

Summary of Hydrogen Sulfide Acceptable Ambient Level Amendment Proposal

By Steve Schliesser, May 22, 2003

In 1986 the current NC Acceptable Ambient Level (AAL) guideline for hydrogen sulfide (H_2S), based on acute irritancy, was established. At that time the studies on the known health effects supported an AAL for H_2S of 2.1 milligrams per cubic meter (mg/m^3) or 1,500 parts per billion (ppb) for a 1-hour average. Based on new health effects data and following the prescribed practice, in late 2001 the NC Scientific Advisory Board recommended a range of AALs rather than one single AAL for consideration by the Air Quality Committee. The three AALs recommended by the Scientific Advisory Board with their corresponding health basis are as follow:

- 40 ppb ($0.056 mg/m^3$) for 1-hour average, Respiratory effects in exposed asthmatics;
- 23 ppb ($0.033 mg/m^3$) for 24-hour average, Eye irritation in exposed workers;
- 83 ppb ($0.120 mg/m^3$) for 24-hour average, Nasal toxicity in exposed rats.

During several Air Quality Committee meetings in late 2002 and early 2003 Division of Air Quality (DAQ) staff presented information related to the technical, regulatory, and economic issues for amending the H_2S AAL. In May 2003 the Environmental Management Commission recommended that three sets of options be taken to public hearings. Below is a summary of the key facts and points covered so far in this rulemaking process; more detail are available in the files with the corresponding titles on the DAQ H_2S AAL web page:

1. Hydrogen sulfide emission inventory in North Carolina. The DAQ 1999 emission inventory showed a statewide total release of 4.2 million pounds of H_2S . Largely from revised data cooperatively submitted by the fertilizer and paper industries, the 2002 emission inventory revealed a statewide total of 11.9 million pounds of H_2S /year. The fertilizer and paper industries account for over 99% of these emissions; the wastewater treatment systems represent nearly 90% of the NC pulp and paper industry H_2S emissions.
2. State survey of hydrogen sulfide Acceptable Ambient Level standards. While the US EPA does not consider it a hazardous air pollutant, NC and at least 31 other states do consider H_2S a toxic or hazardous air pollutant and have developed ambient standards to protect public health. The AALs recommended by the NC Scientific Advisory Board are in the middle of the range of the other states' standards, both on a 1-hour average and a 24-hour average basis.
3. Hydrogen sulfide regulatory practices in other states. DAQ contacted four states: South Carolina, Georgia, Minnesota and Wisconsin. These states show similar characteristics to NC, including:
 - Occurrence of paper/pulp mills and other H_2S -emissive industries, and
 - Air toxics programs with comparable (some higher, some lower) H_2S standards.
4. Hydrogen sulfide emissions from NC hog farms. DAQ along with NC State University have studied hog farm emissions extensively for 5 years. Experts from both organizations have data supporting that H_2S emissions from NC hog farms only represent a small portion (less than 5%) of statewide emissions, though they recognize hog farms in the Midwest can be much more H_2S emissive. However, certain NC industry representatives believe that our hog farms release the majority (roughly 85%) of statewide emissions; and based on this premise, industry argues that it is unreasonable to exempt the most H_2S emissive industry. This controversy may continue until NCSU test results on H_2S emissions from NC hog farms become available, which DAQ plans to report later this year.

5. Sulfur cycling in swine lagoons. An Auburn University professor provides an account of why and how hog farm lagoons produce H₂S emissions. His information indicates that purple sulfur bacteria (PSBs) may reduce the concentration of sulfide in the water, but PSBs would not remove the entire mass of sulfide. Even for hog lagoons with active PSB populations, there will still be substantial hydrogen sulfide releases to the atmosphere. PSB activity is inherently unstable and environmental factors (i.e., light, temperature) and the toxic nature of swine waste (i.e., high ammonia and copper salts) may reduce activity or kill the PSBs outright.
6. Hydrogen sulfide modeling at paper and fertilizer facilities. Dispersion modeling results of the two most H₂S emissive NC industries showed the following property line levels of H₂S:
 - 11,000 ppb (15.3 mg/m³) on a 1-hour average for paper mills, and
 - 1,400 ppb (1.9 mg/m³) on a 1-hour average for phosphate fertilizer.
7. Proposed options on hydrogen sulfide and activated sludge issue. Based on the estimated emissions and modeling, a paper mill is apparently operating with property line ambient air levels exceeding the current H₂S AAL guideline. Its modeled maximum property line concentration is 15.3 mg/m³ compared to the current AAL of 2.1 mg/m³. There is reason to believe that: (1) All NC mills (except Blue Ridge Paper) would likewise model above the current H₂S AAL; and (2) To have their wastewater treatment comply with any of the three proposed AALs, all NC mills (except Blue Ridge Paper) would be forced to convert from aerated stabilization basin to activated sludge treatment, and then add covers, ducting, and an incinerator.

