KRAFT PULP MILL
ODOR SOURCES

A
SUMMARY OF ACCOMPLISHMENT
2001-2008

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TABLE OF CONTENTS

1.0 INTRODUCTION

1.1 PURPOSE

In response to growing public concern, the Camas Mill agreed in February 1994 to complete an evaluation of kraft mill odor sources.[1] The evaluation plan contained a comprehensive list of action steps covering both odor assessment and control. The requirements for the evaluation plan included tracking odor complaints, creating a community advisory panel, setting up a meteorological station, maintaining a total reduced sulfur (TRS) gas inventory, assessing the community impact, and selecting odor control technologies. These items were completed and a summary report was issued in 2001.[2] Since that time, improvements have continued with the installation of a kraft condensate steam stripper, a High Volume Low Concentration (HVLC) gas collection and combustion system, noncondensible gas (NCG) collection system improvements, a NCG Scrubber, and wastewater treatment optimization. The purpose of this document is to report on the progress achieved with these recent projects.[3-7]

1.2 BACKGROUND

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-tetradecadienoic acid) of the black carpet beetle,[8] the camel's ability to smell water,[9,10] and the skunk's defensive scent (butyl mercaptan).[11] 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 (androgenic steroids),[12] chemicals indicative of death or fecal contamination (cadaverine, indole, putrescine, scatole),[13] and the odor of bacterial decomposition (amines, hydrogen sulfide, mercaptans, dimethyl sulfide).[13-19] This sensitivity is the result of countless generations of natural selection and expresses itself at a very early age. Experiments with newborns indicated that babies exposed to fruity or milky odors responded with facial relaxation, smile-like expressions, and sucking or licking movements. Decay or fishy odors, on the other hand, elicited expressions of aversion, often accompanied by spitting and salivation.[12] Odor sensitivity is also gender specific. Human females, for example, generally have a more acute sense of smell. This is particularly true for the volatile compounds found in sweat, urine, and other body secretions. The biological advantage of this sensitivity shows up in many reproductive functions such as menstrual cycle regulation, mate selection, and sexual arousal.[12, 20]

As we have shown, odor perception has a genetic component which determines species, gender, and individual sensitivity to a given volatile chemical. Odor perception also has a contextual aspect, particularly when evaluating a smell's pleasantness or unpleasantness. To illustrate the point we have selected a common example. Most people, especially if they are hungry, would appreciate the aroma of baking bread. But if the odor exists after we have polished off a big meal, it quickly loses its appeal and can become annoying or even objectionable if it is too intense or persists day after day. Odors can also be considered objectionable if they have been associated with a traumatic experience (accident, illness, death, fire, injury, etc.) or repetitive/unpleasant activities (cleaning a bathroom, taking out the garbage, changing a diaper, washing out the cat litter box, etc.). Unfortunately for the papermaker, many of the volatile compounds inadvertently produced in the kraft pulping process are also characteristic of body functions, sewage, and biological decay. This, combined with the low odor threshold (0.5-10 parts per billion, ppb, in air) of the major kraft odor components (dimethyl disulfide, dimethyl sulfide, hydrogen sulfide, methyl mercaptan, etc.), has led to difficult community relations.[12, 20-25]

1.3 DEFINITIONS

ADT – Air dry ton of pulp production. It assumes 10% moisture content.

ASB – Aerated stabilization basin. Used at the Camas Mill for biological wastewater treatment.

BLACK LIQUOR – Black liquor is the highly variable alkaline residue resulting from the kraft cooking of wood. It contains dissolved and degraded cellulose, hemicellulose, and lignin, as well as excess pulping chemicals and other materials. A typical analysis (black liquor solids 15-70%) yields the following: complex organics 8-46%, sodium carbonate 3-22%, sodium thiosulfate <1-6%, sodium sulfide <1-2%, sodium hydroxide <1-2%, sodium sulfate <1%, and water 30-85%.

BOD – Biochemical oxygen demand.

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 6-10 ppb. 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 1-10 ppb. 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 oceanic plankton.

EPA – U. S. Environmental Protection Agency.

GPM – Gallons per minute.

GREEN LIQUOR – A chemical solution in the kraft pulping process obtained by dissolving kraft smelt (the combustion residue from burning black liquor) in water. A typical analysis yields the following-- sodium carbonate 7-15%, sodium sulfide 2-6%, sodium hydroxide 1-4%, sodium sulfate <1-2%, and water 75-85%.

HIGH VOLUME LOW CONCENTRATION (HVLC) – A variable gas mixture containing air, water vapor, methanol, hydrogen sulfide, dimethyl sulfide, dimethyl disulfide, pinene, methyl mercaptan, and sodium hydroxide produced as a byproduct of pulp washing, knotters, screens, deckers, oxygen delignification, and storage tanks..

