emissions appears to be limited in extent to the areas nearest the facility, because the monitors farther away measured much lower levels. Because of the uncertainty in some samples, we cannot determine the duration of the intermittent respiratory hazards.

Elevated hydrogen sulfide (H₂S) levels occurred on two separate occasions close to Weyerhaeuser. Carbonyl sulfide (COS), another respiratory irritant, was present at higher levels than typically found outdoors. Based on the measurements made in Plymouth neither H₂S nor COS individually poses a public health hazard. However, both respiratory irritants were found concurrently with SO₂ and their combined effects may have contributed to respiratory disease in the region. The extent of H₂S contamination also appears to be limited to areas closer to Weyerhaeuser.

The fate and transport of atmospheric sulfides in Plymouth is not well understood. The relative proportions of atmospheric sulfides measured during the EI differ from those found at other kraft mills. The measured levels also differ from those predicted based on Weyerhaeuser emissions. In this investigation, COS and SO₂ were detected at levels above 100 ppb. However, despite the fact that they are often associated with kraft mill emissions, methyl mercaptan, dimethyl disulfide, and dimethyl sulfide were not found during the EI. Additionally, H₂S was detected at high levels on only one day, but monitoring results show low H₂S levels on most days, especially at the sampling location nearest to Weyerhaeuser.

Recommendations

- Children, asthmatics, or people with lung or heart disease should avoid outdoor exertion if they experience respiratory discomfort or smell sulfurous or irritating odors.
- NCDENR should conduct ambient air quality monitoring for sulfur dioxide (SO₂) and total reduced sulfur (TRS) to better characterize SO₂ and TRS levels in the area nearest to the facility.
- NCDHHS should investigate possible correlations between respiratory aggravation levels and elevated SO₂ levels. Emergency room records could be correlated with SO₂ measurements to determine if there is an increase in respiratory distress among Plymouth residents on days following elevated SO₂ measurements. If these measures of respiratory effects are present, NCDHHS should evaluate whether the levels of more severe respiratory and cardiovascular-related effects are also elevated.

- Air quality scientists should consider expanding community air monitoring near kraft mills to include several different sulfides to better characterize the sulfur profile. Sampling should include carbonyl sulfide (COS), Total Reduced Sulfur (TRS), hydrogen sulfide (H₂S), methyl mercaptan, dimethyl sulfide, dimethyl disulfide, and sulfur dioxide (SO₂).

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Appendix A: Sulfur Compound Comparison Tables

Table A1: Comparison Values for Carbonyl Sulfide

<u>Agency/Organization</u>	<u>Exposure Level*</u>	<u>Standard/Exposure Duration</u>
Arizona DEQ	130 ug/m ³ (53.3 ppb)	Ambient Air Quality Standard (AAQS) (1-hour)
	40 ug/m ³ (16.4 ppb)	AAQS (24-hr)
Massachusetts DEQ	0.1 ug/m ³ (0.041 ppb)	AAQS (24-hr)
	0.1 ug/m ³ (0.041 ppb)	AAQS (annual)
DuPont	10 ppm	Worker Harm Level – based on Monsanto study of reproductive effects in mice
	2 ppm	Adverse Exposure Level (AEL) – 40-hr work week
Haskell Laboratory	2 ppm	AEL (8-hr)
	200 ppb	Community Exposure Level (CEL) (24 hr)

* ppm is parts per million (parts hydrogen sulfide per million parts air, by volume);
 ppb is parts per billion (parts hydrogen sulfide per million parts air, by volume)

Table A2: Comparison Values for Hydrogen Sulfide

<u>Agency/Organization</u> *	<u>Exposure Value</u> **	<u>Exposure Duration</u>
ATSDR	0.2 ppm (200 ppb)	Acute Minimal Risk Level (MRL)—value for up to 14 days of continuous exposure. Exposures below this value are not expected to result in non-cancerous adverse health effects
	0.02 ppm (20 ppb)	Chronic MRL—value for longer than 365 days of continuous exposure. Exposures below this value are not expected to result in non-cancerous adverse health effects
NC DHHS	120 µg/m ³ (86 ppb)	Acceptable Ambient Level (AAL) (24-hr)
NC DHHS	33 µg/m ³ (23 ppb)	Recommended Scientific Advisory Board (24-hr)
	56 µg/m ³ (40 ppb)	Recommended Scientific Advisory Board AAL (1-hr)
NIOSH	100 ppm	Immediately Dangerous to Life and Health (IDLH)—based on the ability of a worker to escape an area without loss of life or irreversible health effects
	10 ppm	Worker exposure—40-hr work week; 10-minute ceiling value
AIHA	0.1 ppm	ERPG-1—maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to 1 hour without perceiving a clearly defined objectionable odor
	30 ppm	ERPG-2—maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to 1 hour without developing irreversible or other serious health effects that could impair ability to take protective action
ACGIH	10 ppm	Worker exposure—40-hr work week
	15 ppm	Worker exposure—15-minute ceiling

* ATSDR is the Agency for Toxic Substances and Disease Registry;
 NIOSH is the National Institute for Occupational Safety and Health;
 AIHA is the American Industrial Hygiene Association;
 ACGIH is the American Conference of Industrial Hygienists

** ppm is parts per million (parts hydrogen sulfide per million parts air, by volume);
 ppb is parts per billion (parts hydrogen sulfide per million parts air, by volume).