The technology on the extent and control of H₂S emissions from wastewater treatment is not fully developed. This means there is not enough known about these issues for the paper industry to make a huge commitment in reducing H₂S emissions from wastewater treatment. Until more information is available, DAQ recommends that the paper industry wastewater treatment operations be exempt. Below are three DAQ proposed options for consideration:

- A. Revise the AAL and exempt wastewater treatment systems at paper mills until February 1, 2007, in which case a demonstration of economic hardship may not be necessary.
- B. Revise the AAL, but do not exempt wastewater treatment systems at paper mills, in which case a demonstration of economic hardship would be necessary from each facility.
- C. Do nothing; do not revise the AAL, and do not exempt wastewater treatment systems at paper mills, in which case a demonstration of economic hardship would be necessary from each facility.

In any of the three proposed options, further investigation on the control of all toxic air pollutants from wastewater treatment at paper mills appears necessary. DAQ recommends the paper industry perform and report on such a study. In addition to air quality benefits, industry would evaluate any improvements/ benefits in the quality of wastewater discharge to see if there were any synergy in improving *both* air and water quality with a given technology(s). Industry would report its final findings no later than February 1, 2007.

8. Additional information on hydrogen sulfide and activated sludge issue. During the February 2003 Air Quality Committee Meeting, a number of concerns were raised on H₂S and wastewater treatment. Following is the information compiled by DAQ:
 - DAQ confirmed the industry-provided costs to control H₂S emissions meeting the recommended AALs from the fertilizer and paper industries.

- For a given treatment efficiency, the current method utilized at most of the NC paper mills, called aerated basin, is more economical than activated sludge treatment.
 - However, activated sludge provides higher quality sludge treatment than aerated basin.
 - There is evidence that the paper industry in many instances was able to bear the costs of installing new activated sludge units when necessary to meet environmental standards.
 - Some paper mills have successfully phased in activated sludge treatment while others have not.
 - It appears to be common practice in the paper industry not to report emissions from wastewater treatment; consequently, there is little experience in developing process changes to minimize emissions or in developing cost-effective emission control technologies.
9. Asphalt plant modeling of hydrogen sulfide emissions. There are 15-asphalt terminals in NC. Emission testing performed at an asphalt terminal found 2,400,000 ppb (3,360 mg/m³) H₂S released from the storage tanks. Since then the facility installed activated carbon beds on the storage tanks and maintained the carbon beds controlling the truck loading racks. Dispersion modeling was performed using the DAQ normal compliance determination procedures. A digital map of the September 2001 facility was created, and receptors (or discrete ground level points) were placed around the terminal property boundaries. The predicted maximum impacts were 785 ppb (1.1 mg/m³) for the uncontrolled scenario and 6 ppb (0.009 mg/m³) for the controlled scenario.
10. Economic impact analysis for proposed hydrogen sulfide. Industry provided one aggregate (for the 6 fertilizer and paper facilities in NC) cost estimate to meet the proposed H₂S AALs, but was unable to provide aggregate cost estimates for each of the three SAB recommended AALs because of the basic uncertainty associated with their costs. The threshold determination of annual costs in excess of \$5 million per year is conclusive as the total cost estimate exceeds \$42 million. The proposed H₂S rule change is not expected to cause a state or local fiscal impact. Based on the available cost estimates, the proposed H₂S amendment is considered a significant rulemaking. Either of the proposed alternatives would be filed as resulting in 'substantial economic impact,' which in turn requires detailed explanation of the analysis methodology and requires an additional 30 days for the comment period associated with the public input process. There also appear to be significant public health benefit from the various proposed AALs in terms of reduced ambient concentrations and resulting health costs related to H₂S exposure.
11. Stability of hydrogen sulfide in ambient air. Information in the scientific literature indicates the stability for H₂S in air is generally in the range of 18 hrs to 3 days depending on atmospheric conditions and the levels of ozone and other smog components. A maximum time of 42 days was noted in one reference, but this was in a high latitude location in winter, i.e. very cold, which slows reaction rates. A minimum time of 2 hours was noted in another reference in the presence of "polluted urban air." Additionally, H₂S appears not to react photochemically, meaning that light does not appear to cause a direct reaction in which H₂S is changed to another compound.
12. DAQ slide presentation on hydrogen sulfide issues – February AQC meeting. Somewhat self-explanatory; a summary of the information contained in several files above.
13. DAQ slide presentation on hydrogen sulfide issues – March AQC meeting. Somewhat self-explanatory; a summary of the information contained in several other files above.
14. NC Toxics Rule compliance procedures. Information is provided for the schedules when compliance with the toxics rules must occur for various circumstances. For example:
- A new facility would be required to comply upon startup.

