

CHARACTERIZATION OF ODOROUS COMPOUNDS IN US PULP AND PAPER MILL WASTEWATER TREATMENT PLANTS

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Abstract: Community odor concerns are an ongoing issue for many in the pulp and paper industry and a continuing part of most mill environmental management programs. Anti-nuisance laws and permit requirements that address fugitive odors are becoming more common in the United States. NCASI has developed analytical techniques to identify odors associated with typical reduced sulfur compounds (RSC) and has focused on techniques to help identify non-sulfur and non-typical RSC compounds which may contribute to pulp and paper mill odors. This paper presents the results of an evaluation of gas chromatography/olfactometry-mass spectrometry (GC/O-MS) in combination with purge and trap, direct injection methods for the determination of selected RSCs, NCASI Method RSC-02.01, and GC/FID for the determination of volatile fatty acids (VFAs) for the characterization of odorous compounds at US pulp and paper mill wastewater treatment systems. This research included development of an odor wheel specifically tailored to pulp and paper mill wastewater samples. Mass flows of odorous compounds throughout selected treatment systems were estimated. The analytical tools developed and the data generated were utilized to assist selected US mills implementing odor reduction studies. Findings indicated that sulfur-containing compounds are often associated with odors at pulp and paper mill wastewater treatment systems. In addition, terpenes, aldehydes, ketones, and alcohols were associated with odors at a majority of the mills studied. Although volatile fatty acids were detected in several samples they were not commonly associated with medium to strong odors in the wastewater samples. It was noted that the levels and intensities of odorous compounds decreased as wastewater progressed from the primary treatment to final biological treatment. Several compounds were identified in relationship to odors at the facilities tested but high variability was observed for concentrations of these compounds at various locations in similar mills.

Keywords: dimethyl disulfide, dimethyl sulfide, hydrogen sulfide, methyl mercaptan, dimethyl trisulfide, pulp and paper mill wastewater, odor, volatile fatty acids

Introduction and Background

Community odor concerns are an ongoing issue for many in the pulp and paper industry and a continuing part of most mill environmental management programs. Anti-nuisance laws and permit requirements that address fugitive odors are becoming more common in the United States and Canada. Historically, kraft mill odors have been related to releases of reduced sulfur gases from pulp processing areas; specifically, hydrogen sulfide (H₂S), methyl mercaptan (MESH), dimethyl sulfide (DMS), and dimethyl disulfide (DMDS). As technologies for gas collection and management have improved these releases have been minimized and odors arising from wastewater treatment plants (WWTPs) have received increasing attention. Recent efforts by NCASI have focused on analytical methods to quantify reduced sulfur compounds (RSCs) in aqueous waste streams, and a direct injection method was developed for analysis of these compounds [1,2]. As RSC emissions have declined [3], other compounds that may contribute to odor have gained importance [4]. Analytical methods to make identifications and to monitor the effectiveness of control measures implemented at different facilities are needed. The main objective of this research effort was to develop a set of analytical tools that could be applied to investigate odors from WWTPs at pulp and paper mills. These tools can help track the environmental fate of selected compounds throughout treatment systems. Analytical methods were developed and applied at several US mills in an effort to assess specific compound contributions to overall odor. This paper presents the results of this evaluation using gas chromatography/ olfactometry-mass spectrometry (GC/O-MS) in combination with purge and trap; and direct injection methods for the determination of selected RSCs and volatile fatty acids (VFAs) to investigate odorous compounds at pulp and paper mill WWTPs.

Some potential origins of odorous compounds at pulp and paper mills include process additives; compounds generated during the manufacturing, derivatization, decomposition, and rearrangement of process-generated compounds in effluent treatment; and products of anaerobic decomposition. A review of the literature indicated that non-RSC odorous compounds found in chemical pulp mill