Table A3: Comparison Values for Sulfur Dioxide

Agency/Organization*	Exposure Value**	Exposure Duration
ATSDR	0.01 ppm (10 ppb)	Acute Minimal Risk Level—value for up to 14 days of continuous exposure. Exposures below this value are not expected to result in non-cancerous adverse health effects.
U.S. EPA	0.14 ppm	24-hr National Ambient Air Quality Standard (NAAQS)
	0.03 ppm	Annual arithmetic mean NAAQS
NIOSH	100 ppm	Immediately Dangerous to Life and Health (IDLH)—based on the ability of a worker to escape an area without loss of life or irreversible health effects
	2 ppm	Worker exposure— 40 hour work week
AIHA	0.3 ppm	ERPG-1—maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to 1 hour without perceiving a clearly defined objectionable odor
	3 ppm	ERPG-2—maximum airborne concentration below which it is believed nearly all individuals could be exposed for up to 1 hour without developing irreversible or other serious health effects that could impair ability to take protective action
	15 ppm	ERPG-3—maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to 1 hour without experiencing or developing life-threatening health effects
ACGIH	2 ppm	Worker exposure—40-hour work week
	5 ppm	Worker exposure—15-minute ceiling

* ATSDR is the Agency for Toxic Substances and Disease Registry;
 NIOSH is the National Institute for Occupational Safety and Health;
 AIHA is the American Industrial Hygiene Association;
 ACGIH is the American Conference of Industrial Hygienists

** ppm is parts per million (parts hydrogen sulfide per million parts air, by volume);
 ppb is parts per billion (parts hydrogen sulfide per million parts air, by volume)

Table A4: Air Quality Index for Sulfur Dioxide [DOI and EPA 2005]

Air Quality Index (AQI): Sulfur Dioxide (SO₂)

Index Values	Levels of Health Concern	Cautionary Statements
0-50	Good	None
51-100*	Moderate	None
101-150	Unhealthy for Sensitive Groups	People with asthma should consider reducing exertion outdoors.
151-200	Unhealthy	Children, asthmatics, and people with heart or lung disease should reduce exertion outdoors.
201-300	Very Unhealthy	Children, asthmatics, and people with heart or lung disease should avoid outdoor exertion. Everyone else should reduce exertion outdoors.
301-500	Hazardous	Children, asthmatics, and people with heart or lung disease should remain indoors. Everyone else should avoid exertion outdoors.

* An AQI of 100 for sulfur dioxide corresponds to an SO₂ level of 0.14 parts per million (averaged over 24 hours).

Table A5. Selected Exposure Guidelines for Sulfur Gases

Sulfur Gas	Agency*	Exposure Value **	Exposure Period†
Carbon Disulfide	NIOSH	1 ppm (3 mg/m ³) 10 ppm (30 mg/m ³)	TWA STEL
	OSHA	20 ppm 30 ppm 100 ppm	TWA Ceiling 30-minute maximum peak
Methyl Mercaptan	NIOSH	0.5 ppm (1 mg/m ³)	Ceiling (15-minute)
	OSHA	10 ppm (20 mg/m ³)	Ceiling
Diethyl Sulfate	NIOSH	0.1 ppm (0.5 mg/m ³)	TWA
	OSHA	1 ppm (5 mg/m ³)	TWA
Ethyl Mercaptan	NIOSH	0.5 ppm (1.3 mg/m ³)	Ceiling
	OSHA	10 ppm (25 mg/m ³)	Ceiling
m-Butyl Mercaptan	NIOSH	0.5 ppm (1.8 mg/m ³)	Ceiling
	OSHA	10 ppm (35 mg/m ³)	TWA

* NIOSH is the National Institute for Occupational Safety and Health;

OSHA is the Occupational Safety and Health Administration

** ppm is parts per million (parts hydrogen sulfide per million parts air, by volume);
mg/m³ is milligrams per cubic meter

† TWA is Time-Weighted Average;

STEL is Short-Term Exposure Limit

Appendix B: Hydrogen Sulfide and Carbonyl Sulfide Monitoring, Sampling, and Quality Assurance

Hydrogen Sulfide (H₂S) levels of 1800 ppb and 1200 ppb detected in grab samples collected on October 25, 2004 are not consistent with the concurrent tapemeter readings. These grab samples were analyzed by the RTP laboratory, with quality assurance samples from the lab indicating good recoveries on that day. The tapemeters also showed reliable response rates. While the samples collected on October 25, 2004 appear to be valid, they may represent a very short peak not captured by the tapemeters.

Based on the evidence, it is likely that tapemeter readings for H₂S were in part due to the presence of carbonyl sulfide (COS). Sulfur dioxide (SO₂) was not present at levels required to diminish the H₂S response on the monitor. As a result, the presence of SO₂ is not “blinding” the monitors to H₂S.

Most of the chemicals that can produce false positive readings are not associated with industrial activities at this site [ATSDR 2002]. If present, those sulfur compounds known to produce false positive readings and possibly associated with Weyerhaeuser should have been detected in the EI samples analyzed by two laboratories [Goyer 1990, Zellweger 1994].

Prior to this investigation, available data did not indicate the possibility that COS could produce false positive readings [Zellweger 1994]. Based on the EI findings, ATSDR has contacted Zellweger to review the false positive results and to share the associated quality assurance data. It is possible that moisture in the air allows some COS to hydrolyze to H₂S (inside the sampling port) just before analysis. To date, however, Zellweger has not provided ATSDR with laboratory data to support its conclusion that COS does not cause false positive H₂S readings.

COS was detected in air samples collected at the time of an H₂S tapemeter response. In addition, the detection of H₂S on October 25th indicates that H₂S could be responsible for a portion of the H₂S reading. Therefore, at any given time, the H₂S tapemeters may have been measuring a mixture of both COS and H₂S. It is known, for example, that a TRS (total reduced sulfur) monitor will detect COS, H₂S, and other sulfur compounds with an equal response rate; i.e., each sulfide atom will produce a single response. ATSDR recommends that use of a TRS monitor at future exposure investigations associated with kraft mills.

The peak sulfur compound levels from downwind tapemeter readings combined with the COS results from downwind grab samples suggest that the paper mill is contributing to atmospheric COS in the Plymouth area. However, the “downwind” designation is subjective since it is based on the detection characteristic paper mill odors.