- A modified facility would be required to comply before operation of the modified equipment.
- For a SIC call, a facility would be required to comply in 3 years from date permit is issued.
- For a Director's call, there is no specified compliance time line.
- For a MACT affected facility, compliance deadline occurs with AALs by the same deadline as the last MACT deadline (excluding boiler MACT). Modifications can be made without an air toxics evaluation until permit renewal date (5 year cycle).

15. Proposed 15A NCAC 2D .1104 TAP AAL guidelines for hydrogen sulfide. DAQ recommended the 6 options below for consideration by the Air Quality Committee; the committee selected three for further consideration, marked by an asterisk [*]. (Note: These consist of individual and various combinations of the 3 AALs recommended by the Scientific Advisory Board; also note that the numerical values are given in mg/m³ at 77 °F (25° C) and 29.92 inches (760 mm) of mercury pressure.

Pollutant:	Annual (Carcinogens)	24-hour (Chronic Toxicants)	1-hour (Acute Systemic Toxicants)	1-hour (Acute Irritants)
Hydrogen sulfide				
OPTION 1		<u>0.12</u>		
OPTION 2			<u>0.056</u>	
OPTION 3 *		<u>0.033</u>		
OPTION 4 *		<u>0.033</u>	<u>0.056</u>	
OPTION 5				
<u>New facility</u>		<u>0.033</u>		
<u>Old facility (existing)</u>		<u>0.12</u>		
OPTION 6 *				
<u>New facility</u>		<u>0.033</u>	<u>0.056</u>	
<u>Old facility (existing)</u>		<u>0.12</u>		

16. Proposed 15A NCAC 2D .0702 Exemptions for paper mill wastewater treatment systems. The following exemption was proposed by the Air Quality Committee:
 "A permit to emit toxic air pollutants shall not be required under this Section for wastewater treatment systems at pulp and paper mills until February 1, 2007, at which time this exemption would expire."
17. Steps in developing and adopting a rule. Under Appendix 37 in the North Carolina Air Quality Rules, the various steps in adopting a rule are identified. After consideration by the Air Quality Committee and its recommendation to proceed, a draft rule goes before the Environmental Management Commission (EMC) for request to go to the public hearing stage. If the draft rule is approved by the EMC, Hearing Officers are appointed and public hearings are arranged with public notice at least 30 days before the public hearings in newspapers and at least 15 days before the public hearings in the NC Register.

Then public hearings across the state are held to obtain input and comments from the interested public on the three proposed H₂S AAL options. A record of the public hearing(s) is prepared for and approved by the Hearing Officers before being presented to the EMC. In this rulemaking, the Hearing Officers will make a recommendation for the H₂S AAL, based on their

judgment of public input. If approved by the EMC, the recommended rule with any technical corrections would go to the Rules Review Commission (RRC) and through other administrative steps before going into effect.

18. Rulemaking process timeline. A timeline with each of the rulemaking steps is illustrated in a figure in the corresponding file on the DAQ web page. It shows that the H₂S AAL rule amendment would become effective in late 2004, if approved by the EMC and RRC.
19. Typical comment procedures. All persons interested in the rule change are invited to attend the public hearing(s). Any person desiring to comment is welcome to submit a written statement of their opinion on this issue before, during, or after the public hearing. The hearing record will remain open to receive written statements for a minimum of 60 days after the public hearing process is initially announced in the North Carolina Register. The date when the hearing record will close will be clearly announced at each public hearing.
20. May Environmental Management Commission (EMC) Meeting. During the meeting the EMC decided to take three sets of options through public hearings across the state to obtain input and comments. The three sets of options are as follow:

A. Five H₂S AAL options. The EMC decided to take to public hearing five AAL options. These consist of individual and various combinations of the 3 AALs recommended by the Scientific Advisory Board and the 3 options recommended by the Air Quality Committee; note that the numerical values are given in mg/m³ at 77 °F (25° C) and 29.92 inches (760 mm) of mercury pressure. For a complete copy of the EMC proposed H₂S AAL options, see <http://daq.state.nc.us/rules/draft/1104n.pdf>.