effluents include acetic acid, butyric acid, formic acid, propionic acid, valeric acid, terpenes, ammonia, sulfur dioxide, and nitric oxide [5]. Volatile fatty acids (acetic, propionic, and butyric) contribute to odor in recycled paper mill systems and paper [6]. One study indicated that odors associated with effluent treatment system residuals at chemical and non-chemical mills were due to products of anaerobic decomposition, including volatile fatty acids (VFAs), p-cresol, indole, and skatole [7]. In addition to those mentioned, other compounds identified in pulp and paper samples are known to have relatively low odor thresholds. A literature review was conducted to compile an odor potential database specific to the pulp and paper industry. The database lists compounds potentially released from chemical and non-chemical pulp and paper mills along with available published odor threshold data. Odor threshold data are limited for some compounds, and for many compounds reported odor thresholds vary by several orders of magnitude because the determination of odor is subjective. Methods that could be applied to analyze for compounds with low odor thresholds were investigated. Isolation, identification, and quantitative determination of the components of a mixture that result in a specific odor is a complex problem. Compounds that cause odors are not always major constituents of a sample and can often be difficult to identify and monitor. Therefore, a “tool box” approach using a variety of analytical methods was pursued.

GC/FID analysis with simultaneous sniffing has been utilized in the fragrance and flavor industry for some time to help isolate, identify, and evaluate compounds related to specific odors [8]. This technique was recently applied to investigate odors at kraft and mechanical pulp mills [7]. GC/O-MS with a two column system was used to determine off-odor compounds in extrusion coatings of polyethylene [9]. Techniques which utilize a one-column approach to GC/O-MS analyses have also been applied [10,11,12]. Several factors need to be considered when utilizing olfactory GC techniques, including the subjective nature of odor descriptors; the within and between individual variability of odor sensitivities; rapid changes in odor perception due to concentration; different perceptions of odor resulting from GC separation; rearrangement and decomposition in the instrument; uncertainty in knowing if each peak represents only one compound or a mixture; or determining whether the compounds which contribute to odor are amenable to GC analysis. Due to the complex nature of pulp and paper matrices, the pursuit of a method which would allow for unknown compound identification and odor intensity simultaneously was preferred; therefore GC/O-MS was investigated. It was proposed that most of the compounds responsible for odor at a pulp and paper facility would be amenable to purge and trap methods, so the combination of purge and trap and GC/O-MS was evaluated and applied.

Experimental Methods and Materials

The mills for which GC/O-MS, RSCs, and VFAs were characterized are listed in Table 1 along with general information regarding location in the US, wood furnish, process type, bleaching sequence, WWTP, and condensate management (hardpiping or steam stripping). Sample collection sites were mill specific and in most cases included samples from the outlet of the primary clarification, the front portion of the aerated stabilization basin (ASB), the midpoint of the ASB, and the final effluent. At mills hardpiping condensates a sample of the hardpipe condensate was analyzed to assess the overall contribution of odorous compounds from this input.

Table 1. Mill WWTPs characterized for odorous compounds via GC/O-MS, RSC-02.01, and VFA

Mill Code	Region ^a	Furnish ^b	Process Type	Bleaching Sequence ^c	WWTP ^d
A	NW	SW	kraft	O2-D-Eop-D-DP	ASB ^e
C	NW	SW/OCC	kraft, recycling	unbleached	ASB ^e
D	SE	SW	kraft	D-Eop-D-E-D, D-Eo-H-E-D	ASB ^e
E	NW	SW/OCC	kraft, recycling	unbleached	ASB
G	SE	SW/HW	kraft	D-E-H-D-E-D, D-Eo-D-Ep-D	ASB ^e
J	NW	HW, SW	kraft	unbleached	ASB ^e
K	SW	HW, SW	kraft	D-Eop-D, D-Eo-D-E-D	ASB ^e

^a northwest (NW), southeast (SE), southwest (SW) United States

^b softwood (SW), hardwood (HW), old corrugated container (OCC)

^c chlorine (C), chlorine dioxide (D), alkaline extraction (E), oxygen (O), hydrogen peroxide (P), hypochlorite (H)

^d activated sludge (AS), aerated stabilization basin (ASB)