If the presence of COS were responsible for the H₂S tapemeter readings, then based on the results of equipment testing, nearly 1000 ppb of COS would be required to create false H₂S reading of 20 ppb. COS levels near or exceeding 1000 ppb were detected by the lab in two samples. Also, the color of the stain on the corresponding tapemeter tapes indicates the possibility of something other than H₂S. Also note that H₂S produces a 1 ppb to 1 ppb reading while other sulfur compounds produce a much poorer response. Although sulfur

compounds are found in fertilizers and surfactants used in nearby farming area [FCM 1999], their presence should have been detected in the laboratory samples.

Quality Assurance Data

There are questions about the results from samples collected on October 25, 2004. The RTP lab detected high levels of COS and H₂S while the DataChem lab found no sulfur compounds. The RTP lab showed good quality results with “spiked” and blank samples. Although no spikes were sent to the DataChem labs that day, several subsequent spikes indicated poor recoveries by DataChem.

COS was detected in all other samples collected on other days, albeit at lower levels. No other H₂S was detected (by labs) during the investigation. However, it is important to note that the laboratory detection levels are above the levels recorded by the monitors.

Because the laboratory frequently detected COS and seldom detected H₂S, ATSDR tested the tapemeters to find out if they would falsely identify COS as H₂S. The result was that 97 ppb of COS was falsely identified as up to 2 ppb H₂S; 193 ppb COS was falsely identified as up to 4 ppb H₂S. This response is considered acceptable data quality. Nevertheless, for field application in Plymouth the tapemeter may over estimate H₂S by a small amount due to COS.

The amount of the overestimate is uncertain because the stain formed on the tape by the COS reaction was grayish and the stains in the field were white or pink. (See the description of detection in methods section.) It seems clear that the field measurements were not solely from COS.

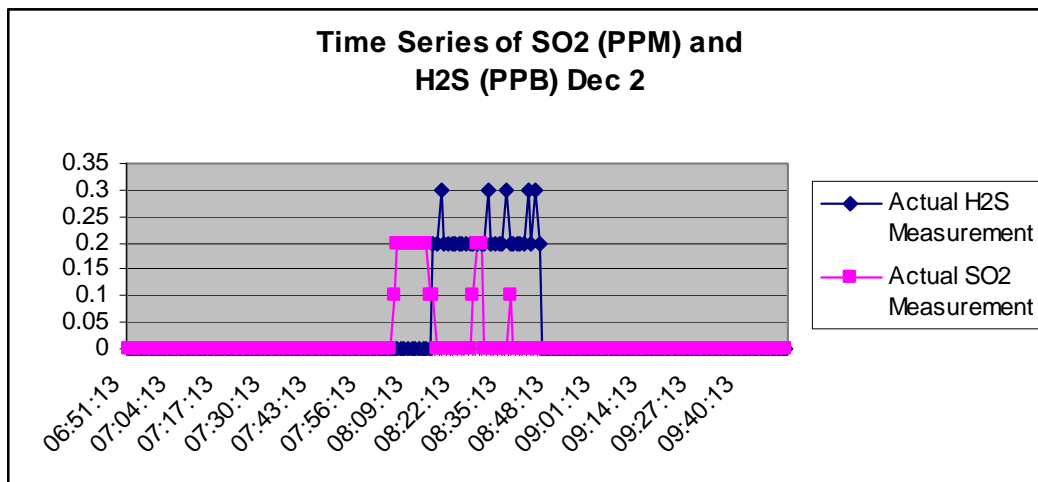
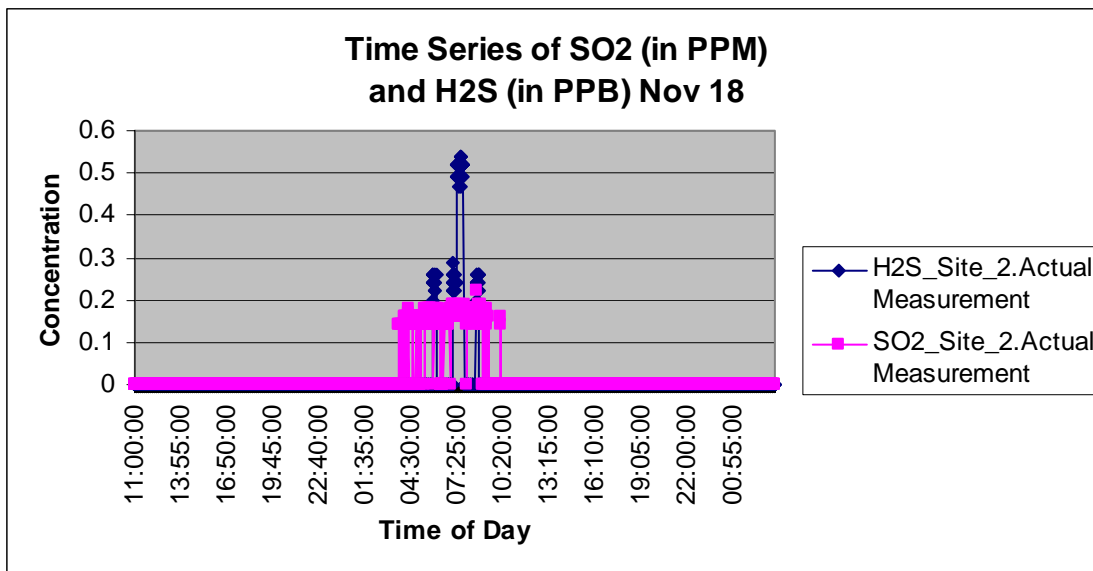
SO₂ (and other oxidizers) at concentrations near 1000 ppb have been shown to produce a negative response on the H₂S tapemeter. In other words, levels near 1000 ppb may reduce H₂S measurements by a few ppb. Since SO₂ was never detected near 1000 ppb, it should not have interfered with the readings.

