U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
CENTER FOR DISEASE CONTROL
NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH
CINCINNATI, OHIO 45226

HEALTH HAZARD EVALUATION DETERMINATION
REPORT HE 79-79-611

GREAT NORTHERN PAPER COMPANY
MILLINOCKET, MAINE

August 1979

I. TOXICITY DETERMINATION

An environmental and medical investigation was conducted by The National Institute for Occupational Safety and Health (NIOSH) May 8 and 9, 1979, at the Pollution Plant of Great Northern Paper Company to determine if sludge and/or water treatment operations were exposing workers to significant concentrations of toxic vapors and gases. From this investigation it was determined that workers in the Pollution Plant were not being over exposed to toxic airborne emissions including sulfur dioxide (SO_2) and hydrogen sulfide (H_2S). Sample results as indicated in Tables I and II are all well within the evaluation criteria. However, it should be mentioned that the results of this investigation are based only on data collected during (regular operations) May 8 and 9, 1979, and the potential for increased exposure problems may exist.

Medical interviews with ten employees revealed that 5 had a history of a popular puritic rash which may have been occupationally related. Five people had experienced occasional headaches or nausea probably secondary to excessive H_2S exposure, and 2 people had suffered near syncopal episodes after probable H_2S overexposure.

Recommendations presented in Section V of this report are offered for the control of potential or increased exposures that may result from production processing and waste treatment operations.

II. DISTRIBUTION AND AVAILABILITY

Copies of this Determination Report are currently available upon request from NIOSH, Division of Technical Services, Information Resources and Dissemination Section, 4676 Columbia Parkway, Cincinnati, Ohio 45226. After 90 days the report will be available through the National Technical Information Service (NTIS), Springfield, Virginia. Information regarding its availability through NTIS can be obtained from the NIOSH Publications Office at the Cincinnati address.

Copies of this report have been sent to:

a) Safety Supervisor
b) Mill Manager
c) President UPIU, Local 12
d) L.V. Treasury 471
e) President, Local 658 C&J
f) U.S. Department of Labor (OSHA) - Region I
g) NIOSH - Region I

III. INTRODUCTION

Section 20(a)(6) of the Occupational Safety and Health Act of 1970, 29 U.S.C. 669(a)(6), authorizes the Secretary of Health, Education and Welare, following a written request by any employer or authorized representative of employees, to determine whether any substance normally found in the place of employment has potentially toxic effects in such concentrations as used or found.

The National Institute for Occupational Safety and Health received such a request from an authorized representative of the United Paper Workers International Union, Local 12, on April 5, 1979. The request alleged that employees working at the Pollution Plant were being exposed to substances that were causing sore throats, bronchitis, and headaches. Two of the substances identified by the requestor as being present at the site were hydrogen sulfide and sulfur dioxide.

During June 1979, an Interim Report was forwarded to GNP as well as, to union members which included preliminary results of the investigation, future action to be taken by (NIOSH) and recommendations.

IV. HEALTH HAZARD EVALUATION

A. Plant Description

The Great Northern Paper Company (GNP), located in Millinocket, Maine, produces over 820,000 tons of paper per year. Their paper products include printing papers, business forms, workbooks, magazines, mail-order catalogs, paperback books and telephone directories. These products are produced in two mills (Millinocket East and Millinocket) which employs over 4000 persons. Processing operations at these Millinocket mills begin in a Wood Yard where both tree length logs and pulpwood are cut into four foot bolts. The bolts are conveyed into four revolving drums for bark removal. After debarking, the logs are ground into pulp or conveyed to a chipper for sulfite pulp production and/or refined groundwood. During the sulfide pulp operations gases collected from burned molten sulfur are added to magnesium-base liquids to form bisulfite acid (liquor) which is used for cooking wood chips. The chips are cooked under pressure in digesters and then pumped through a series of

screens to remove oversized fibers. The resulting pulp is sent through washers to remove excess acids then rescreened, cleaned, thickened and stored in tanks until further use. Processed pulp and refined groundwood products are conveyed to a Paper Room where light weight printing grade papers are manufactured. Rolls to be coated are moved to a Coating Mill where a thin opaque film made of kaolin clay and starch is applied. Final preparation takes place in the Finishing Room. In this area the paper rolls are inspected, weighed, wrapped and loaded for shipment.