^e condensate management includes hardpiping of evaporator condensates

NCASI Method RSC-02.01 was employed for quantitative determination of total sulfide, methyl mercaptan, dimethyl sulfide, dimethyl disulfide, and dimethyl trisulfide [1,2]. This method utilizes two different sample preservative schemes. The first uses zinc acetate at pH 11 to bind the sulfide for storage stability and shifts the equilibrium back to sulfide just prior to analysis by acidification to pH 2.5 with phosphoric acid. The second technique uses the addition of ascorbic acid at pH 3 with

phosphoric acid to prevent oxidation of the remaining target RSCs for a period of two weeks. Samples are analyzed via gas chromatography-pulsed flame photometric detection (GC/PFPD). A 2 μL sample was injected in split mode onto a GC equipped with a Crossbond[®] 6% cyanopropylphenyl/ 94% dimethyl polysiloxane fused silica capillary column (J&W DB-624, 30 m x 0.25 mm i.d. with 1.4 μm film). Calibration ranged from 20 to 1000 μg S/L. Quality control during this study included analysis of a method blank, calibration check sample, fortification of each sample with a surrogate to assess recovery from a matrix, and sample duplicate and matrix spike experiments with each set of samples.

NCASI staff developed a direct injection method using GC/MS to measure acetic, propionic, isobutyric, butyric, isovaleric, and valeric acids in aqueous samples to support previous research [13]. For the purpose of this investigation a flame ionization detector (FID) was used. Samples did not incorporate preservation other than refrigeration with a two week holding time. Five hundred microliters of aqueous sample was diluted with 10 μL of 1:3 phosphoric acid (to ensure protonation) in isopropanol to a final volume of 1 mL at a dilution factor of 1 (50:50 isopropanol:water) in GC autosampler vials. Prior to analysis the diluted samples were fortified with d_5 -phenol as the internal standard. Calibration standards were prepared and analyzed in the same manner as aqueous samples over a range of 5 to 200 mg/L for acetic acid and 0.5 to 200 mg/L for the other acids. Samples and standards were analyzed by direct injection of a 1 μL aliquot of the dilutions onto a GC/FID equipped with a nitroterephthalic acid modified polyethylene glycol (DB-FFAP) GC column (30 m x 0.32 mm x 0.25 μm). Each analyte or internal standard was identified by the GC retention time based on authentic standards. Target compounds were quantified using the average response factors from the calibration curve. Each sample set was analyzed in conjunction with a calibration check sample, method blank, duplicate, and matrix spiked sample to assess quality control. One microliter of each sample was injected (splitless, 8.2 psi, purge time 0.8 min) onto the GC with an initial temperature of 70°C for 1 min, followed by 2°C/min to 90°C, then 20°C/min to 150°C and 35°C/min to 240°C held for 2 minutes, for a total run time of 20.57 minutes. The injection port was at 220°C and the detector was at 250°C.

Ten milliliters of sample was placed in the purge tube and 5 μL of a bromofluorobenzene (BFB) standard stock at a concentration of 61.8 $\mu\text{g}/\mu\text{L}$ was added to each tube. Samples were spiked with 5 μL of geosmin standard stock at a concentration of 33 $\text{ng}/\mu\text{L}$ for comparison of odor intensity and correlation of odor to peak elution. Purging was conducted at room temperature using helium at 45 mL/min for 22 minutes. Purged compounds were trapped on a Supelco Vocab 3000 and thermally transferred to a HP 5890 GC. The sample was split 1:10 using a 2 mm splitless glass liner and injection port temperature of 220°C. Detection was accomplished via GC/O-MS.

An olfactory device was installed directly at the interface of the GC/MS, similar to the procedure utilized by Qian [10,12]. A gas chromatograph (Hewlett Packard (HP) 5890A) was equipped with a Restek Corporation Crossbond[®] trifluoropropylmethyl polysiloxane capillary column (RTX[®]-200, 60 m x 0.32 mm (i. d.) with a 0.5 μm (d. f.)). A HP 5970B mass selective detector equipped with a HP G1034C revision 3.0 ChemStation data system was used. The mass spectrometer was scanned from 33 to 500 m/z at a cycle of 0.77 sec. The ion source temperature was 200°C and the electron ionization potential was 70 eV. The outlet of the capillary column was split into two portions at the end of the GC column using an MKT Y-union connector with a silcosteel treatment for inertness.

