QUESTIONS AND ANSWERS

ABOUT

KRAFT PULP MILL ODOR

Author: S. R. Young

JUNE 2008

GEORGIA-PACIFIC
CONSUMER PRODUCTS (CAMAS) LLC
CAMAS, WASHINGTON

Manual 75

WHAT IS KRAFT PULP MILL ODOR?

Kraft pulp mill odor typically consists of four reduced sulfur gases including dimethyl sulfide, dimethyl disulfide, hydrogen sulfide, and methyl mercaptan. Of these, methyl mercaptan and hydrogen sulfide are the predominant components. These gases are notable because there is a wide concentration range between the odor threshold and actual health concerns. For example, the odor threshold for hydrogen sulfide is around 0.5 parts per billion (0.0005 ppm), while the occupational exposure guideline for this chemical is 10,000 parts per billion (10 ppm).

HOW ARE THESE REDUCED SULFUR GASES FORMED?

In the kraft process, wood chips or sawdust are cooked under pressure in a solution containing sodium hydroxide, sodium sulfide, and sodium carbonate. An unavoidable consequence of this cooking is the production of reduced sulfur gases. These gases, collectively known as TRS (total reduced sulfur gas) can evolve from washing the digested wood pulp, evaporating the spent pulping liquid, and burning the spent liquid for chemical and energy recovery.

HOW DOES THE MILL CONTROL REDUCED SULFUR GASES?

More than 96% of the TRS generated by the mill is collected and burned in one or more of the mill's large combustion units. The combustion exhaust gas is then scrubbed to remove additional pollutants. The collection and combustion processes are regulated by the mill's air operating permit.

HAS THE MILL CONTROLLED HVLC SOURCES?

In 2006, the Camas Mill completed a comprehensive multiyear program to collect and burn air emissions from miscellaneous process vents. These vents are known as high volume low concentration (HVLC) sources. TRS reductions exceeding 95% were achieved with this project.

WHAT ARE THE REMAINING SOURCES OF TRS EMISSIONS AT THE MILL?

The only significant untreated source of TRS left at the Camas Mill is the wastewater treatment system on Lady Island. We control emissions from this source by steam stripping the kraft condensates, minimizing spills in the pulp mill, and ensuring that there is adequate aeration in the wastewater treatment basin.

WHAT IS THE CONCENTRATION OF REDUCED SULFUR GASES IN THE BIG MILL STACKS?

Many Camas Mill systems have continuous emission monitors or CEMs which measure the concentration of total reduced sulfur gas (TRS) in the stacks. The 2007 stack concentrations of TRS by source are as follows:

Source	Total Reduced Sulfur Gas – ppm		
	Stack Concentration		Permit Limit
	Average	Range	12-Hour Average
No. 3 Kraft Recovery Furnace	1	0-3	5
No. 4 Kraft Recovery Furnace	1	0-5	5
No. 4 Lime Kiln	4	0-8	8

These concentrations meet the conditions of the mill's air operating permit. After leaving the stack, the gases rapidly disperse in the ambient air.

WHAT IS THE CONCENTRATION OF TOTAL REDUCED SULFUR GASES AT THE WASTEWATER TREATMENT SYSTEM?

The calculated annual average concentration for 2007 was 0.006 ppm (83% less than in 2000). Individual measurements ranged from zero (not detected) to 3 ppm (parts per million).

WHAT ARE OTHER SOURCES OF REDUCED SULFUR GASES?

Reduced sulfur gases are common in the environment. The major sources (based on annual emissions) are natural in origin and include animals and their wastes, composting vegetation, decaying plankton, human wastes, natural gas, petroleum, stagnant water, sulfur springs, volcanoes, and wetlands. Potential municipal and industrial sources of reduced sulfur gases are dairies, food processing plants, leather tanneries, livestock feedlots, municipal landfills, petroleum refineries, poultry farms, rayon factories, and sewage treatment plants.

HOW MIGHT I BE EXPOSED TO REDUCED SULFUR GASES?

The primary route of exposure to reduced sulfur gases is through inhalation. Since the majority of these gases are the product of nature, TRS (total reduced sulfur gas) is present in ambient air all over the world. Typical concentrations range from less than 0.001 ppm (parts per million) at remote sites to over 0.097 ppm in urban locations. Air near active geothermal areas, marshes, or sulfur hot springs may contain 0.005 to 2.5 ppm TRS. Concentrations near industrial processes such as pulp mills are typically less than 1 ppm TRS. Concentrations many times these levels (often exceeding 400 ppm) can occur in enclosed or poorly ventilated places where TRS is produced by bacteria. Some common examples are septic tanks, sewers, latrines, and manure storage areas. You are also exposed to the TRS (up to 5 ppm) that is generated by bacteria that assist food digestion in your own intestines. Bacteria in your mouth also generate TRS with breath containing 0.007-0.886 ppm and “bad breath” in healthy individuals containing as much as 18.4 ppm.

WHAT ARE THE SHORT-TERM (ACUTE) HEALTH EFFECTS OF EXPOSURE TO REDUCED SULFUR GASES?