HYDROGEN SULFIDE (H_2S) – Hydrogen sulfide is a colorless, flammable gas with an offensive odor reminiscent of rotten eggs. The odor threshold is in the range of 0.5-10 parts per billion (ppb). The gas is heavier than air (Molecular weight = 34lb/lb Mol, Air = 29 lb/lb Mol) and slightly soluble in water (one gram will dissolve in 242 ml of water). 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.

KRAFT FOUL CONDENSATE STRIPPING SYSTEM – The foul condensate stripping system collects wastewater from the evaporators, concentrators, and miscellaneous streams from the kraft pulping process. These streams are steam stripped in a distillation tower. The stripper off-gases or SOGs are piped to either No. 5 Power Boiler or the No. 4 Lime Kiln for combustion. The clean condensate can then be used in mill processes requiring hot water.

KRAFT NONCONDENSIBLE GASES (NCGs) – Kraft noncondensible gas is the residual gas remaining after condensing digester or evaporator vent gases. This highly variable and potentially explosive mixture can be characterized by the following composite analysis: dimethyl sulfide <1-6%, dimethyl disulfide <1-6%, pinene <1-5%, methyl mercaptan <1-33%, ethanol <1-2%, propanol <1-1%, hydrogen sulfide <1-1%, methanol <1-1%, water vapor, air.

KRAFT SMELT – Kraft smelt is the molten ash that collects in the bottom of the recovery furnace. It flows into the dissolving tank where it mixes with weak wash or water to form green liquor. A typical analysis yields the following: sodium carbonate 53-75%, sodium sulfide 4-21%, sodium hydroxide 1-20%, sodium sulfate <1-10%, potassium carbonate 1-8%, sodium chloride <1-4%.

METHYL MERCAPTAN (CH_4S) – Methyl mercaptan is a colorless, flammable gas with a characteristic odor reminiscent of decayed cabbage. The odor threshold is in the range of 0.5-8 ppb. The gas is heavier than air (Molecular weight = 48 lb/lb Mol, Air = 29 lb/lb Mol) and slightly soluble in water (2.3 g/100 mls water). 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.

MGD – Million gallons per day.

MG/L – Milligrams per liter.

OSHA – The Occupational Safety and Health Administration. Part of the U.S. Department of Labor. The regulatory and enforcement agency for safety and health in most U.S. industrial sectors.

PSIG – Pounds per square inch, gauge.

PPM – Parts per million.

SOGs – Stripper off-gases. The gases produced by the kraft foul condensate steam stripper. The gases are burned in the No. 5 Power Boiler or the No. 4 Lime Kiln. They have the following approximate composition: methanol 40-45%, methyl mercaptan 1-4%, hydrogen sulfide <2%, dimethyl sulfide <1-2%, dimethyl disulfide <1%, turpene compounds <1%, and water 40-45%.

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

WASTEWATER TREATMENT PLANT – A facility containing a series of tanks, screens, filters, and other processes by which pollutants are removed from water.

WDOE – Washington Department of Ecology.

WEAK WASH – Weak wash is an aqueous solution resulting from the washing and dewatering of lime mud. It has the following approximate composition: sodium hydroxide <1-2%, sodium sulfide <1%, sodium carbonate <1%, and sodium sulfate <1%. Weak wash is commonly added to the smelt dissolving tank.

WHITE LIQUOR – A corrosive chemical solution used in the kraft process to cook wood in the digester. A typical analysis yields the following: sodium hydroxide 6-11%, sodium sulfide 2-6%, sodium carbonate 1-3%, sodium sulfate <1-2%, and water 9-78%.

2.0SUMMARY AND CONCLUSIONS

- Total reduced sulfur gas (TRS) emissions from all mill sources have been reduced by about 90% since 2001 and 99% since 1970.

- The kraft condensate steam stripper and Best Management Practices (BMP) have reduced wastewater treatment inlet total reduced sulfur (TRS) load by 98% from an estimated 426 tons/year in 1995 to about 7.5 tons/yr in 2007.

- Citizen odor complaints have declined by 98% since 2001.

- The current rate of citizen complaints attributed to mill odor has dropped from 108 in 2001 to 2 in 2007.

- Noncondensible gas (NCG) venting has been reduced by 88% since 2001 and 98% since 1998.

- Based on what is known about the mechanisms of toxicity of reduced sulfur compounds, it appears highly unlikely that significant adverse health effects would result from exposures to current ambient TRS levels within the Camas Mill or the surrounding community.