One of the union outlets was connected to a HP 5970 MSD using 0.66 m of 0.1 mm i.d. deactivated fused silica capillary column at a flow rate of 0.8 mL/min and 280°C interface. The other union outlet was connected to 1.66 m of 0.18 mm i.d. deactivated fused silica capillary column for the olfactometry portion with a flow rate of 1.2 mL/min. A stream of humidified air (flow rate 15 mL/min) was introduced using a 1/8" stainless steel T inside the GC oven connected to two 1/8" x 24" stainless steel tubes at 90 degrees from each other and exiting the oven with 18" protruding [14]. The capillary column was inserted into the tubing and extended just beyond the end, and was sealed with a ferrule to the T connector. This sniffing port was insulated with glass tubing and wrapped with heat tape to maintain a regulated temperature of 185°C in order to eliminate condensation. Compounds were tentatively identified based on a Q-value of greater than 80% and identification in both duplicate runs at the same retention time (± 0.1 min), similar odor intensity, and odor description. The Q-value is an assessment of how well the spectrum of the unknown compound agrees with the spectrum of an authentic standard (Q=100 indicates greatest agreement). Tentative identifications were confirmed using authentic standards for all compounds except those noted in the results.

Personnel who participated as sniffers in this study were selected based on their ability to detect and describe odors from solutions of standard stocks containing acetic acid, methyl ethyl ketone, propionic

acid, isobutyric acid, butyric acid, alpha-pinene, isovaleric acid, valeric acid, beta-pinene, limonene, p-cymene, phenol, o-cresol, m-cresol, p-cresol, guaiacol, iso-borneol, borneol, alpha-terpineol, indole, geosmin, methyl indole, hydrogen sulfide, MESH, DMDS, and DMTS. Efforts were made to formulate an odor wheel based on descriptions obtained during assessment of standard stocks and pulp and paper mill samples to assist in standardizing odor descriptions (Figure 1). Odor intensity was described as threshold (T), weak (W), moderate (M), or strong (S). An odor standard of geosmin was injected into all the samples analyzed using GC/O-MS to provide a reference for odor intensity and consistent descriptors. Geosmin is reported to have a threshold detection limit by sensory GC of 0.02 ng [15]. GC/O-MS analyses were conducted in duplicate using two individual sniffers. The instrument was isolated from the laboratory, and the individuals conducting the sensory assessment were segregated from other staff when conducting assessments. Compounds detected in the method blank were excluded from the data.

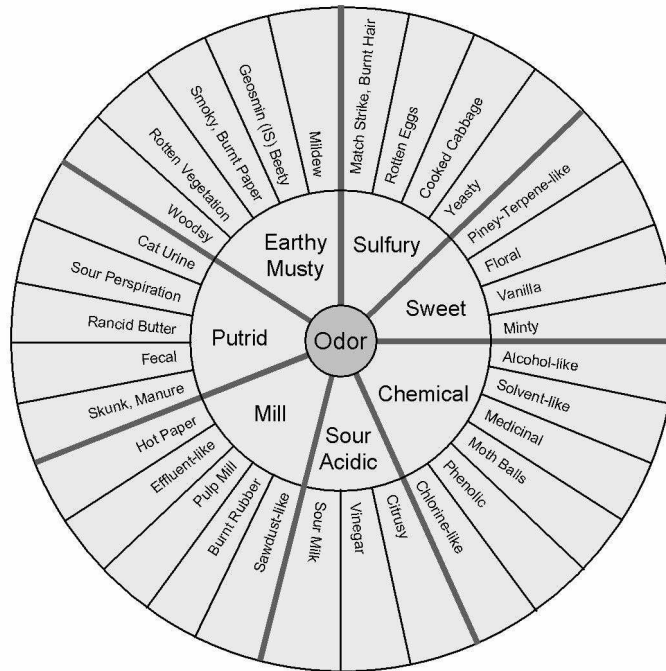


Figure 1. Pulp and paper mill odor wheel

Results and Discussion

Table 2 summarizes the odor-active compounds identified or detected at the mills surveyed during this investigation using GC/O-MS, along with CAS numbers, compound names, odor descriptions, and odor thresholds available in the literature [16,17,18]. Odor descriptors are subjective and can vary by individual sniffers and concentrations in a sample. Tables 3 through 6 summarize the compounds identified in the primary clarifier, front of the ASB, mid-point of the ASB, and final effluent, respectively, along with the intensity of odor indicated by each sniffer during the duplicate analyses. The majority of compounds associated with odors in these samples were sulfur-containing compounds, terpenes, and a group of aldehydes, ketones, and alcohols. Four unidentified compounds with strong intensity were detected at four mills at retention times of 16.8, 18.2, 20.4, and 28.8 minutes. Generally, the number and intensity of odiferous compounds detected in the samples decreased as the waste stream progressed to the final effluent. The odors associated with medium to strong odors remained similar from the primary clarifier outlet to the mid-point of the ASB. The front of the ASB contained the largest number of odorous compounds.