Exposure to low levels of reduced sulfur gas (in air), such as the exposure associated with kraft odor, may in some individuals result in difficult breathing, headache or nausea. In general, these effects are not noted at the levels released from the major mill sources. Much higher concentrations are likely to result in eye and respiratory tract irritation that becomes more severe as the exposure time increases. Please see the following table for concentration ranges.

WHAT ARE THE LONG-TERM (CHRONIC) HEALTH EFFECTS OF EXPOSURE TO REDUCED SULFUR GASES?

Reduced sulfur gases are rapidly metabolized and do not accumulate in the body. The available scientific literature suggests that long-term exposures of one ppm (parts per million in air) or less will result in no adverse effects to the eyes, skin or lungs. In addition, there is no indication of other health effects such as cancer, cardiovascular disease, and reproductive or developmental problems.

POTENTIAL PHYSIOLOGIC EFFECTS FOR HUMAN EXPOSURE TO TOTAL REDUCED SULFUR GASES

Potential Physiologic Effects[a]	Concentration[b] – ppm			
	Dimethyl Disulfide	Dimethyl Sulfide	Hydrogen Sulfide	Methyl Mercaptan
Odor threshold	0.006-0.090	0.001-0.020	0.0005-0.030	0.0005-0.008
Mill stacks, no dilution			1-4	
Airway irritation, headache (asthmatics)			2-5	
Occupational exposure guideline (TLV)[c]			10	0.5
Occupational exposure limit (PEL)[d]			10	0.5
Cough, headache, insomnia, nausea (workers)			10-20	4-8
Strongly offensive odor			20-30	
Eye irritation			20-100	1,500
Sickeningly sweet odor			30	
Respiratory irritation	150[b]	>150[b]	50-100	
Immediately dangerous to life and health (IDLH)[e]			100	150
Rapid unconsciousness, death within 15 minutes			700-900	1600 – 2200
Immediate collapse, respiratory paralysis, neural paralysis, death			1,000	10,000

[a] See reference section.

[b] Animal studies suggest that dimethyl disulfide and methyl mercaptan are slightly less toxic then hydrogen sulfide. Dimethyl sulfide is about 100 times less toxic than the other reduced sulfur gases discussed here.

[c] Threshold Limit Values (TLVs) are airborne concentrations of substances under which it is believed that nearly all workers may be repeatedly exposed day after day without adverse health effects. Both TLVs are based on irritation.

[d] The Permissible Exposure Limits (PELs) listed are the maximum legal occupational exposures allowed. For both hydrogen sulfide and methyl mercaptan, they are the 8 hour time weighted averages (TWA).

[e] Immediately dangerous to life and health (IDLH) as defined by NIOSH (National Institute for Occupational Safety and Health) is the concentration of an airborne contaminant that is likely to cause death, permanent adverse health effects, or the prevention of escape (within 30 minutes) from such an environment.

GLOSSARY

DIMETHYL DISULFIDE (DMDS) – Dimethyl disulfide ($C_2H_6S_2$) is a colorless, flammable liquid with a characteristic odor of decayed fish. The odor threshold is in the range of 0.006 – 0.090 ppm. Most of the DMDS present in the atmosphere results from biological decomposition.

DIMETHYL SULFIDE (DMS) – Dimethyl sulfide (C_2H_6S) is a colorless, flammable, slightly water soluble (2 g/100 ml of water) liquid with a characteristic odor of decayed vegetables. The odor threshold is in the range of 0.001-0.020 ppm. Dimethyl sulfide has the unique capability of enhancing and intensifying other odors. This property has prompted its use in warning odorants and odor masking agents. Most of the DMS present in the atmosphere is the result of biological decomposition, especially of oceanic plankton.

HVLC – High volume low concentration sources of total reduced sulfur gases. Some examples are bleach plant tower vents, pulp washer hood vents, seal tank vents, washer filtrate tank vents, etc.

HYDROGEN SULFIDE (H_2S) – Hydrogen sulfide is a colorless, flammable gas with an odor reminiscent of rotten eggs. The odor threshold is in the range of 0.0005-0.030 ppm. Approximately 95% of hydrogen sulfide present in the atmosphere is produced naturally from volcanic eruptions, sulfur springs, undersea vents, swamps, stagnant bodies of water, and biological decomposition.

IDLH – Immediately Dangerous to Life and Health as defined by the National Institute for Occupational Safety and Health (NIOSH) is the concentration of an airborne contaminant that is likely to cause death, permanent adverse health effects, or the prevention of escape (within 30 minutes) from such an environment.

METHYL MERCAPTAN (MeSH) – Methyl mercaptan (CH_4S) is a colorless, flammable gas with a characteristic odor reminiscent of decayed cabbage. The odor threshold is in the range of 0.002-0.008 ppm. Methyl mercaptan is evolved naturally from mineral deposits, natural gas, petroleum, and biological decomposition. It is also an essential flavor component of several vegetables (especially onion and garlic), nuts, and cheeses.