3.0 TRS INVENTORY

3.1 KRAFT MILL SOURCE DESCRIPTION

The United States consumes more paper and paperboard than any other country in the world and most of that is produced by the sulfate or kraft process. This process can produce a strong pulp from almost any wood species. That, coupled with the favorable economics of chemical recovery (which incidentally reduces water pollution by 90+%), have made it the predominant pulping technique.[26] In the kraft process, wood is cooked under pressure in a solution consisting of sodium hydroxide, sodium sulfide, and sodium carbonate. An undesirable consequence of the use of alkaline sodium sulfide is the demethylation of cellulose and the subsequent production of reduced sulfur gases.[26-29] The most prevalent compounds are methyl mercaptan (MeSH), dimethyl sulfide (DMS), dimethyl disulfide (DMDS), hydrogen sulfide (H_2S), and a variety of lesser volatile organic sulfides. Collectively, these gases are referred to as total reduced sulfur (TRS) gas and are the major objectionable components of kraft mill odor. TRS can be detected by the human nose in concentrations at or below one part per billion (ppb) in air.[2, 20-22]

Kraft mill odor is formed in the digester during cooking and is released when spent pulping liquor is evaporated and burned for both chemical and energy recovery. Historically, the major odor sources (in descending order of importance) were the recovery furnace (where the concentrated black liquor is burned), the liquor evaporators (where water is removed from the black liquor so it will burn), the digester, the brown stock washers, the smelt dissolver, the lime kiln, and various miscellaneous sources. This is illustrated in Table 3 which lists the magnitude of TRS emissions by process unit. At the present time the Camas Mill has three continuous digesters, one for hardwood and softwood chips and two for sawdust. All of them use the kraft process. Weak black liquor is washed out of the brown stock and is thickened to about 50% solids in one of two multiple effect evaporator sets. It is then processed in a concentrator to raise the solids to about 70%. Strong, odorous, noncondensible gases (NCGs) from the digesters, evaporators, and concentrators are captured and combusted in the No. 5 Power Boiler or the No. 4 Lime Kiln.[2]

The recovery furnace burns the concentrated black liquor and is of contemporary low odor design with noncontact liquor concentration, electrostatic precipitation, and cross flow exhaust gas scrubbing. After combustion, the resulting inorganic smelt is dissolved in weak wash to form green liquor. The green liquor is then treated with lime to form white liquor which is returned to the digester for cooking the next batch of wood residue (chips or sawdust).[2]

3.2 HIGH VOLUME LOW CONCENTRATION (HVLC) COLLECTION SYSTEM

The HVLC collection system consists of a main collection conduit and feeder lines from the digesters, washers, screenrooms, oxygen delignification systems, and kraft recovery areas. The collection header consists of a HVLC cooler, mist eliminator, fan, and steam coil air heater. From there the HVLC gas is transported to the No. 4 Recovery Furnace for combustion. The fan maintains a negative draft in the main conduit and all feeder lines to ensure collection.[6] Phase I of the HVLC collection system was completed in 2005. Phase II, the final phase, was completed in 2006. With the completion of these two phases, the mill has reduced organics and TRS emissions from these sources by at least 97%.

3.3 NONCONDENSIBLE GAS (NCG) SYSTEM

3.3.1. Collection

The NCG collection system consists of a main collection conduit and seven feeder lines. The main collection header begins at the southwest side of the kraft mill next to the secondary condenser and ends at the block valves at the east end of the lime kiln. At that point, the line branches with arms extending to the No. 5 Power Boiler and the No. 4 Lime Kiln. A negative draft is maintained in the main collection conduit to ensure collection. The beginning of the collection pipe has a large opening with an adjustable orifice to control dilution air entering the main header. The dilution air keeps the concentration of NCGs well below the lower explosive limit. There are also several other points in the system where dilution air enters the NCG collection system. Generally, these additional dilution sources are located at points where NCGs enter the system and are insignificant compared to the main source of dilution air at the beginning of the pipe.[6]

Along the header, there are several condensate drains. The drains have a seal leg to prevent the negative draft from interfering with the flow of the condensate. Water is added at each seal leg to keep it flooded. Water seals are also present in various locations in the system to prevent direct discharge of the gas to the atmosphere. The water seal allows for minor changes of pressure within the collection system. The seals are broken if the collection system experiences a positive or negative pressure change that exceeds 6 inches water column.[6]

NCGs from the steam stripper feed tank and black liquor fuel tank are cooled before entering the collection header. Cooling makes the gases less volatile, decreasing the risk of system over pressurization and lessening the total NCG emission should venting occur. Condensate generated during the cooling process is directed to the intake of the steam stripper feed pumps.[6]

3.3.2 NCG Scrubber

The NCG pre-conditioning scrubber was installed in September 2003 to remove a majority of the TRS gas from the kraft NCG stream prior to combustion in the No. 5 Power Boiler or the No. 4 Lime Kiln. The purpose was to reduce ambient odor if atmospheric venting should occur, reduce stack opacity, and improve lime kiln operating reliability when burning NCGs.[3]