Odorous compounds associated with hard piped condensates were assessed at Mills C and K. The condensates were found to contain medium to strong intensity odors associated with all of the compounds listed in Table 4 except limonene, terpinenol-4, 2-furfurylmethylsulfide, and MIBK.

Table 2. Odor-active compounds identified in kraft WWTPs

CAS Number	Compound	Odor Descriptors ^a	Odor Threshold (mg/m ³) ^b
<u>Reduced Sulfur Compounds</u>			
7783-06-4	total sulfide (hydrogen sulfide)	rotten eggs	0.0007
74-93-1	methyl mercaptan	rotten eggs, sulfur like, pulp mill	0.00004
75-18-3	dimethyl sulfide	rotten vegetables, sour milk, rancid	0.0025
624-92-0	dimethyl disulfide	rotten eggs, burnt rubber	0.0001
3658-80-8	dimethyl trisulfide	putrid/rancid, rotten eggs, burnt rubber	0.0073
5756-24-1	dimethyl tetrasulfide	rotten vegetables, moth balls	NA
10152-76-8	3-(methylthio)-1-propene	asparagus, manure, rotten vegetables	NA
20333-39-5	ethyl methyl disulfide	rotten eggs, rotten vegetables	0.062
88-15-3	2-acetylthiophene	hot paper, burnt	NA
1438-91-1	2-furfurylmethylsulfide	burnt rubber, smoky	NA
6628-18-8	1,2-bis (methylthio) ethane	pulp/paper mill, rotten vegetables, putrid	NA
<u>Terpenes</u>			
138-86-3	limonene	woody	0.01
80-56-8	alpha pinene	chemical, medicinal, pine like	0.016
127-91-3	beta pinene	rotten vegetables, skunk like	(140 ppb in water)
562-74-3	terpinenol-4	chemical, saw dust	0.01 to 0.39
76-22-2	camphor	rotten vegetables	0.02 to 45
99-87-6	p-cymene	medicinal	0.012
<u>Others</u>			
108-10-1	4-methyl-2-pentanone (MIBK)	sweet, vanilla, phenolic	0.3
90-05-1	guaiacol	phenolic, sweet, smoky	0.0025
75-07-0	acetaldehyde	solvent like	0.0002

^a see Figure 1^b detection thresholds in air (unless otherwise stated); ranges shown where reported values differ significantly
NA not available in the literature**Table 3.** Odor-active compounds identified at the primary clarifier outlet^a

Compound	Mill A	Mill C	Mill D	Mill DII	Mill E	Mill G	Mill J ^a	Mill K
hydrogen sulfide							s, s	
methyl mercaptan	m, m			m, m		s ⁺	m, s	m, s
dimethyl sulfide			w		m, s	s, s ⁺	m, s	s, s ⁺
3-(methylthio)-1-propene								m, m
dimethyl disulfide		s, s			w, w	m, s		s, s ⁺
beta-pinene		w, w		s, s ⁺⁺				w, m
limonene		w, m	m, m					
dimethyl trisulfide	m, s			m, s	s, s	m, s ⁺⁺	s, s	s, s ⁺⁺
2-furfurylmethylsulfide						s, s ⁺⁺		
1,2-bis(methylthio)ethane ^a	m					m, s ⁺		s, s ⁺
guaiacol	m	m, s	m, s ⁺	m, s ⁺⁺	s, s ⁺	s, s ⁺	m, s ⁺	m, s ⁺⁺
dimethyl tetrasulfide ^a								s, s