ATSDR provided other quality assurance testing to determine whether there is a loss or decay of samples during the sampling, shipping, and analysis process. A mixture containing known quantities of sulfur compounds sent to each laboratory (DataChem and RTP) for analysis showed that some sample loss occurs. DataChem never detected methyl mercaptan in any sample (including the spiked samples) and had unreliable recoveries of dimethyl disulfide. DataChem detected COS in the spiked samples; although, the data indicates a COS half life of about one day in the canisters. Specifically, a spike sample of 100 ppb of COS was sent to the lab and 42 ppb was detected the first day, 25 ppb on the second day, and none was detected on the third day.

Ambient COS levels measured by DataChem were about one-half that measured by RTP, also indicating a half life of 1 day. As a result, atmospheric COS in Plymouth is likely to be closer to the levels measured at RTP, which appeared to be reliable. The apparent absence of methyl mercaptan in Plymouth may actually be due to DataChem’s inability to detect it in samples and RTP’s higher detection levels.

Appendix C: Examples of Associated Sulfur Dioxide and Hydrogen Sulfide Measurements

On occasion, there appear to be associations between the sulfure dioxide (SO_2) and hydrogen sulfide (H_2S) measurements. The following time series graphs show peak measurements of SO_2 and H_2S at Site 2 on each of the following days: November 18, 2004, December 2, 2004, and January 13, 2005.



The time series graphs imply an association between the two chemicals and appear to indicate a plume. These time series can be contrasted with the concentrations measured on January 13, 2005.

Appendix D: **Laboratory Reports**



ANALYTICAL REPORT

Form ARF-AL
 Page 1 of 3
 Part 1 of 2
 05030522341867X

Date MAY 04 2005
 Laboratory Group Name 05T-1643-01
 Account No. 07051

USPHS/FOH
 Attention: Clifford Moseley
 2165 West Park Court
 Suite C
 Stone Mountain, GA 30087

FAX (770) 469-8623
 Telephone (770) 498-3449
 E-mail cmoseley@psc.gov

Sampling Collection and Shipment

Sampling Site _____ Date of Collection May 02, 2005

Date Samples Received at Laboratory May 03, 2005

Analysis

Method of Analysis DCL Method

Date(s) of Analysis May 03, 2005

Analytical Results

Field Sample Number	Laboratory Number	Sample Type	n-Butyl Mercaptan Ppb (v/v)	t-butyl Mercaptan Ppb (v/v)	Carbon Disulfide Ppb (v/v)	Carbonyl Sulfide Ppb (v/v)	Diethyl sulfide Ppb (v/v)	Dimethyl Disulfide Ppb (v/v)	Dimethyl Sulfide Ppb (v/v)	Ethyl Mercaptan Ppb (v/v)
ERG1QC1	05I15267	AIR	ND	ND	ND	42	ND	23	ND	ND
ERG1QC2	05I15268	AIR	ND	ND	ND	ND	ND	ND	ND	ND
Limit of Detection			20	20	10	20	20	10	20	20

† See comment on last page.
 ND Parameter not detected above LOD.
 NR Parameter not requested.
 NA Parameter not applicable.

** See comment on last page.
 () Parameter between LOD and LOQ.

Analyst: Steven J. Sagars
 Reviewer: Mila V. Potekhin



ANALYTICAL REPORT

Form ARF-C
Page 3 of 3
05030522341867X

Date MAY 04 2005
Laboratory Group Name 05I-1643-01

General Lab Comments

The results provided in this report relate only to the items tested.
Samples were received in acceptable condition unless otherwise noted in the General Set Comments above.
Samples have not been field blank corrected unless otherwise noted in the General Set Comments above.
This test report shall not be reproduced, except in full, without written approval of DataChem Laboratories, Inc.
This page is the concluding page of the report.



DATA CHEM

LABORATORIES, INC.

ANALYTICAL REQUEST FORM

1. REGULAR Status 121-111301

RUSH Status Requested - ADDITIONAL CHARGE
RESULTS REQUIRED BY _____

DATE

CONTACT DATACHEM LABS PRIOR TO SENDING SAMPLES

2. Date 5/2/05 Purchase Order No. 7003 (ATSDR) 4. Quote No. _____
 3. Company Name Sec Paul Pope - for details DCL Project Manager Paul Pope
 Address _____ 5. Sample Collection _____
 Person to Contact Scott Sholar Sampling Site _____
 Telephone (919) 468-7951 Industrial Process Ambient
 Fax Telephone (919) 468-7803 Date of Collection 2:55 5/2/05
 E-mail Address scott.sholar@erg.com Time Collected 3:30 PM
 Billing Address (if different from above) see Paul Pope for details Date of Shipment 2:55 5/2/05
 Chain of Custody No _____

Send data to

6. REQUEST FOR ANALYSES

Laboratory Use Only	Client Sample Number	Matrix*	Sample Volume	ANALYSES REQUESTED - Use method number if known	Units**
USE 15207	ER61Q1	Air	6L	Speciated Sulfur Compounds	ppbV
108	ER61Q2	Air	6L	by Chemeluminiscence Analysis	108317
* Expedited Analysis Reactive Compounds					

* Specify: Solid sorbent tube, e.g. Charcoal; Filter type; Impinger solution; Bulk sample; Blood; Urine; Tissue; Soil; Water; Other

** 1 ug/sample 2 mg/m³ 3 ppm 4 % 5 _____ (other) Please indicate one or more units in the column entitled Units**

Comments Charges go to Greg Zarus (ATSDR) - see Paul Pope.
data goes to Scott Sholar@ERG scott.sholar@erg.com

