



Paprican

Impact of Volatile Organic Acids on Activated Sludge Microbiology

Michael Paice

8th IWA Symposium on Forest Industry Wastewaters
Vitoria, Brazil April, 2006

Co-authors

Carl Pelletier, now with Nexia Biotech, Montreal

Sophie Deschênes, FF Soucy, Québec

Mary Ann Fitzsimmons, Paprican, Montreal

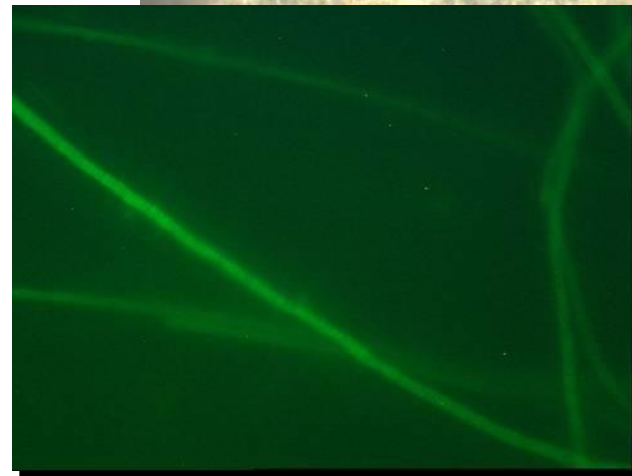
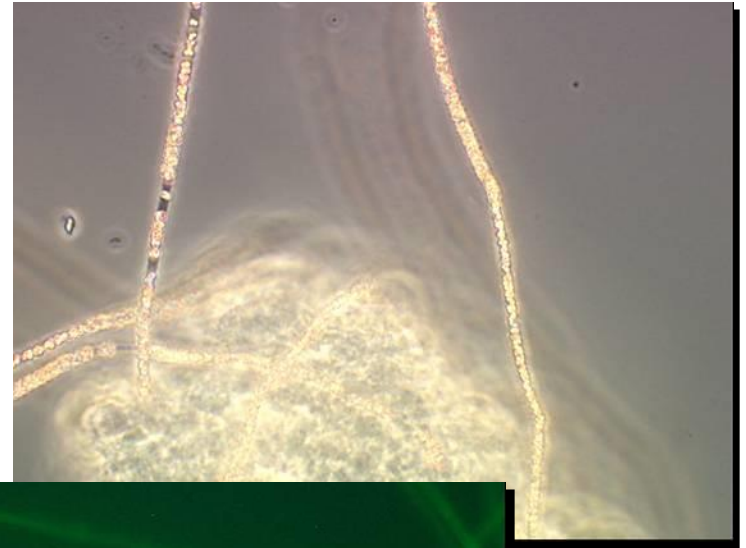


Impact of Septic Compounds on Filament & Floc Formation

- Volatile organic acids (VOA)
 - Acetic : CH_3COOH
 - Propionic : $\text{CH}_3\text{CH}_2\text{COOH}$
 - Butyric : $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$
- Reduced sulfur compounds
 - Sulfide : S^{2-}
 - Thiosulfate : $\text{S}_2\text{O}_3^{2-}$
- Cause primary clarifier odour and activated sludge filamentous bulking

Type 021N / *Thiothrix* Bulking

- Type 021N is a common bulking filament
- Identified by:
 - Microscopy
 - Fluorescent in-situ hybridization (FISH)
- Now looking at quantitative polymerase chain reaction (qPCR)



