North Carolina Division of Air Quality (DAQ) Progress Report on the Study for Estimating Hydrogen Sulfide and Total Reduced Sulfur Compounds Emissions from Wastewater Treatment Systems (WWTS) at Kraft Paper Mills; Prepared for March 8, 2006 NC Air Quality Committee Meeting

1. Rule Requirements of the Study

On April 1, 2005 a rule change, proposed by the NC Environmental Management Commission (EMC), became effective to reduce the hydrogen sulfide Acceptable Ambient Level (AAL). The rule change was to reduce the hydrogen sulfide AAL from 2.1 to 0.12 milligrams per cubic meter (or from 1,500 to 83 parts per billion) under 15A NCAC 2D .1104.

Included in the new rule were provisions to exempt paper mill wastewater treatment systems from the new hydrogen sulfide AAL, provided the paper industry submit the following two reports relative to their wastewater treatment systems, both subject to DAQ approval:

- Monitoring studies for estimates of hydrogen sulfide, methyl mercaptan, and total reduced sulfur emissions through industry monitoring studies by November 1, 2005. In deciding approval of the estimates, DAQ shall consider field validation procedures including the number of valid samples taken, when measurements are made, quality assurance procedures, and other information necessary in producing accurate and precise measurements. DAQ shall report information on the monitoring study to the EMC by January 1, 2006 [15A NCAC 2D .1104(1)].

- Results of air dispersion modeling using the monitoring study data. If the modeling analysis demonstrates that predicted hydrogen sulfide concentrations are below the acceptable ambient levels, no further action is required to maintain the exemption. The favorable modeling results must be submitted by July 1, 2006, and DAQ shall report information on the modeling analysis to the EMC by September 1, 2006 [15A NCAC 2D .1104(2)].

However, if the modeling results are not favorable and show the hydrogen sulfide acceptable ambient level is exceeded, then the paper industry must submit an ambient air monitoring plan to assess actual hydrogen sulfide levels by September 30, 2006. The monitoring may be performed at each mill or one mill DAQ determines to be representative. The DAQ shall make the decision regarding approval of the monitoring plan by December 31, 2006 [15A NCAC 2D .1104(3)].

2. Conduct and Reporting of the Monitoring Study

The minimum scope of the monitoring study to satisfy the rule was to:
- Identify points / areas of sulfur gas release from each paper mill WWTS, and
- Measure hydrogen sulfide, methyl mercaptan, and other total reduced sulfur (TRS) compounds (*i.e.*, dimethyl sulfide and dimethyl disulfide) emission rates from such areas at typical WWTS.

Industry was also interested in expanding the study scope to include the following:
- Identify points of generation and release in WWTSs from three paper mill WWTS;
- Measure all TRS compounds, methane, and carbonyl sulfide gas emission rates;
- Determine ability of sulfur material balance approach to estimate TRS emissions;
- Develop an understanding of factors affecting WWTS sulfur compound emissions; and
- Calibrate and/or develop mechanistic models to predict emissions.

The initial study (Phase I) approach was to quantify emission rates of several compounds from three individual paper mill WWTS: Weyerhaeuser mills at Plymouth and New Bern, and the International Paper mill at Roanoke Rapids.. The procedures for ambient air sampling emission monitoring created by Esplin were followed involving measuring air concentrations across the full plume width.[1,2] Plume sampling occurred directly downwind of the sources at four elevations above ground with a mobile cart and a tethered balloon. Process data and meteorological data at 6- and 30-foot heights were collected at each study site. Sample analyses were performed using gas chromatography and pulsed flame photometric detection for all four TRS compounds and methane.

Initial Study Schedule (Phase I):

First site:	Weyerhaeuser-Plymouth	April 2005
Second site:	Weyerhaeuser-New Bern	May 2005
Third site:	International Paper-Roanoke Rapids	August 2005
Report Submittal	Both International Paper and Weyerhaeuser	November 2005

3. DAQ Review of the Paper Mill Monitoring Study Reports

DAQ approved the sampling and emission calculation methodology in the monitoring study reports. However, DAQ questioned the validity of most of the analytical data, given that a key quality assurance criterion stated in the approved plan was not routinely met. Then DAQ hired a consultant to serve as an expert analyst with first-hand experience in performing the same analytical procedure with the same sulfur compounds in ambient air as performed in the study. A meeting was held between the paper industry and DAQ on January 17, 2006 to discuss the data quality problems and plans for conducting additional studies. DAQ concluded that most of the analytical data and resulting emission estimates in the Phase I reports to be unacceptable for the purpose of meeting 15A NCAC 2Q .0714. However, analytical data and emission estimates from two International Paper-Roanoke Rapids sources were found to be acceptable. The US EPA also reviewed the reports and found the analytical data "questionable" bearing the same uncertainty as information existing before the study. , and "hopes that a more suitable H_2S study will be conducted … in the near future."

In early February 2006 the paper industry submitted their revised study plan (Phase II) in terms of the proposed scope of work and analytical quality assurance procedures. DAQ found all but one proposed detail in their submittal acceptable, being firm that analyses must include dimethyl sulfide and dimethyl disulfide along with hydrogen sulfide and methyl mercaptan [*i.e.*, all four compounds are defined as TRS in 15A NCAC 2D .0528 and required in the study under 15A NCAC 2Q .0714(1)]. Industry plans are to complete the Phase II monitoring study in time to submit emission estimates and dispersion modeling results by July 2006. The schedule for the Phase II monitoring study and modeling analysis is the following:

Phase II Study Schedule:

First site:	Weyerhaeuser-Plymouth	March 2006
Second site:	International Paper-Roanoke Rapids	April 2006
Report Submittal (with emission estimates and dispersion modeling results)		July 1, 2006

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

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