Possible Contamination and/or Chemical Hazards _____

7. Chain of Custody (Optional)

Relinquished by <u>Scott Sholar</u>	Date/Time <u>5/2/05</u>
Received by <u>TRN</u>	Date/Time <u>5/3/05</u>
Relinquished by _____	Date/Time _____
Received by _____	Date/Time _____
Relinquished by _____	Date/Time _____
Received by _____	Date/Time _____



ANALYTICAL REPORT

Form ARF-C

Page 3 of 3
05050500452670X

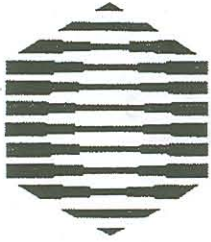
MAY 05 2005

Date _____

Laboratory Group Name 05I-1665-01

General Lab Comments

The results provided in this report relate only to the items tested.
Samples were received in acceptable condition unless otherwise noted in the General Set Comments above.
Samples have not been field blank corrected unless otherwise noted in the General Set Comments above.
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This page is the concluding page of the report.



DATA CHEM

LABORATORIES, INC.

ANALYTICAL REQUEST FORM

1. REGULAR Status (ST-1105-01)

RUSH Status Requested - ADDITIONAL CHARGE

RESULTS REQUIRED BY _____ DATE _____

CONTACT DATACHEM LABS PRIOR TO SENDING SAMPLES

2. Date 5/3/05 Purchase Order No. 07003 (ATSDR - Greg Zarus) 4. Quote No. _____

3. Company Name See Paul Pope for details DCL Project Manager Paul Pope

Address _____ 5. Sample Collection

Person to Contact S. H. Sholar Sampling Site _____

Telephone (114) 468-7951 Industrial Process Ambient

Fax Telephone (914) 468-7803 Date of Collection 5/2/05

E-mail Address s10th.sholar@ercy.com Time Collected 3:30 PM

Billing Address (if different from above) see Paul Pope for details Date of Shipment 5/3/05

Chain of Custody No _____

send data to

6. REQUEST FOR ANALYSES

Laboratory Use Only	Client Sample Number	Matrix*	Sample Volume	ANALYSES REQUESTED - Use method number if known	Units**
SL 1520	ERG/RL3 ¹⁰⁸⁸¹⁹	Air	6L	Specialty Sulfur Compounds by Chemluminescence	ppbV
<p>A Expedited Analysis Reactive Compounds</p>					

* Specify: Solid sorbent tube, e.g. Charcoal; Filter type; Impinger solution; Bulk sample; Blood; Urine; Tissue; Soil; Water; Other

** 1. ug/sample 2 mg/m³ 3 ppm 4. % 5. _____ (other) Please indicate one or more units in the column entitled Units**

Comments charges go to Greg Zarus (ATSDR) -
data goes to S10th Sholar @ ERG s10th.sholar@ercy.com

Possible Contamination and/or Chemical Hazards _____

7. Chain of Custody (Optional)

Relinquished by <u>Scott Blah</u>	Date/Time <u>5/3/05</u>
Received by <u>[Signature]</u>	Date/Time <u>5/04/05</u>
Relinquished by _____	Date/Time _____
Received by _____	Date/Time _____
Relinquished by _____	Date/Time _____
Received by _____	Date/Time _____

DataChem Laboratories, Inc.
CANISTER CHAIN-OF-CUSTODY AND FIELD DATA RECORD

Client: Eastern Research Group
Account No: 07003

Project/Job/Task: ATSDR Weymouth, NC

Please do not apply adhesive labels directly on Canisters
Manilla tags are provided, attached to Canisters for your convenience, to apply adhesive labels

Canister Serial No.	Date Cleaned	Initial Vacuum (Inches of Hg Vacuum)	VFR flow rate (ml/min)	Initials:	Field Vacuum before sampling (Inches of Hg vacuum)	Final Vacuum after sampling (Inches of Hg vacuum)	Client Sample Identification	Other Client Information	DataChem Labs use only
<u>108619</u>	<u>4-25-05</u>	<u>22.5</u>		<u>mt</u>	<u>29.5</u>	<u>0.44</u>	<u>ERG/AC-3</u>		
<u>108808</u>							<u>Expedited Analysis</u>		
							<u>Reactive Compounds</u>		
VFR Serial No.									

Original Field Sample Chain-of-Custody

Relinquished By: (Signature)	Date/Time	Received By: (Signature)	Reason for Transfer/Storage Location
<u>Andrew Hogan</u>	<u>4-28-05 15:00</u>	<u>E.H. Blum</u>	
<u>BT & Colby</u>	<u>5/3/05</u>		

Return to:
DataChem Laboratories, Inc.
960 W. LeVoy Drive
Salt Lake City, UT 84123
800-356-9135

Please do not apply adhesive labels directly on Canisters
Manilla tags are provided, attached to Canisters for your convenience, to apply adhesive labels



**DATA
CHEM**
LABORATORIES, INC.

ANALYTICAL REQUEST FORM

1. REGULAR Status
 RUSH Status Requested - ADDITIONAL CHARGE
 RESULTS REQUIRED BY _____ DATE _____
 CONTACT DATACHEM LABS PRIOR TO SENDING SAMPLES

2. Date 1/12/05 Purchase Order No. AT:DR Airt 7003 4. Quote No. _____
 3. Company Name _____ DCL Project Manager _____
 Address _____
 Person to Contact 700 # chet
 Telephone (tit) 405 7451
 Fax Telephone (tit) 405 7403
 E-mail Address th. holder@ery.com
 Billing Address (if different from above) Paul Piper, D.L.
 5. Sample Collection Site Site 2/way 1 Plymouth, NC
 Industrial Process Amk. it
 Date of Collection 11/17/04 1/12/05
 Time Collected 10:00 AM →
 Date of Shipment _____
 Chain of Custody No. 1