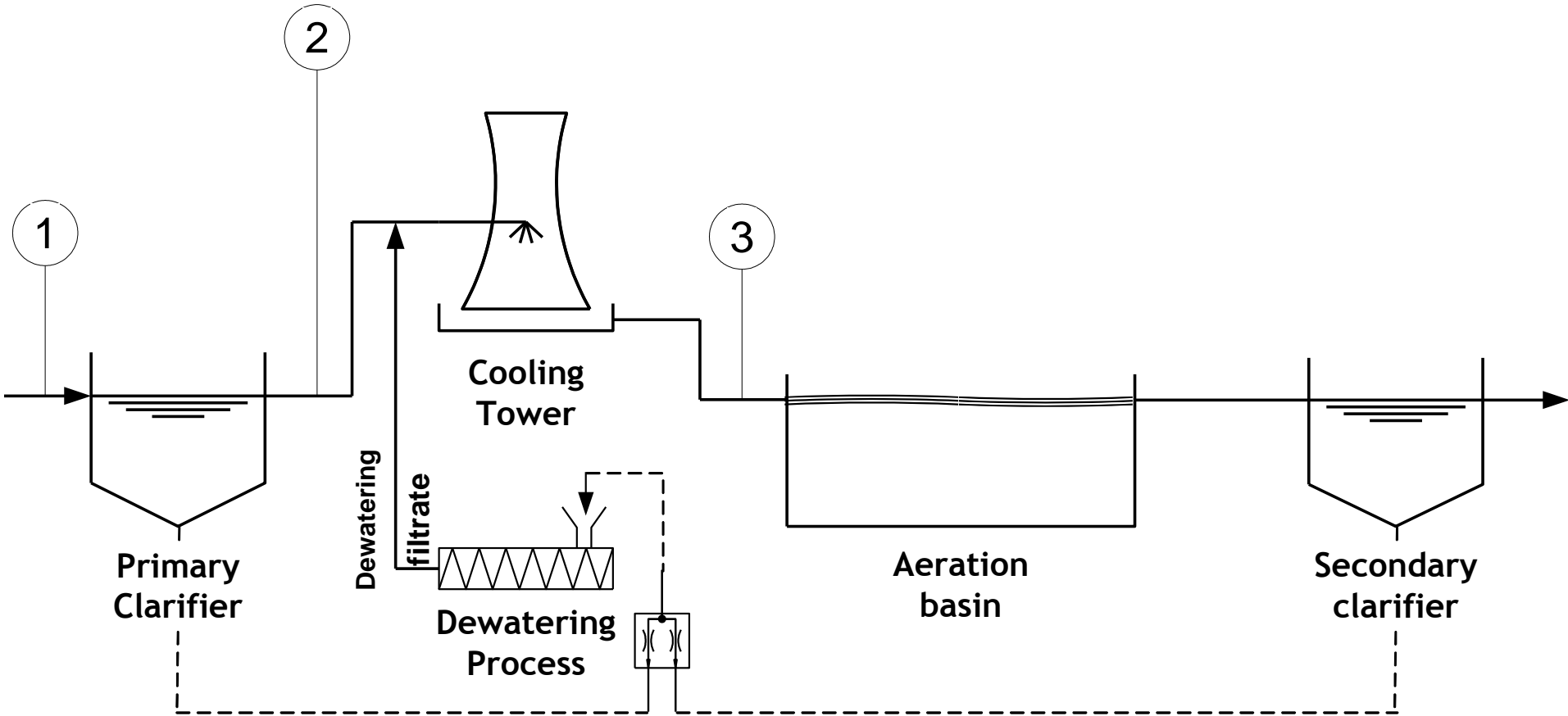
What Triggers Type 021N / *Thiothrix* Bulking?

- Low F/M ratio
 - (for 021N only)
- Low dissolved oxygen < 2.0 mg/L
- Nutrient deficiency (nitrogen & phosphorous)
- Septicity
 - Organic acids
 - Reduced sulfur compounds
 - Others readily biodegradable substrate
 - Alcohols, amino acids with sulfur, glucose

What Triggers Type 021N / *Thiothrix* Bulking?