NATURAL GAS ODOR – The warning odorant currently used in natural gas supplies in our area is about 75% t-butyl mercaptan and 25% methyl ethyl sulfide. This odor is often confused with kraft odor at concentrations near the odor threshold.

ODOR THRESHOLD – Odors play an important role in the animal kingdom. They provide a method of communication, they attract mates, and they enhance the chances of survival. Some examples are the recruiting (geraniol and citral) and alarm (isoamyl acetate) odors of the honey bee, the sexual attractant (trans-3-cis-tetradecaienoic acid) of the black carpet beetle, the camel's ability to smell water, and the skunk's defensive scent (butyl mercaptan). Man too has developed a higher

sensitivity to certain classes of volatile compounds, among them the aromas of edible plants and fruits, reproductively significant scents, chemicals indicative of death or fecal contamination, and the odor of bacterial decomposition.

Just as there are tremendous differences in odor perception between animal species there are also significant differences in human odor perception based on age, gender, ethnic background, familiarity, and individual sensitivity. Take hydrogen sulfide for example. A hydrogen sulfide concentration of 0.0005 ppm is considered to be the threshold of odor perception. At this concentration, only about 2% of adults can detect it. If the concentration is raised four fold to 0.002 ppm, approximately 14% of adults can smell it. By the time we reach a concentration of 0.03 ppm, 83% of adults can smell it but most don't find it to be objectionable.

PERMISSIBLE EXPOSURE LIMIT (PEL) – An occupational exposure limit that is enforced as a legal standard by state or federal agencies.

ppb – Parts per billion in air by volume.

ppm – Parts per million in air by volume. One ppm is equal to 1000 parts per billion.

THRESHOLD LIMIT VALUE (TLV) – TLV's are airborne concentrations of substances under which it is believed that nearly all workers may be repeatedly exposed day after day without adverse health effects.

TOTAL REDUCED SULFUR GASES (TRS) – The sum of hydrogen sulfide, mercaptans, dimethyl sulfide, dimethyl disulfide, and other volatile sulfides expressed as hydrogen sulfide.

REFERENCES

Kangas, J.; Jappinen, P.; and Savolainen, H., “Exposure to Hydrogen Sulfide, Mercaptans, and Sulfur Dioxide in the Pulp Industry,” Am. Ind. Hyg. Assoc. J, 45, 12, December 1984.

Sax, N. I., et al., “Dangerous Properties of Industrial Materials, Sixth Edition,” Van Nostrand Reinhold, New York, NY, 1984.

Sweet, D. V., Editor, “Registry of Toxic Effects of Chemical Substances,” NIOSH, Washington, D. C., April 1987.

Goyer, N., “Evaluation of Occupational Exposure to Sulfur Compounds in Paper Pulp Kraft Mills,” Am. Ind. Hyg. Assoc. J, 51, 7, July 1990.

“Documentation of the Threshold Limit Values and Biological Induces, 6th Edition,” American Conference of Governmental Industrial Hygienists, Cincinnati, OH, 1991.

Kerger, B. D., and L. Barfield, “Current Understanding of Hydrogen Sulfide Toxicity with Specific Reference to Regulatory Policies and Pulp and Paper Mill Emissions,” McLaren/Hart Environmental Engineering, Irvine, CA, July 31, 1992.

Bhambhani, Y., et al., “Comparative Physiological Responses of Exercising Men and Women to 5 ppm Hydrogen Sulfide Exposure,” Am. Ind. Hyg. Assoc. J, 55, 11, November 1994.

Tatum, V. L., “Health Effects of Reduced Sulfur Gases,” NCASI, New York, NY, Technical Bulletin No. 691, February 1995.

Budaveri, S., et al., “The Merck Index, 12th Edition,” Merck & Company, Whitehouse Station, NJ, 1996.

Harris, R. L., Editor, “Patty’s Industrial Hygiene, Fifth Edition,” John Wiley & Sons, New York, NY, 2000.

Bingham, E.; Cohrssen, B.; and C. H. Powell, Editors, “Patty’s Toxicology, Fifth Edition,” John Wiley & Sons, New York, NY, 2001.

“NIOSH Pocket Guide to Chemical Hazards,” NIOSH, U. S. Dept. of Health & Human Services, Washington, D.C., January 2003.

Warner, T., “Summary of Community Health Concerns, Georgia-Pacific Pulp And Paper Mill, Clark County, Washington”, Washington State Department of Health, Olympia, WA, February 26, 2004.

Beers, M. H., et al., “The Merck Manual of Diagnosis and Therapy, 18th Edition,” Merck & Company, Whitehouse Station, NJ, 2006.

REFERENCES
(Continued)

"Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices," American Conference of Governmental Industrial Hygienists, Cincinnati, OH, 2008.

Diaz, E., "Summary of Air Quality Issues and Identification of Information Needed to Address Community Health Concerns – Port Townsend Paper Corporation, Jefferson County, Washington", Washington State Department of Health, Olympia, WA, April 2008.

Cook, D., "Summary of Industry Experience With Odor Minimization At Wastewater Treatment Plants", NCASI, Research Triangle Park, NC, Technical Bulletin No. 949, May 2008.