^a primary clarifier outlet sample was the only sample assessed using GC/O-MS for Mill J^b authentic standard of this compound not available for confirmation; identification based on Q value >90%**Table 4.** Odor-active compounds identified in front of the aerated stabilization basin^a

Compound	Mill A	Mill C II	Mill D	Mill D II	Mill E	Mill K
hydrogen sulfide						m, s
methyl mercaptan		s, s	m, s	m, s	s, s	s, m
acetaldehyde			s, s	w, s		
dimethyl sulfide		s, s	s, s	s, s ⁺	s, s ⁺⁺	m, s
3-(methylthio)-1-propene		m, s	m, w	m, s ⁺	s, s ⁺	
dimethyl disulfide		s, m	m, s ⁺	s, s ⁺	s, s ⁺⁺	
ethyl methyl disulfide		w, m	m, w			
4-methyl-2-pentanone		m, m		m, s ⁺		
alpha-pinene				w, m		
beta-pinene				s, s ⁺		
limonene			w, m			
dimethyl trisulfide		s, s	s, s ⁺	s, s	s ⁺⁺ , s ⁺⁺	s, s
2-furfurylmethylsulfide				s, s	s, s ⁺	
1,2-bis(methylthio)ethane ^b		s, s	m, s ⁺⁺	s, s ⁺⁺	m, s	
guaiacol		m, s	m, s ⁺	s	s, s ⁺⁺	s, s ⁺
terpinen-4-ol			m, s			
dimethyl tetrasulfide ^b			m, s	s, m	m, s	
camphor						s

^a Mill G not sampled at this location^b authentic standard of this compound not available for confirmation; identification based on Q value >90%

Table 5. Odor-active compounds identified in mid-point of the aerated stabilization basin

Compound	Mill A	Mill C	Mill D	Mill D II	Mill E	Mill G ^a	Mill K
hydrogen sulfide				m			
methyl mercaptan	m, w	s, s	s, s+	s, s	m, m	s, s	w, s
acetaldehyde							m, s
dimethyl sulfide	s, s	s, s	s, s	s, s+	m, s	m, s	m, m
3-(methylthio)-1-propene	t, m	w, w	m, s+	m, s			
dimethyl disulfide	s, s	s, s	s, s+	m, s+		w, m	
4-methyl-2-pentanone	m, m	m, s+	s, m				
alpha-pinene			s+	m, m			m
beta-pinene			s++			s, s+	m, m
limonene	t, m	w, m					
dimethyl trisulfide	s, s	m, s	s, s++	s, s++	s, s+	s, s+	m, s+
o-cymene or p-cymene			m, m				
2-furfurylmethylsulfide			m, s	s, s++		s, s+	
1,2-bis(methylthio)ethane ^b	s, s	s, s+	s, s++	s, s+		m, s	
guaiaicol	m, m	m, s	m, s	m, s		m, s+	
terpinenol-4				s, s++			
dimethyl tetrasulfide ^b		m		s, s			

^a results for two ASB ponds combined for this assessment

^b authentic standard of this compound not available for confirmation; identification based on Q value >90%

Table 6. Odor-active compounds identified in final effluent

Compound	Mill A	Mill C	Mill D	Mill D II	Mill E	Mill G	Mill K
hydrogen sulfide				m			
methyl mercaptan		m, m		m, s	w		
dimethyl sulfide	s, w				m, m	m, m	
dimethyl disulfide						w, m	
beta-pinene						s, m	
dimethyl trisulfide	s, m		m, s			s, s	m, s
2-furfurylmethylsulfide			m, s	s		s, s	
1,2-bis(methylthio)ethane ^a	s, m					m, s+	
guaiaicol						s	s+
2-acetylthiophene	s, m						

^a authentic standard of this compound not available for confirmation; identification based on Q value >90%

RSC data for sampling sites common to all the mills sampled are summarized in Table 7. Repeat samplings occurred at several of the sites assessed to investigate variability of the RSCs. RSC levels have been demonstrated to vary over time and with process fluctuations. This variability is especially noted in samples collected at the front portion of the WWTP. The median calculations were assessed using a value of zero to replace all non-detects. This result will represent a low bias median of the results.