Pollutant:	Annual (Carcinogens)	24-hour (Chronic Toxicants)	1-hour (Acute Systemic Toxicants)	1-hour (Acute Irritants)
Hydrogen sulfide				
OPTION 1		<u>0.033</u>		
OPTION 2			<u>0.056</u>	
OPTION 3				
<u>New facility</u>		<u>0.033</u>		
<u>Old facility (existing)</u>		<u>0.12</u>		
OPTION 4		<u>0.12</u>		
OPTION 5		<u>0.12</u>	<u>0.056</u>	

B. Two timeline options for Wastewater Treatment System Exemptions. The EMC decided to take to public hearing two exemption options: one with a sunset provision and one without a sunset, as indicated below. For a complete copy of the EMC proposed WWTS exemption options, see <http://daq.state.nc.us/rules/draft/new702.pdf>.

15A NCAC 02Q .0702 EXEMPTIONS

- (a) A permit to emit toxic air pollutants shall not be required under this Section for:

OPTION A

(24) Wastewater treatment systems at pulp and paper mills until February 1, 2007, at which time this exemption shall expire (sources covered under this exemption may be covered under Rule .0714 of this Section); [this would mean that mills would have until February 2010 to reduce WWTS emissions to comply with H₂S AAL or until EMC elects to undergo another rulemaking to extend or otherwise change the exemption.]

OPTION B

(24) Wastewater treatment systems at pulp and paper mills (sources covered under this exemption may be covered under Rule .0714 of this Section); [this would mean that the WWTS would be exempt on a permanent, indefinite basis, or until EMC elects to undergo another rulemaking to remove or otherwise change the exemption.]

C. Two options to study Wastewater Treatment Systems (WWTS) emissions. The EMC decided to take to public hearing two options dealing with the nature and extent of the study to evaluate WWTS emissions, the resulting air quality, and environmental and health benefits, as indicated below. For a complete copy of the proposed study options, see <http://daq.state.nc.us/rules/draft/0714new2.pdf>.

Option A	Option B
Test WWTS for emissions of H ₂ S, methyl mercaptans, and total reduced sulfur and report using sufficiently accurate methods approved by the DAQ Director by August 1, 2005.	Estimate WWTS emissions of H ₂ S, methyl mercaptans, and total reduced sulfur and report using suitable methods developed from industry studies and approved by the DAQ Director by August 1, 2005.
Provide engineering evaluation and report of installing activated sludge as a WWTS, including its cost and an assessment of the environmental and health benefits to water quality and air quality of activated sludge as a WWTS by August 1, 2006.	Using the above emission estimates, perform air dispersion modeling of all H ₂ S emission sources. If modeling predicts levels below the AAL, then no further action is required to maintain the WWTS exemption; submit results to the DAQ Director by July 1, 2006.
DAQ Director will report the above findings to the EMC within 60 days.	If modeling predicts levels above the AAL, then submit an ambient air quality monitoring plan to assess actual ambient H ₂ S levels typical of pulp and paper operations for DAQ approval; the plan may be undertaken at each mill, or at the option of the affected mills, it may be performed at one NC mill the DAQ Director determines to be representative of the industry. Implement the monitoring plan within 180 days of DAQ Director's approval.
	Complete the ambient monitoring plan and report the results to the DAQ Director and the EMC Chairperson within 18 months of the start of the study.
	DAQ Director will report the above findings to the EMC within 60 days.
Except mills with activated sludge for WWTS	Except mills with activated sludge for WWTS

ACRONYMS

AAL	Acceptable Ambient Level
AQC	Air Quality Committee
DAQ	Division of Air Quality
EMC	Environmental Management Commission
EPA	U.S. Environmental Protection Agency
H ₂ S	Hydrogen sulfide
mg/m ³	milligram per cubic meter
NC	North Carolina
NCSU	North Carolina State University
NCAC	North Carolina Administrative Code
MCIC	Manufacturing and Chemical Industry Council of NC
ppb	Parts per billion
PSB	Purple sulfur bacteria
RRC	Rules Review Commission
SAB	Scientific Advisory Board
TAP	Toxic Air Pollutant
WWTS	Wastewater treatment system