- Nutrient deficiency
 - Nitrogen
 - < 1.0 mg/L of TIN
- Septicity
 - Organic acids (acetic, propionic, butyric)
 - VOA > 100 to 200 mg/L
 - Reduced sulfur compounds (TRS)
 - Hydrogen sulfide > 1 to 3 mg/L
 - Thiosulfate $> ?$ mg/L (021N only)

Newsprint Mill 14-Week Sampling Campaign



This mill has experienced chronic sludge bulking problems (Type 021N)

Measured Septic Compounds at Sampling Sites 1, 2 & 3 (average of 14 samples)

	VOA _{total} (mg/L)	Sulfide (mg/L)	Thiosulfate (mg/L)
1-Prim. Clarifier In	77	0.5	1.4
2-Prim. Clarifier Out	140	0.8	2.5
3-After Cooling Tower (pressate included)	146	0.3	1.2

Correlation Between Filaments Bacteria Counts and Septic Compounds in the Effluent

	Filaments ^α	VOA _t *	Sulfide *	Thiosulfate*
n	14	14	11	14
Average	3.4E+06	146	0.3	1.2
Std. Dev.	9.5E+05	32	0.2	0.9
Pearson r	-	0.43	0.40	0.23

() Pearson r significance test passed

*mg/L

^α int. / g MLSS

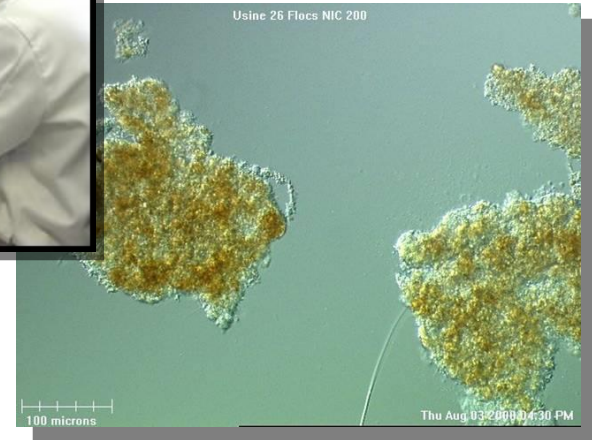
VOAs Entering Aeration Basin: Correlation with Filament Abundance (average of 14 samples)

Acid	Average*	%	r Pearson
Formic	5	3.7	0.12
Acetic	119	82.1	0.39
Propionic	8.6	5.9	(0.59)
Butyric	12.1	8.3	0.35
Total	146	100.0	0.43