Table 7. Reduced sulfur compound concentrations in WWTP samples ($\mu\text{g S/L}$)

Sampling Location	Total Sulfide ^a	Methyl Mercaptan	Dimethyl Sulfide	Dimethyl Disulfide	Dimethyl Trisulfide
			Range (median) n ^b		
Primary clarifier outlet	270 – 20100 (8600) 12	<20 – 2490 (154) 12	<20 – 3060 (28.7) 14	<20 – 2710 (NA) 13	<20 – 470 (NA) 13
Front of ASB	60 – 16200 (7100) 15	<20 – 13900 (282) 15	<20 – 4680 (198) 16	<20 – 8410 (137) 19	<20 – 2500 (NA) 19
Mid-point of ASB	130 – 5730 (1000) 12	<20 – 2370 (19.3) 14	<20 – 1020 (NA) 14	<20 – 2000 (NA) 15	<20 – 280 (NA) 15
Final effluent	<20 – 197 (84.2) 9	<20 – 221 (0) 15	<20 – 119 (NA) 13	<20 – 113 (NA) 19	not detected n=12
Hardpiped condensates	10600 – 117000 (68800) 9	2190 – 151000 (61850) 8	25.9 – 21900 (11105) 8	548 – 12700 (4715) 8	<20 – 694 (127) 8

^a concentration of total sulfide measured using this method represents total amount of sulfide in sample volatile at pH 2.5; it is believed that this includes all freely dissolved sulfide plus sulfide weakly associated with either dissolved organic matter or certain transition metals; if sample pH is greater than 2.5, actual sulfide concentration in solution might be less than concentration measured by this method

^b some sampling sites sampled and analyzed more than once to assess variability, therefore n may be greater than 7
NA median of zero determined based on substitution of zero for non-detects

Samples from Mills A, C, D, E, and G were analyzed for VFAs. Table 8 contains a summary of the range and median of VFA concentrations determined in the samples collected at each site. The median calculations were assessed using a value of zero to replace all non-detects. This result will

represent a low bias median of the results. Valeric and isobutyric acids were not detected in any of the samples analyzed. The most commonly detected VFA was acetic acid. The VFAs were not identified as odiferous compounds during the GC/O-MS analyses because the concentrations in the samples were well below the low odor thresholds of 2.5 mg/m³ (acetic acid) and 0.02 mg/m³ (propionic acid) for these compounds.

Table 8. Volatile fatty acid concentrations in WWTP samples (mg/L)

Sampling Location	Acetic Acid	Propionic Acid	Butyric Acid	Isovaleric Acid
			Range (median) n	
Primary clarifier outlet	21.5 – 122 (71.8) 5	1.59 – 10.5 (6.8) 5	<0.5 – 1.55 (0.4) 5	<0.5 – 0.52 (NA) 5
Front of ASB	<5.0 – 154, (19.1) 5	<0.5 – 5.76 (1.4) 5	<0.5 – 2.02 (NA) 5	<0.5 – 0.92 (NA) 5
Mid-point of ASB	<5.0 – 25.7 (3.8) 5	<0.5 – 3.63 (0.9) 5	ND	<0.5 – 0.79 (NA) 5
Final effluent	<5.0 – 5.32 (2.6) 5	<0.5 – 3.6 (NA) 5	ND	ND

NA median of zero determined based on substitution of zero for non-detects

ND not detected above lowest calibration limits: 5 mg/L for acetic acid; 0.5 mg/L for propionic acid, isobutyric acid, butyric acid, isovaleric acid, and valeric acid

Quality Control

During these analyses assessments of quality control were included with each sample set (<14 samples) analyzed. These included a method blank, calibration verification, surrogate recovery experiments (RSC-02.01), and matrix spike recovery and duplicate analyses to assess precision and accuracy. None of the target compounds were detected in the method blanks. Instrument calibration was verified with each set of samples by analyzing a reagent water sample fortified with the target compounds at known concentrations. The recovery of the target compounds ranged from 72 to 134% for the RSCs and 84 to 117% for the VFAs. Surrogate recoveries of thioanisole (RSC-02.01) in all samples ranged from 73 to 131%, with an average of 106%. Matrix spike recoveries for the VFAs ranged from 84 to 128% for all of the target compounds. Average matrix spike recoveries for total sulfide, MESH, DMS, DMDS, and DMTS were 93, 106, 102, 112, and 96%, respectively. The relative percent differences observed between duplicate analyses of the same sample ranged from 1.3 to 21% for the VFAs. The pooled RPDs across all duplicate analyses for the RSCs ranged from 5.6 to 12.3%. These results indicate consistently good analytical performance throughout the studies.