The complete system consists of a horizontal scrubber body, air atomizing nozzles, a mist eliminator, a scrubbing liquid supply system, a liquid drain system, and flow control system. The NCG stream is saturated with a caustic solution sprayed into the scrubber by three atomizing nozzles where the fine mist (60 μm aerodynamic diameter) provides excellent surface area for gas/liquid contact. After the scrubbing section, the gas passes through a chevron style mist eliminator. Liquid droplets, including the reaction products from scrubbing, are removed from the gas stream resulting in a 70 – 80 % reduction in TRS gases. The scrubbed gas then passes through a fan and is combusted in the No. 4 Lime Kiln or the No. 5 Power Boiler.[3]

3.3.3 NCG Reliability

In recent years, the mill has greatly improved the effectiveness of NCG destruction. This has been accomplished by providing two combustion units, installing a switching system to automatically move the NCGs from one combustion unit to another, improving operator training, and increasing the breadth and frequency of system inspections. In addition, if both NCG combustion units are unavailable, procedures are in place to immediately shut down the NCG sources. These improvements have reduced NCG venting by 98% since 1998. Our progress since 2001 is illustrated in Figure 2.

3.4 STEAM STRIPPER

The kraft foul condensate steam stripping system collects wastewater from the evaporators, concentrators, and miscellaneous streams from the kraft pulping process. These streams are steam stripped in a distillation tower. The stripper off- gases (SOGs) are piped to either the No. 5 Power Boiler or the No. 4 Lime Kiln for combustion.[2] The steam stripper destroys TRS compounds that would be emitted by the wastewater treatment system if they were not captured in the mill. Following stripping, the hot clean condensate is used to wash the pulp.

3.5 WASTEWATER TREATMENT

Pulp and paper manufacturing processes utilize large volumes of water to digest, wash, bleach, and clean pulp and distribute it evenly on the paper machine wire. Most of this water is recycled, but residual streams remain which must be treated to preserve the multiple uses of our rivers, lakes, and streams. Wastewater treatment was pioneered at the Camas Mill when in 1960 one of the first treatment basins in the Northwest was installed. Since that time, the system has received regular upgrades and expansions including the installation of primary treatment and sludge dewatering in 1967, secondary treatment Phase I in 1975, secondary treatment Phase II in 1977, primary sludge landfill cells in 1987, 1988 and 1992, and secondary sludge removal in 1989, 1990, 1997, 1999, 2001, and 2005. The company has also spent a great deal of time and money over the years investigating new treatment methods (aeration alternatives, fixed film reactors, hydraulic optimization, system seeding, nutrients, etc.) and surveying the quality of the Columbia River to ensure that the waste treatment systems were operating properly.[5]

In 2003, the mill implemented a best management practices (BMP) plan. The BMP's primary objective is to prevent leaks and spills of spent pulping liquors, soaps, and turpentine. As part of the BMP plan, the mill implemented early detection systems to limit the magnitude of a spill or leak, conducts process inspection, and has planned system maintenance. The mill also optimizes aeration, nutrient addition, and flow control measures. Since the implementation of the BMP, the mill's wastewater treatment facility has seen a 77% reduction TRS loads. Figure 3 shows the decline in TRS going to the wastewater treatment plant since 2003.

3.6 COMMUNITY OUTREACH

3.6.1 Community Advisory Panel

A Community Advisory Panel (CAP) was created by the Camas Mill in 2001. The panel members are representative of the community's diverse residents and interests. In this advisory capacity, the CAP has discussed and addressed such subjects as community involvement, community support, mill water use, permit renewals, mill environmental improvements, and the community–wide warning system. Mill management values the CAP's input, and has taken action on many of the group's recommendations, particularly with respect to the mill's contact and interaction with area residents.[7]

3.6.2 Community Information

The community warning notification system was updated in 2003 as part of the mill's continuing commitment to safety and community outreach. The mill has two electronic sirens, one installed at each end of the mill's property that can broadcast a warning 360° within one mile of the mill. These sirens will be used to alert the community to an emergency that may require people to evacuate or stay inside until an all-clear is given. Examples of such emergencies are earthquakes, severe weather, train derailments, hazardous materials spills, and volcano eruptions. Georgia-Pacific worked closely with the Camas police and fire departments to create this community-wide system.[7] The Camas Mill also created a web site to provide the public with information about environmental performance, emergency warning, kraft odor, NCGs, and weather conditions. It can be accessed at www.gpcamas.com.