* mg/L

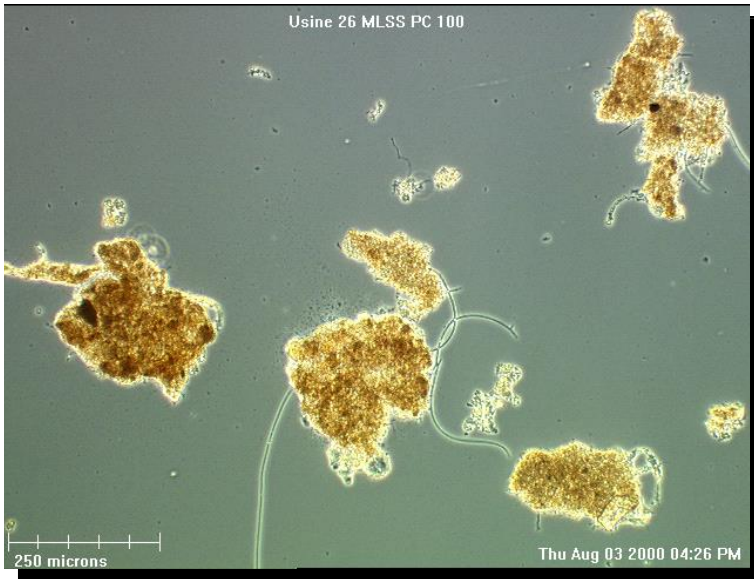
() Pearson r significance test passed

Measuring Floc Size Distribution



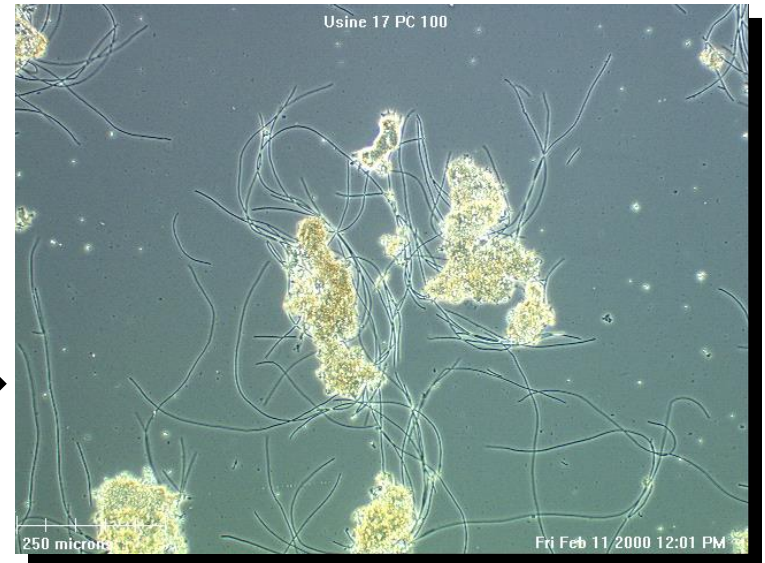
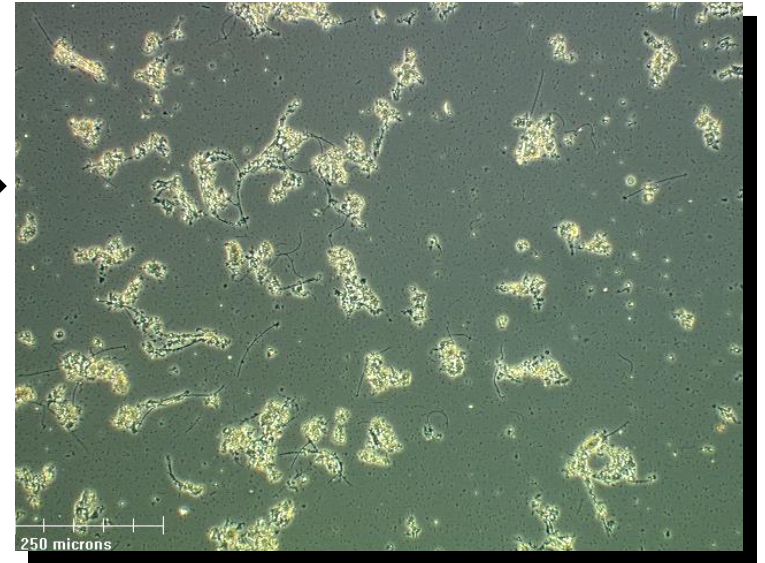
Viewing Toxic Effects

< 50 μm , 50 – 150 μm , 150 – 500 μm →



150 – 500 μm , 50 – 150 μm , < 50 μm

50 – 150 μm , < 50 μm , 150 – 500 μm →



Correlation of Septic Compounds with Floc Size Distribution (14 samples)

	Formic acid	Acetic acid	Propionic acid	Butyric acid	Total sulfur	Thiosulfate
< 50 μm	0.03	0.23	(0.57)	0.24	-0.30	-0.30
50-149 μm	-0.26	0.10	-0.01	0.16	0.13	0.16
150-500 μm	0.22	-0.36	(-0.56)	-0.42	0.23	0.12
> 500 μm	0.38	0.25	0.37	0.22	0.12	-0.12

() = Pearson r significance test passed ($t_r > t_{0.05}$)

Correlation of Floc Size Distribution with Confounding Factors

	TIN ^{1*} α	BOD : N	O-PO ₄ ^{2*} α	BOD : P	F/M Ratio ³	D.O. ⁴ α
< 50 μm	-0.26	0.37	-0.40	0.08	-0.14	-0.08
50-149 μm	0.30	-0.20	0.30	-0.21	0.05	0.03
150-500 μm	-0.05	-0.13	0.07	0.19	0.04	0.07
> 500 μm	-0.45	0.10	-0.32	-0.19	0.32	-0.21