Estimates of Mass Flows

Several mass balances have been undertaken in the course of these surveys. These balances have been in the form of measuring the loads of RSCs in wastewater at various points in the treatment system and assessing the net generation and loss of reduced sulfur within each zone. An example is shown in Figure 2. This treatment system consists of a primary clarifier, three smaller sized aerated equalization ponds, and two aerated stabilization basins.

As shown, reduced sulfur compounds are generated in the primary clarifier and in equalization ponds 2 and 3. During sampling, dissolved oxygen levels in the equalization ponds were very low. There was an overall loss of reduced sulfur from the two ASBs. These data, and those collected at other WWTPs, suggest that reduced sulfur generated during wastewater treatment is associated with anoxic zones with higher levels of oxygen demanding substances. It is likely that those areas where reduced sulfur generation is at its highest are also the areas where the potential for emissions and odor are highest. However, actual emission rates depend on several physical properties of the zone, such as surface area to volume ratio and level of turbulence. Further, the loss of sulfur in some treatment zones (e.g., the ASBs in case shown in Figure 2) may be due to volatilization or to oxidation of RSCs by chemical or biological processes. The latter mechanisms would reduce actual emissions. The inability to project emission rates from water mass balance studies provides strong motivation to coordinate wastewater column studies with direct basin emissions measurements, and to develop a more thorough understanding of reduced sulfur generation and oxidation/precipitation mechanisms. These studies are currently underway by NCASI.

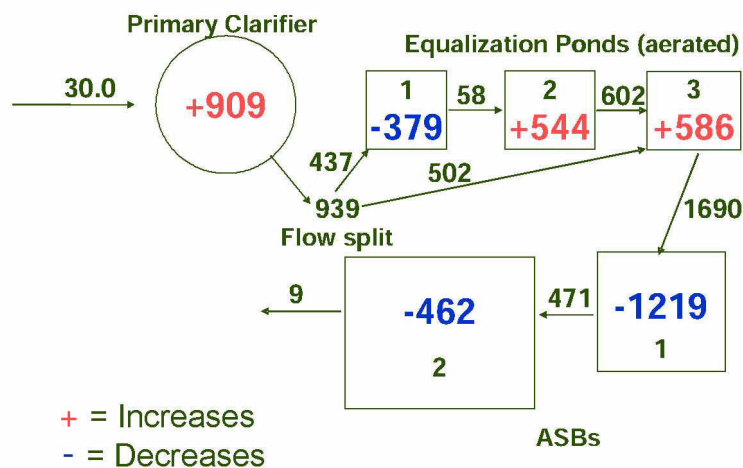


Figure 2. WWTP total sulfide mass flows (lb S/day)

Conclusions

Control of reduced sulfur compound emissions from pulping operations has greatly decreased the discharge of odor associated with kraft pulp mills. Efforts to understand the sources of remaining odors have demonstrated that WWTPs may be a potential source. The findings of this study indicate that purge and trap GC/O-MS coupled with quantitative analyses for VFAs and RSCs can provide useful information regarding the compounds related to odors in aqueous samples from pulp and paper mill WWTPs. This research demonstrates that RSCs account for the majority of odorous compounds detected during purge and trap GC/O-MS of WWTP samples. In addition, medium to strong odors were often related to terpenes, aldehydes, ketones, and alcohols. The RSC analyses conducted to confirm concentrations indicate high variable from mill to mill at similar sampling locations. Examining the data for trends in odorous compounds throughout the WWTPs suggests that the profile of each location is somewhat unique. Analyses of samples for VFAs in conjunction with GC/O-MS results demonstrate a lack of odor associated with these compounds in the aqueous phase of the WWTP. Future research efforts will focus on the application of these analytical techniques to examine odor issues, estimate and model emissions, and suggest potential control strategies for pulp mills seeking to reduce odorous emissions.

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