4.0COMMUNITY IMPACT ASSESSMENT

4.1 CITIZEN ODOR COMPLAINTS

As other sources of air pollution have come under increasing control, environmental professionals have faced a new challenge. In many air pollution control districts, concerns about disagreeable odors dominate the complaint log. Based on a U.S. Environmental Protection Agency national study, about 29 odor complaints can be expected each year for every 100,000 population. A lightly industrialized city like San Francisco is typical of the national average. Odor complaints in large cities run the gamut of sources from commercial bakeries, coffee roasters, dry cleaners, restaurants (especially barbecue), and food preparation plants to uncollected garbage, clogged sewers, sanitary landfills, and wastewater treatment facilities. As the level of industrialization increases, the number of odor complaints rise accordingly. Los Angeles, for example, reports 54 odor complaints/100,000 population/year. The excess over a city like San Francisco is attributed to oil production, oil refining, aerospace, and chemical manufacturing. The relative effect of a pulp mill can be gauged by looking again at California. Humboldt County in the northern portion of the state did, until recently, support two kraft pulp mills. In the 1970s, Humboldt County recorded 748 odor complaints/100,000 population/ year. Most of the complaints were directed at the pulp mills.[20] During this period of time, neither mill had wastewater treatment or low odor recovery technology making them similar to the Camas Mill in 1970 (see the emissions inventory in Table 2). In 2007 the Camas Mill had 0.5 odor complaints/100,000 people (based on Clark County's population of 413,000 people in 2006). As a combined result of the odor reducing projects the mill has seen a dramatic reduction of odor complaints, 98% since 2001. While we do not have access to Ecology's citizen complaint logs, this would appear to be lower than the expected rate for a large urban area and much less than the experience in other pulp mill communities. Figure 1 illustrates the Camas Mill's odor complaint decline since 2001.

4.2 HEALTH EFFECTS FROM ODOROUS COMPOUNDS

Citizens who call the mill about odor often have a number of questions to ask concerning the source, planned duration, and components of the odor. A frequently asked question is "What effect does this odor have on my health?" The health consequences of exposure to a kraft odor components such as hydrogen sulfide are well documented. Methyl mercaptan has also been examined, but the body of knowledge concerning dimethyl sulfide and dimethyl disulfide is less robust. Table 1 provides a summary of the physiological effects of human exposure to these compounds. The immediate conclusion drawn from this table is that recognizable acute health effects begin to occur many times above the odor detection threshold. Mill TRS emission points typically have TRS concentrations at the source in the <1-8 ppm range (examples include the recovery furnace 1-2 ppm, lime kiln 3-8 ppm, wastewater treatment <1-3 ppm, etc.). This suggests that during normal operation, mill emissions are not likely to elicit acute health effects.[11, 12, 30-42]

Also of interest to the citizen, is the effect of long term exposures to lower levels of reduced sulfur gases. Very little specific research has been conducted in this area, but it is possible to form a conclusion from a general understanding of human physiology. We know that the components of TRS are naturally occurring, rapidly metabolized, easily excreted, and have not been shown to be cumulative toxicants. Epidemiological studies have repeatedly failed to demonstrate that significant health effects or an increased risk of cancer occurs in kraft pulp mill workers or in residents of communities near pulp mills or natural gas refineries (also a source of TRS). In fact, a recent John Hopkins study found pulp and paper mill workers to be substantially healthier than the general population. Based on what is known about the mechanisms of toxicity of reduced sulfur compounds, it appears highly unlikely that significant adverse health effects would result from exposures to current ambient TRS levels within the Camas Mill or the surrounding community.[12, 40]