Of particular importance at the Mill site was the Secondary Treatment or Pollution Plant which is located Southeast of the Millinocket operations. Materials in slurry form are received at the treatment plant in a five million gallon clarifier. The clarifier, with a skimmer and rakecom system processes 30 million gallons of sludge per day. Solids removed from the bottom of the clarifier are conveyed to coil filters where they form sheets. The sludge sheets are then dissevered, conveyed to a press (1800 psi) to remove excess liquids, conveyed to the outside, loaded onto trucks and then hauled to a landfill. Liquids from the press as well as those from the clarifier are piped to a 10 acre lagoon site where ammonia is added for pH control. The liquids settle in the lagoon for 24 hours and are then treated for four to five days in an aeration pond. From the aeration pond all treated waters are pumped into the Penobscot River.

B. Evaluation Method

1. Environmental

Both breathing zone (BZ) and general area (GA) air samples were collected to determine sulfur dioxide and organic vapor levels. These samples were obtained for analyses by using special impregnated charcoal tubes connected, via tygon tubing to sampling pumps calibrated at 200 cubic centimeters per minute (cc/m). MSA personal sampling pumps operating at 1.0 and 2.0 liters per minute (ℓ/m) were used to collect the more polarorganic materials as well as the sulfuric acid mists. The polar compounds such as amines were collected on large silica gel tubes while the acid mists (H_2SO_4) were collected on AA millipore filters. In addition, detector tube measurements were obtained as a quick screening method for chlorine, oxides of nitrogen, sulfur dioxide, ammonia, and hydrogen sulfide. All long term samples along with bulk materials from the sludge press were submitted to the laboratory for qualitative analysis.

2. Medical

NIOSH medical personnel interviewed 7 men presently employed in the Secondary Treatment plant and 3 former drivers who discontinued working at the treatment plant because of various medical reasons.

C. Evaluation Criteria

1. Evaluation Toxicology

Sulfur dioxide - A colorless gas at ordinary temperatures which is a mucous membrane irritant. Exposure to high levels is intolerable and causes chemical bronchopneumonia or death by asphyxiation. Levels low enough so that working is tolerable may still result in eye discomfort, sneezing, coughing, alteration of taste and smell, difficulty in breathing, and fatigue. Research shows that 80% of exposed persons become acclimatized to such levels. Chronic exposure has been associated with impaired pulmonary function and respiratory diseases.[1,2]

Toluene - Prolonged excessive exposure to this agent may acutely cause headache, weakness, fatigue, unconsiousness, loss of coordination, nausea, vomiting anorexia, acute dermatitis and irritation of skin and mucous membranes.

Terpenes - High vapor concentrations are irritating to the eyes, nose, and bronchi. Turpentine vapor in acute concentrations may cause central nervous system depression. Symptoms include headache, anorexia, anxiety, excitement, mental confusion, and tinnitus. Turpentine vapor also produces kidney and bladder damage. Chronic nephritis with albuminuria and hematuria has been reported as a result of repeated exposures to high concentrations. Predisposition to pneumonia may also occur from such exposures. Recovery usually takes from a few days to a few weeks. Several animal experiments of chronic low level exposure have produced no ill effects to the central nervous system, kidneys, bladder, or blood.[4]