Reactive Compounds Expedited Analysis Required

6. REQUEST FOR ANALYSES

Laboratory Use Only	Client Sample Number	Matrix*	Sample Volume	ANALYSES REQUESTED - Use method number if known	Units**
	S2-CAN-1/12/05	Air	6L	Speciated Sulfur Compounds	
	S3-CAN-1/12/05	Air	6L	" " "	
	S5-CAN-1/12/05	Air	6L	" " "	

* Specify: Solid sorbent tube, e.g. Charcoal; Filter type; Impinger solution; Bulk sample; Blood; Urine; Tissue; Soil; Water; Other
 ** 1. ug/sample 2. mg/m³ 3. ppm 4. % 5. _____ (other) Please indicate one or more units in the column entitled Units**
 Comments Chet Piper AT:DR (Guy Z...) Airt # 7003
Date to: Dave Dayton, ERG

Possible Contamination and/or Chemical Hazards _____

7. Chain of Custody (Optional)

Relinquished by 700 # chet Date/Time 1/12/05 1:30 PM
 Received by _____ Date/Time _____
 Relinquished by _____ Date/Time _____
 Received by _____ Date/Time _____
 Relinquished by _____ Date/Time _____
 Received by _____ Date/Time _____

Research Triangle Park Laboratories, Inc.
8109 Ebenezer Church Road
Raleigh, NC 27612



NELAC Accredited



919 510-0228 Telephone
919 510-0141 Fax

Web Site: www.rtp-labs.com

June 9, 2005

Greg Zarus, Principal Investigator
Agency for Toxic Substances and Disease Registry
1600 Clifton Road, NE
Mail Stop, E-32
Atlanta, GA 30333

Project: Weyerhaeuser Exposure Investigation – Plymouth, NC
Purchase Order Number: HHSP23300400612P
MOU: D8H04HE34100
FOH Tracking Number: ATSDR-4-04-NC853
Client Task: 98FED16234-11
RTP Labs Tracking Number: 05-047

Enclosed with this letter is the report on the chemical analysis for the samples received May 18 - 20, 2005 for a same day analysis and a normal turnaround for the report. Two Tedlar bags were received on May 18, one on May 19 and one on May 20. All samples were in good condition with chain-of-custody forms completed. The samples were analyzed the same day as received for the listed target sulfur compounds by EPA Modified Method 15/16 by GC/FPD. No problems were encountered with the analysis.

This report is a correction to the report submitted on May 25, 2005. The reporting limit was changed from 0.5 ppmv to 0.2 ppmv to reflect previous reporting limits. The 0.5 ppmv value is the lowest point on the calibration curve.

Please note that ND means not detected at the reporting limits expressed.

Sincerely,

Amy Gordon,
Chemist

Attachments: GC/FPD report, COC forms.

Research Triangle Park Laboratories, Inc.

8109 Ebenezer Church Road
Raleigh, NC 27612



NELAC Accredited



919 510-0228 Telephone
919 510-0141 Fax

Web Site: www.rtp-labs.com

Client ID: ATSDR
Sample Date: 5/18/05
Date Received: 5/18-20/05

Contact: Greg Zarus
Matrix: Tedlar bag
Analysis Date: 5/18-20/05

Client Proj. #: Weyerhaeuser
RTP Labs Proj. #: 05-047

EPA Modified Method 15/16 for Sulfurs by GC/FPD

Compound	ERG/QC 1	ERG/QC2	ERG/QC 2	ERG/QC3	ERG/QC 4	Reporting Limit
Hydrogen Sulfide (H ₂ S)	ND	ND	ND	ND	ND	0.2 ppmv
Carbonyl Sulfide (COS)	ND	ND	ND	ND	ND	0.2 ppmv
Carbon Disulfide (CS ₂)	ND	ND	ND	ND	ND	0.2 ppmv
Methyl Mercaptan (CH ₄ S)	ND	ND	ND	ND	ND	0.2 ppmv
Ethyl Mercaptan (C ₂ H ₆ S)	ND	ND	ND	ND	ND	0.2 ppmv
Methyl Sulfide (C ₂ H ₆ S)	ND	ND	ND	ND	ND	0.2 ppmv
Dimethyl Disulfide (C ₂ H ₆ S ₂)	ND	ND	ND	ND	ND	0.2 ppmv

ND = Non detected at the Reporting Limit
Note: QC2 sample was injected twice for precision.

Research Triangle Park Laboratories, Inc.
8109 Ebenezer Church Road
Raleigh, NC 27612

919 510-0228 Telephone
919 510-0141 Fax




NELAC Accredited NJ# NC003

November 24, 2004

Greg Zarus, Principal Investigator
Agency for Toxic Substances and Disease Registry
1600 Clifton Road, NE
Mail Stop, E-32
Atlanta, GA 30333

Project: Weyerhaeuser Exposure Investigation – Plymouth, NC
Purchase Order Number: HHSP23300400612P
MOU: D8H04HE34100
FOH Tracking Number: ATSDR-4-04-NC853
Client Task: 98FED16234-11
RTP Labs Tracking Number: 04-191 and 04-202

Enclosed with this letter is the report on the chemical analyses for the samples received November 11, and November 17, 2004 for a same day analysis and normal turnaround for the report. Two Tedlar bags were received on November 11 and three received on November 17. All samples were in good condition with chain-of-custody forms completed. The samples were analyzed the same day as received for the listed target sulfur compounds by EPA Modified Method 15/16 GC/FPD. No problems were encountered with the analysis.

Please note that ND means not detected at the reporting limits expressed.

Sincerely,

Alston Sykes, Principal Chemist

Attachments: GC/FPD report, COC form.