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6.0 APPENDIX

FIGURES

TABLES

FIGURE 1. CAMAS MILL ODOR COMPLAINTS, 2001–2008

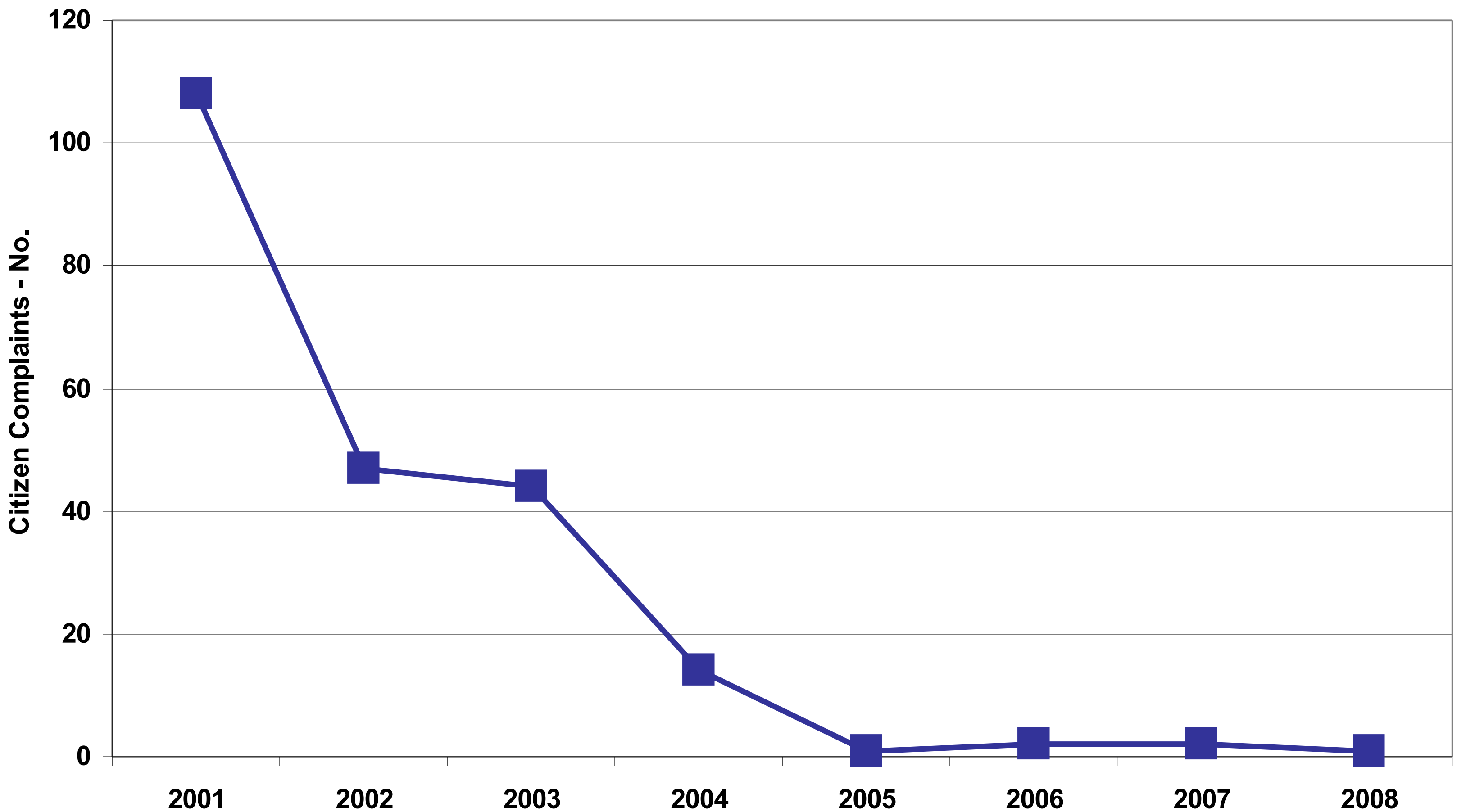

FIGURE 2. CAMAS MILL NON-CONDENSIBLE GAS (NCG) VENTING, 2001-2008

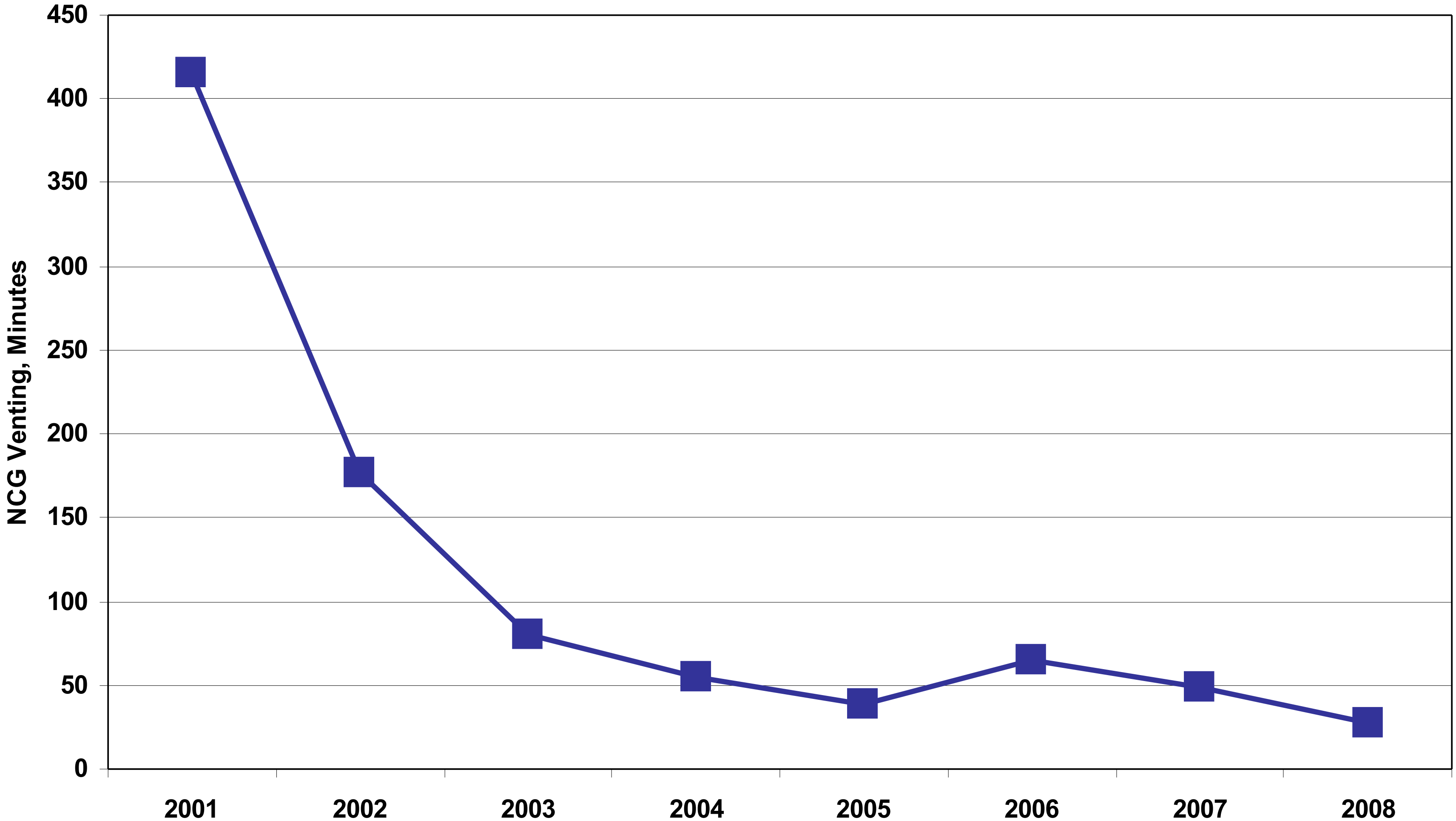

FIGURE 3. CAMAS MILL TOTAL REDUCED SULFUR GAS INVENTORY

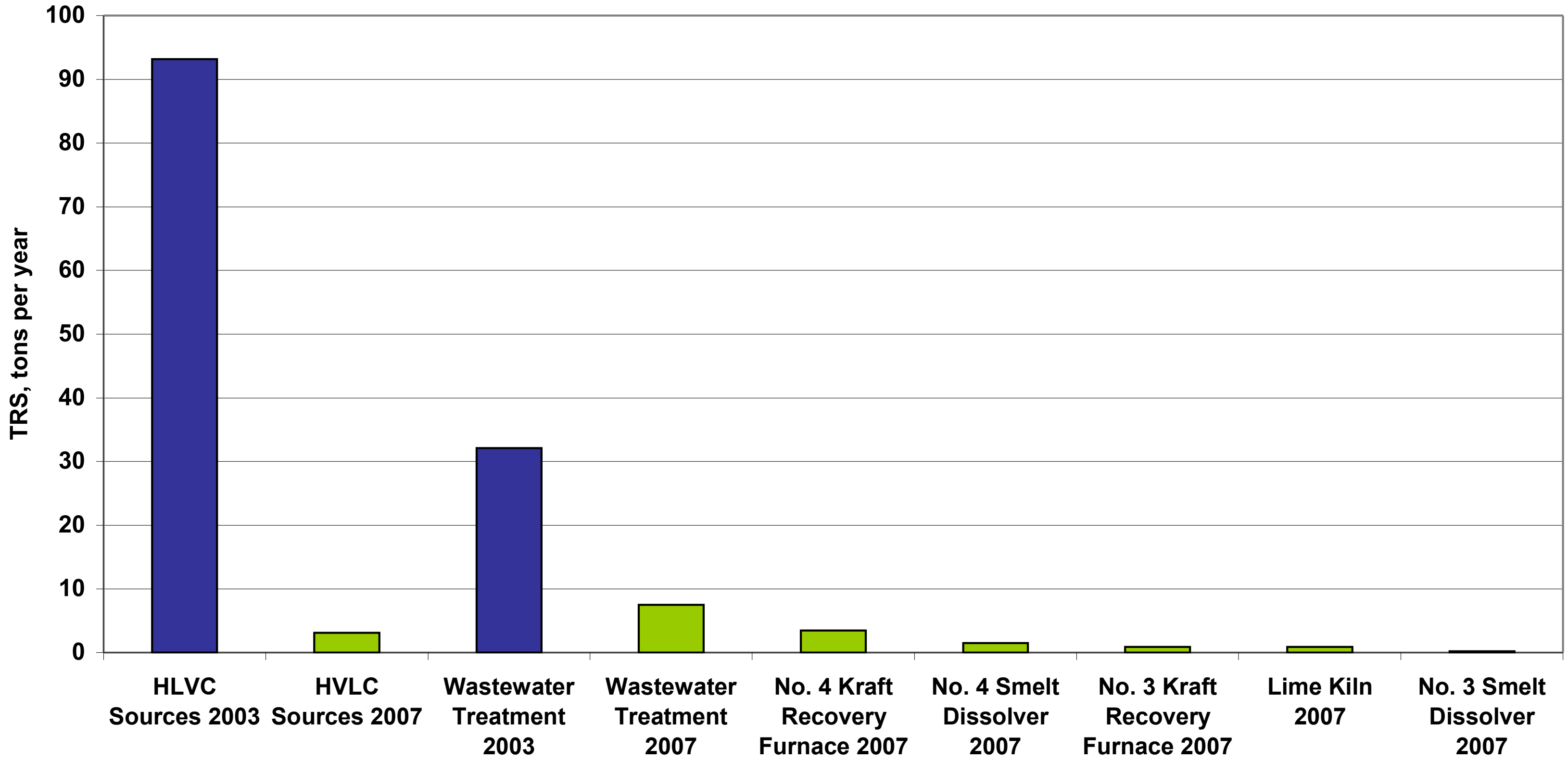

TABLE 1. POTENTIAL PHYSIOLOGIC EFFECTS FOR HUMAN EXPOSURE TO TOTAL REDUCED SULFUR GASES

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 <u>less</u> 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.

TABLE 2. A TOTAL REDUCED SULFUR GAS EMISSION INVENTORY FOR 1970–2007

Source	TRS Emission Inventory - Tons/Year				
	1970[a]	1980[a]	1999[a]	2000[a]	2007[a]
Batch Digester Air Evacuation	3.4	3.4	3.4	3.7	1.0
Black Liquor Storage Tank Vents	4.3	4.3	3.0	3.0	0.7
Brown Stock Washers: North	--	--	4.0	4.0	0.0
Brown Stock Washers: South	22.2	12.8	2.3	2.3	0.0