Hydrogen Sulfide - H_2S is detectable as low as 0.025 ppm and is offensive and moderately intense at 3-5 ppm. Concentrations of 70-100 ppm may cause irritation of the mucous membranes of the eyes and respiratory tract. Exposures from 250-600 ppm may cause headache, dizziness, excitement, nausea, dryness and sensation of pain in the nose, throat and chest and coughing. When the amount of hydrogen sulfide absorbed in the blood stream exceeds that which is oxidized, systemic poisoning results, with a general action on the nervous system, hypernea occurs, and respiratory paralysis may follow. Unless fresh air is made available within a few minutes, death occurs.[5]

2. Environmental Criteria

Airborne exposure limits for the protection of the health of workers have been recommended or promulgated by several sources. These limits are established at levels designed to protect workers occupationally exposed to a substance during an 8-hour day, 40-hours per week based over a normal working lifetime. For this investigation, the criteria used to assess the degree of health hazards to workers were selected

from three sources: 1) NIOSH: Criteria for a Recommended Standard ... Occupational Exposure to various substances. 2) Threshold Limit Values (TLV): Guidelines for Airborne Exposures as Recommended by the American Conference of Governmental Industrial Hygienists (ACGIH) for 1977. 3) OSHA Standards: The air contaminant standards by the U.S. Department of Labor - Occupational Safety and Health Administration as found in the Federal Register - 29 CFR 1910.1000 (Tables Z-1, Z-2).

Whenever possible, the NIOSH recommended standard will be the environmental criteria applied since it represents the most recent knowledge concerning a substance. If one does not exist, the next most stringent recommended level or legal standard will be used.

Substance	NIOSH	ACGIH	OSHA
Sulfur Dioxide	0.5 ppm	5 ppm	5 ppm
Toluene	100 ppm	100 ppm	200 ppm
Turpentine-Terpenes (organics)	-	100 ppm	100 ppm
Hydrogen Sulfide	10(c) ppm	10 ppm	20(c)

*Concentrations, in parts of substance per million parts of air (ppm) are based on an 8-hour Time Weighted Average exposure (TWA). Values designated (c) represent concentrations which should not be exceeded as commonly measured in a 15-minute period.

D. Evaluation Results and Discussion

1. Environmental

The results of the long term air sampling for sulfur dioxide, sulfuric acid mists, toluene and other organic gas emissions are presented in Table I. All levels of airborne gases and vapors were well within the current recommended and legal (OSHA) standards. Only samples CT-1,2,4, and 5 had any detectable concentrations. These samples had a naptha pattern similar to kerosene which ranged (in concentration) from 4.14 ppm to 8.59 ppm. CT-2 and 5 had an additional component identified as toluene which ranged from 0.03 ppm to 0.10 ppm. The bulk sludge and water samples were analyzed for volatiles by heating portions of each sealed vial in a water bath at 65°C. Headspace aliquots were obtained by gas tight syringes and injected into a GC/mass spectrometer (MS) for analysis. The only component found were 2-3 terpens (MW136, C10 H16) such as terpinenes or pinenes (derivaties of pine resins). No quantifiable amounts of sulfur dioxide, sulfuric acid, carbon monoxide-dioxide, chlorine, or oxides of nitrogen were detected in any of the air samples submitted for analysis.

2. Medical

Results from the findings of the ten persons interviewed indicated that 3 persons had probable and 2 had possible work related skin disorders. The majority of those affected described their lesions which were most generally found on the scalp, as small puritic papules. Improvement of these lesions were noted during the monthly shift change when the workers

were scheduled for a 5 day "weekend". There were no typical lesions present at the time of the investigation, however, 1 employee was under observation by a dermatologist for diagnosis, should the lesions reappear. Five employees reported experiencing moderately severe headaches which appeared to be related to the periodic exacerbations of odor, (probably H_2S since this odor was reported most frequently). Occasional nausea was also reported when "odor" levels were readily noted. Two other workers reported symptoms of excessive cough and phlem productions which could possibly have been aggravated by work exposure(s). Frequent sore throats that would markedly improve when away from work were described by 3 workers. Two employees reported suffering near syncopal episodes while working alone during periods of potentially high exposure to H_2S. These episodes could have resulted in serious accidents had the employees not managed to escape from the contaminated areas. One employee suffered a severe urticarial reaction while at work which was felt to be caused by some substance at the work site so he transferred to another area of the paper plant.