File: ATSDR_04-191&202.doc/als

Research Triangle Park Laboratories, Inc.
8109 Ebenezer Church Road
Raleigh, NC 27612

919 510-0228 Telephone
919 510-0141 Fax



Web Site: www.rtp-labs.com



NELAC Accredited NJ# NC003

Client: ATSDR
Sample Date: 11/11/2004
Date Received: 11/11/2004

Contact: Greg Zarus
Matrix: Tedlar bag
Analysis Date: 11/11/2004

Client Proj. #: Weyerhauser
RTP Labs Proj. #:04-191

*This is a pre-investigation
QA/QC sample
lab test
using spheres*

EPA Modified Method 15/16 for Sulfurs by GC/FPD

Compound	ERG/QC-1	ERG/QC-2	Reporting Limit
Hydrogen Sulfide (H ₂ S)	ND	16.3	0.2 ppmv
Carbonyl Sulfide (COS)	0.39	ND	0.2 ppmv
Carbon Disulfide (CS ₂)	ND	ND	0.2 ppmv
Methyl Mercaptan (CH ₄ S)	ND	ND	0.2 ppmv
Ethyl Mercaptan (C ₂ H ₆ S)	ND	ND	0.2 ppmv
Methyl Sulfide (C ₂ H ₆ S)	ND	ND	0.2 ppmv
Dimethyl Disulfide (C ₂ H ₆ S ₂)	ND	ND	0.2 ppmv

ND = Non detected at the Reporting Limit

Independent Quality Control Audit Results

Independent blind audit samples of H₂S in Tedlar bags were analyzed on 11/12/2002 with the following results:

Audit concentration	RTP Labs Results	% Difference
10 ppmv	10.3 ppmv	3.0 %
30 ppmv	28.4 ppmv	5.3 %

File: ATSDR_04191&202.doc/als

Research Triangle Park Laboratories, Inc.
8109 Ebenezer Church Road
Raleigh, NC 27612

919 510-0228 Telephone
919 510-0141 Fax



NELAC Accredited NJ# NC003

Client: ATSDR
Sample Date: 11/17/2004
Date Received: 11/17/2004

Contact: Greg Zarus
Matrix: Tedlar bag
Analysis Date: 11/17/2004

Client Proj. #: Weyerhaeuser
RTP Labs Proj. #: 04-202

EPA Modified Method 15/16 for Sulfurs by GC/FPD

<u>Compound</u>	<u>S1</u>	<u>S2</u>	<u>S3</u>	<u>Reporting Limit</u>
Hydrogen Sulfide (H ₂ S)	ND	ND	ND	0.2 ppmv
Carbonyl Sulfide (COS)	0.07 *	0.18 *	0.15 *	0.2 ppmv
Carbon Disulfide (CS ₂)	ND	ND	ND	0.2 ppmv
Methyl Mercaptan (CH ₄ S)	ND	ND	ND	0.2 ppmv
Ethyl Mercaptan (C ₂ H ₆ S)	ND	ND	ND	0.2 ppmv
Methyl Sulfide (C ₂ H ₆ S)	ND	ND	ND	0.2 ppmv
Dimethyl Disulfide (C ₂ H ₆ S ₂)	ND	ND	ND	0.2 ppmv

* = Detected below the Reporting Limit.

ND = Non detected at the Reporting Limit

File: ATSDR_04191&202.doc/als

Research Triangle Park Laboratories, Inc.
8109 Ebenezer Church Road
Raleigh, NC 27612

919 510-0228 Telephone
919 510-0141 Fax



NELAC Accredited NJ# NC003



Chain of Custody Record

NELAP Accredited NJ #NC003
ISO 17025



Research Triangle Park Laboratories, Inc
8109 Ebenezer Church Road
Raleigh, North Carolina 27612-7307
Phone: 919-510-0228 Fax: 919-510-0141
Web Site: www.rtp-labs.com

Client (Billing) Ones Zanus-ATSDR		Send Report To Attention: David Deyouk	Phone Number 468-7883	Fax Number 468-7803	Date: 11/11/04						
Address 2165 West Park Ct, Suite C		City Stone Mountain	State GA	Zip Code 30087	Page 1 of 1						
Contract/Purchase Order No.:		Project Name: ATSDR-WEY.	RTP Labs Proj. Tracking No.: 04-191 Client Tracking No.:								
Comments: Sample ID No. & Description 1 ELG/QC-1-11104 2 EBG/QC-2-11104 3 4 5 6 7 8 9 10	Matrix Air Ambient Liquid/Solid Source	Time 10:00 10:00	Date Sampled 11/11/04 11/11/04	Compliance Test # of Containers Preservatives GCTPD/sulfur Spec.	Canisters vacuum or pressure Field Initial Final Lab Receipt Final Lab Sample ID Fraction 0491-1 2						
						Turn Around Time Requested for Report: Business Days: *Rush Multipliers (Xx) <input type="checkbox"/> 1 day*(4x) <input type="checkbox"/> 2 days*(3x) <input type="checkbox"/> 3 days*(2x) <input type="checkbox"/> 5 days*(1.5x) <input type="checkbox"/> 10 days*(1.1x) <input checked="" type="checkbox"/> 15 days		Data Pack: Std <input type="checkbox"/> Full <input type="checkbox"/> 1.1x surcharge Electronic Deliverable: <input type="checkbox"/> 1.1x surcharge	QC Requirements: Screen Standard <input type="checkbox"/> EPA Level IV for Compliance <input type="checkbox"/> Requires approved QAPP sent to lab		
						Relinquished By: Sam Duto	Date: 10:50	Time: 11/11/04	Received By: Alton Lopez	Date: 11/11/04	Time: 10:36
						Relinquished By:	Date:	Time:	Received By:	Date:	Time:

Research Triangle Park Laboratories, Inc.
 8109 Ebenezer Church Road
 Raleigh, NC 27612

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 ISO 17025

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 Raleigh, North Carolina 27612-7307
 Phone: 919-510-0228 Fax: 919-510-0141
 Web Site: www.rtp-labs.com



Client (Billing) 6118 Zorus Send Report To Attention: Dave Denton - EL6 Phone Number: (919) 468-7887 Fax Number: _____ Date: 11/17/04

Address ATSOR State _____ Zip Code _____

Contract/Purchase Order No.: _____ Project Name: ATSOR - Wey. Plywood H.