Contaminated Condensate Tank Vent	0.5	0.5	0.5	0.5	0.0
NCGs and Miscellaneous Vents	260.7	8.2	1.7	2.7	2.8
Nos. 1 – 3 Lime Kilns	94.4	--	--	--	--
No. 4 Lime Kiln	--	1.5	1.3	1.0	0.9
No. 5 Power Boiler	--	--	--	--	0.3
Nos. 1 and 2 Recovery Furnaces	842.0	--	--	--	--
No. 3 Recovery Furnace	256.0	5.0	2.0	2.2	0.9
No. 4 Recovery Furnace	--	19.0	3.1	3.8	3.5
Nos. 1 and 2 Smelt Dissolvers	1.3	--	--	--	--
No. 3 Smelt Dissolver	1.4	1.4	0.9	0.8	0.2
No. 4 Smelt Dissolver	--	2.0	1.2	1.1	1.5
Wastewater Treatment	--	312.0[b]	301.0[b]	106.7	7.5
	1486.2	370.1	324.4	131.8	19.3

[a] Monthly and annual air emission reports submitted to the Washington Department of Ecology.

[b] Emission data from Reference 2 adjusted for liquor spills (ASB Inlet BOD 1980: 113,000 lbs/day, 1995: 131,000 lbs/day, 1999: 109,000 lbs/day). Primary wastewater treatment installed in 1967, secondary wastewater treatment installed in 1975-1977.

TABLE 3. TYPICAL TOTAL REDUCED SULFUR GAS EMISSION RATES FROM KRAFT PULP MILL SOURCES