V. CONCLUSIONS AND RECOMMENDATIONS

A. Environmental

Although levels of toxic exposures found at the Secondary Treatment Plant were within the current recommended (NIOSH) and legal (OSHA) standards, the potential for increased concentrations does exist. One such area is the sludge loading space, where moist sludge which gives off heat while accumulating can ferment and thus emit potentially toxic gases and/or vapors (H_2S, SO_2, toluene, etc). In addition, paper products run at the primary plant do have different exposure potentials which may present increased risk problems. Variables influencing these risks include wind direction, temperature, humidity and product production.

B. Medical

Irritative symptoms such as sore throats have been experienced by some of the waste treatment plant employees. Additionally, 2 employees who reported near syncopal episodes were performing duties which exposed them to increased H_2S levels. The frequent headaches are likely secondary to intermittent excessive H_2S exposure. The bronchitic symptoms and sore throats are possibly exacerbated by H_2S as well as by chemical contaminants such as SO_2 which are reported to be occasionally carried by the wind to the waste treatment facility from the main plant. The skin rashes are potentially work related although none of the known chemical exposures are reported to cause a popular rash. The majority of employees agreed that fewer symptoms were being experienced at the time of the NIOSH visit and they felt this decrease in symptoms was due to the newly enacted practice of adding more lime to the wastewater prior to clarifier entry. The increased alkalinity appears to decrease the formation of hydrogen sulfide (H_2S).

C. Recommendations

1. The application of increased lime materials for purification purposes should be continued since this technique appears to decrease H_2S formation.

2. Moisture and heat given off while the sludge accumulates causes fermentation to take place thus releasing toxic gases and vapors. Therefore, the pressed sludge materials should be removed from the plant area every two to three days rather than being allowed to accumulate.

3. An H_2S meter along with an audible alarm system should be installed in the pressed sludge piling area. A probe from this meter should be located near the western wall along-side the sludge pile and an alarm should be set (when 10 ppm is detected) to sound inside the control room as well as the outside loading area. The meter should be observed regularly and calibrated at least monthly.

4. Personal emergency escape units should be provided to the drivers and other heavy equipment operators who load or unload sludge materials. In addition operators inside the plant should be equipped with personal protective devices to be donned in emergency situations. Training in proper use and maintenance of these units should be provided to each Pollution Plant employee.

5. The Pollution Plant's H_2S emergency procedure memo dated May 1978, should be updated to include donning of respirators when 10 ppm H_2S levels are indicated by the H_2S meter and/or alarm.

6. Paper products being processed at the primary plant should be correlated with "worst conditions" situations found at the Pollution Plant in effort to determine if particular paper and pulping operations are responsible for increased gas and/or vapor exposure problems. With such data a written safety action plan could be incorporated into the employee's work schedule to help reduce the potential for unhealthy work conditions.

VI. REFERENCES

1. U.S. Department of Health, Education, and Welfare, PHS, NIOSH: Occupational Diseases - A Guide to Their Recognition, U.S. Government Printing Office, June, 1977.

2. Criteria for a Recommended Standard - Occupational Exposure to Sulfur Dioxide. HEW Publication No. (NIOSH) 74-111. U.S. Department of HEW, CDC, NIOSH, 1974.

3. IBID - 1.

4. IBID - 1.

5. Criteria for a Recommended Standard, Occupational Exposure to Hydrogen Sulfide, U.S. Department of HEW, PHS, CDC, NIOSH, May, 1977.