Comments: ATSOR - Greg Zorus

Sample ID No. & Description	Date Sampled	Time	Matrix		Compliance Test	# of Containers	Preservatives	Canisters			Lab Sample ID	Fraction	
			Air	Liquid/Solid				vacuum or pressure	Field Initial	Lab Receipt Final			
1 S2-BAG-111704	11/17	8:00	✓			1						04202-1	
2 S3-BAG-111704	11/17	8:50	✓			1						04202-2	
3 S1-BAG-111704	11/17	9:30	✓			1						04202-3	
4													
5													
6													
7													
8													
9													
10													

Requested Analyses: _____

QC Requirements: Screen Standard
 EPA Level IV for Compliance
 Requires approved QAPP sent to lab

Turn Around Time Requested for Report: Business Days; *Rush Multipliers (Xx)
 1 day*(6x) 2 days*(3x) 3 days*(2x) 5 days*(1.5x) 10 days*(1.1x) 15 days

Relinquished By: Dave Denton Date: 11/17/04 Time: _____
 Received By: Melissa Englebert Date: 11-17-04 Time: 1:03 PM

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Raleigh, NC 27612

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October 27, 2004

Greg Zarus, Principal Investigator
Agency for Toxic Substances and Disease Registry
1600 Clifton road, NE
Mail Stop, E-32
Atlanta, GA 30333

Project: Weyerhaeuser Exposure Investigation – Plymouth, NC
Purchase Order Number: HHSP23300400612P
MOU: D8H04HE34100
FOH Tracking Number: ATSDR-4-04-NC853
Client Task: 98FED16234-11
RTP Labs Tracking Number: 04-176

Enclosed with this letter is the report on the chemical analyses for the samples received October 25, 2004 for a same day analysis and quick turnaround. Two Tedlar bags were received in good condition with a chain-of-custody form completed. The samples were analyzed the same day as received for the listed target sulfur compounds by EPA Modified Method 15/16 GC/FPD. No problems were encountered with the analysis.

Please note that ND means not detected at the reporting limits expressed.

Sincerely,

Alston Sykes, Principal Chemist

Attachments: GC/FPD report, COC form.

File: ATSDR_04176.doc/als

Research Triangle Park Laboratories, Inc.
8109 Ebenezer Church Road
Raleigh, NC 27612

919 510-0228 Telephone
919 510-0141 Fax



RTPLabs
NELAC Accredited NJ# NC003

Client: ATSDR
Sample Date: 10/25/2004
Date Received: 10/25/2004

Contact: Greg Zarus
Matrix: Tedlar bag
Analysis Date: 10/25/2004

Client Proj. #: Weyerhaeuser
RTP Labs Proj. #: 04-176

EPA Modified Method 15/16 for Sulfurs by GC/FPD

<u>Compound</u>	<u>S1</u>	<u>S2</u>	<u>Reporting Limit</u>
Hydrogen Sulfide (H ₂ S)	1.8	1.2	0.2 ppmv
Carbonyl Sulfide (COS)	1.3	0.9	0.2 ppmv
Carbon Disulfide (CS ₂)	ND	ND	0.2 ppmv
Methyl Mercaptan (CH ₄ S)	ND	ND	0.2 ppmv
Ethyl Mercaptan (C ₂ H ₆ S)	ND	ND	0.2 ppmv
Methyl Sulfide (C ₂ H ₆ S)	ND	ND	0.2 ppmv
Dimethyl Disulfide (C ₂ H ₆ S ₂)	ND	ND	0.2 ppmv

ND = Non detected at the Reporting Limit

File: ATSDR_04176.doc/als

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 Raleigh, NC 27612

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Chain of Custody Record

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Research Triangle Park Laboratories, Inc
 8109 Ebenezer Church Road
 Raleigh, North Carolina 27612-7307
 Phone: 919-510-0228 Fax: 919-510-0141
 Web Site: www.rtp-labs.com

Client (Billing) CDC - Weyerhaeuser Phone Number 919-468-7383 Fax Number 468-7803 Date: 10/25/04

Address ATSDR City _____ State _____ Zip Code _____

Contract/Purchase Order No.: ATSDR - Greg Zorus Project Name: ATSDR - WEY. Plymouth

Comments: _____

Requested Analyses: _____

RTP Labs Proj. Tracking No.: 04-176
 Client Tracking No.: _____

Sample ID No. & Description	Date Sampled	Time	Matrix		Compliance Test	Preservatives	# of Containers	Canisters		Lab Sample ID Fraction
			Air	Liquid/Solid				Field Initial	Lab Receipt Final	
1 <u>51-BAG-102504</u>	<u>10/25</u>	<u>09:00</u>	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<u>Specific Sulfur Compounds</u>		<u>1</u>	<u>vacuum or pressure</u>	<u>04176-1</u>	<u>1</u>
2 <u>52-BAG-102504</u>	<u>10/25</u>	<u>10:45</u>	<input checked="" type="checkbox"/>	<input type="checkbox"/>			<u>1</u>		<u>04176-2</u>	<u>2</u>
3										
4										
5										
6										
7										
8										
9										
10										

QC Requirements: Screen Standard EPA Level IV for Compliance Requires approved QAPP sent to lab

Turn Around Time Requested for Report: Business Days; *Rush Multipliers (X)
 1 day*(4x) 2 days*(3x) 3 days*(2x) 5 days*(1.5x) 10 days*(1.1x) 15 days

Relinquished By: Debra Engled Date: 10-25-04 Time: 2:06 PM

Relinquished By: _____ Date: _____ Time: _____