Source	Emission Rate, lbs/ADT[a]				
	H_2S	CH_4S	DMS	DMDS	TRS[b]
Digester, Batch, Blow Gases	0-0.3	0-3.9	0.2-12.8	0.3-11.7	0.3-18.5
Digester, Batch, Relief Gases	0-0.1	0-0.9	0.2-3.1	0.3-5.9	0.3-6.6
Digester, Continuous	0-0.2	1.5-3.0	0.2-1.9	0.3-2.3	1.4-5.0
Brown Stock Washer, Hood Vent	0-0.02	0.2-3.0	0.2-1.9	0.3-2.3	0.4-4.8
Brown Stock Washer, Seal Tank	0-0.02	0-0.03	0-0.2	0-0.2	0-0.2
Evaporator, Hot Well	0.1-3.2	0.2-2.4	0.2-3.9	0.3-5.9	0.5-11.2
Black Liquor Oxidation, Tower Exhaust	0-0.02	0-0.3	0-1.5	0-1.8	0-2.3
Recovery Furnace, With Direct Contact Evaporation	0-53	0-6	0-3.9	0-1.8	0-60.7
Recovery Furnace, Without Direct Contact Evaporation	0-2	0-0.03	0-0.04	0-0.06	0-2.1
Smelt Dissolver, Tank Vent	0-2	0-2.4	0-0.2	0-1.8	0-5.1
Lime Kiln, Exhaust Stack	0-1.1	0-0.6	0-0.4	0-0.3	0-1.9
Lime Slaker Vent	0-0.02	0-0.03	0-0.04	0-0.06	0-0.1

[a] Emission in pounds per air dry ton of pulp. Source: Reference 29.

[b] Total reduced sulfur gas expressed as hydrogen sulfide.