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TABLE

Results of Air Samples Collected During the Second and Third Shifts
Great Northern Paper Co.
Millinocket, Maine

May 8, 1979

	Field No.	Temp & Humidity	Volume	Sample Type	Location	Concentration in parts of gas per million parts of air (ppm)	
Sulfur Dioxide	SO_2 #1	73° F RH 40-45%	61.4(ℓ)	Personal	Clairifier Operator - take samples	Below limit of detection	
	SO_2 #2	" "	62.2(ℓ)	Personal	Millwright (maintenance)	" "	
	SO_2 #3	" "	61.5(ℓ)	Personal	Operated front end loader	" "	
	SO_2 #4	" "	68(ℓ)	G. Area	Conveyor (above press)	" "	
	SO_2 #5	" "	64.2(ℓ)	G. Area	" " "	" "	
Sulfuric Acid Mists	AM #1	" "	300(ℓ)	G. Area	Conveyor (above press)	Below limit of detection	
	AM #2	75° F RH 49-52%	335(ℓ)	G. Area	Under rotary drier	" "	
	AM #3	" "	Blank	-	-	" "	
Organic Compounds (Amines) including Hydrogen Sulfide	SG #1	" "	310(ℓ)	G. Area	Conveyor above hopper/press	Non detectable levels	
	SG #2	" "	402(ℓ)	G. Area	Conveyor above press	" "	
	SG #3	" "	400(ℓ)	G. Area	Operator Control room	" "	
						Toluene	Total Hydrocarbons
Organic Compounds Toluene and Total Hydrocarbons	CT #1	76° F RH 50-55%	58.2ℓ	Personal	Operator (takes samples)	<.08 ppm	4.1 ppm
	CT #2	" "	67.3ℓ	Personal	Millwright (maintenance)	.10 ppm	11.0 ppm
	CT #3	" "	61.1ℓ	Personal	Operated front end loader	<.08 ppm	<0.2 ppm
	CT #4	" "		Damaged		NA	8.6 ppm
	CT #5	77° F RH 45-50%	402.(ℓ)	G. Area	1st floor under rotary drier	.03 ppm	5.71 ppm
	CT #6	" "					
	CT #7			G. Area		NA	

TA II

Results of Air Samples for Various Gases
Via Direct Reading Indicator Tubes
Great Northern Paper Co.
Millinocket, Maine

May 8-9, 1979

Date and Shift	Location	Sample Time	Concentration (ppm)[1]							Temp.[3]	Humidity
			CO[4]	Cl_2*	CO_2	NO_x*	SO_2*	NH_3*	H_2S*		
May 8, 2nd Shift	Above press	10:15 a.m.	<5.0	ND[2]	<1000	ND	ND	ND	ND	73° F	40-45%
May 8, 3rd Shift	Outside near sludge pile	10:35 a.m.	<5.0	ND	<1000	ND	<0.2	ND	ND	64° F	30-35%
May 8, 3rd Shift	Inside	1:45 p.m.	ND	-	<1000	ND	ND	-	ND	77° F	40-45%
	Outside near loading area	2:00 p.m.	ND	-	<1000	ND	ND	-	ND	70° F	28-32%
	Inside loader cab	2:15 p.m.	ND	-	<1000	ND	-	-	ND	70° F	28-32%
May 9, 1st Shift	Outside near sludge pile	6:30 a.m.	ND	-	<1000	ND	ND	-	ND	-	-
	2nd floor above press	8:55 a.m.	ND	ND	<1000	ND	ND	ND	1.0	-	-
Evaluation Criteria											
NIOSH			35	0.5	10,000	1.0	0.5	50(c)	15(c)[5]		
ACGIH			50	1.0	5,000	5.0	5.0	25	10		
OSHA			50	1.0	5,000	5.0	5.0	50	20(c)		

1. Concentration in parts of gas per million parts of air by volume (ppm)
2. N.D. - non detectable
3. Temperature
*4. CO-carbon monoxide, Cl_2-chlorine, CO_2-carbon dioxide, NO_x-oxides of nitrogen, SO_2-sulfur dioxide, H_2S-hydrogen sulfide
c5. Ceiling (TLV-C) the concentration should not be exceeded.