¹ Total inorganic nitrogen

³ kg BOD / kg MLSS.day

() Pearson r significance test passed

² Orthophosphate

⁴ Dissolved oxygen

* Residual

α mg/L

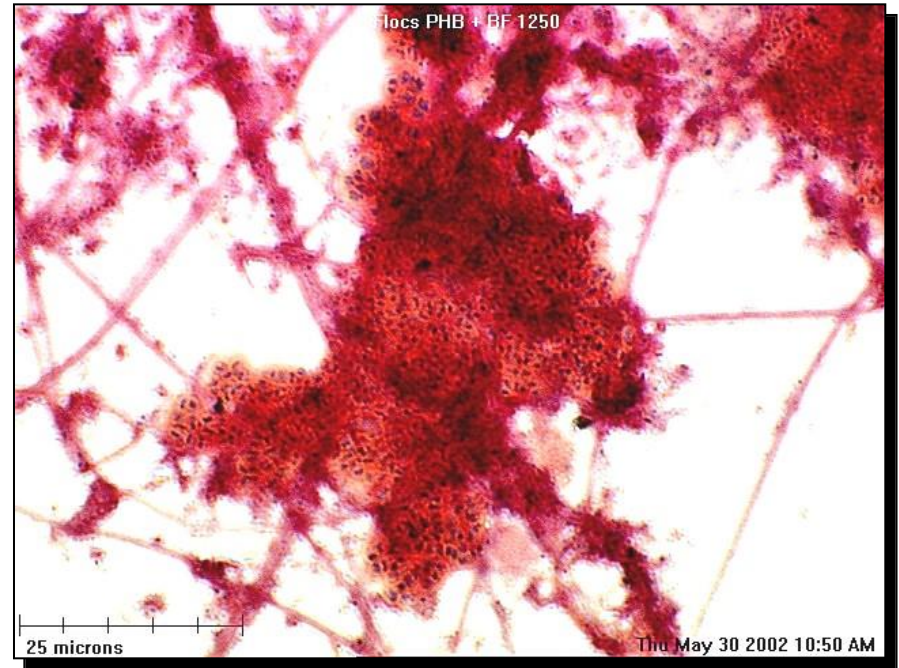
Propionic Acid (PA) Toxicity Impact

- Average PA concentration in primary clarified effluent was 8.6 mg/L for 14 samples collected
 - Literature indicates toxic effect appears between 5 to 10 mg/L
-

1. PA interferes with biosynthesis and accumulation of poly- β -hydroxybutyrate (PHB) in some species of flocculating microorganisms
2. PA also interferes with metabolic activity of biomass by reducing respiration rate

Propionic Acid Inhibits PHB Storage

- Major carbon storage mechanism
- Results in competitive disadvantage of flocs during nutrient deprivation



Sudan Black / Safranin O stain

PA Reduces Respiration Rate of Flocculating Bacteria

- BOD and nutrient uptake by flocs decreases
- Flocs grow more slowly
- More nutrients and BOD become available for filamentous bacteria (competitive advantage)
- Filamentous bacteria progressively out-grow flocculating bacteria, SVI increases

Summary

- Correlation between propionic acid and filamentous bulking is due to floc inhibition
- Inhibition of floc-forming bacteria allows filaments such as Type 021N to out-compete flocs, causing bulking
- Need to prevent propionic acid formation in primary clarifier and during sludge pressing

How to Minimize Propionic Acid Formation?

- Prevent seeding of mill streams and clarifiers
 - Biocide programs
 - Minimize phosphate availability
- Keep redox potential high in clarifiers
 - Pure oxygen or peroxide
- Perform pH shock
 - Must be sufficient to inhibit growth

Microorganisms pH Range

Bacteria Type

Operational pH Range

Sulfate Reducing Bacteria

Desulfobulbus, Desulfovibrio, etc.

5.5 - 9.0

Fermentative Bacteria

Clostridium spp. Propionibacterium spp.

4.5 - 9.5

Coliforms

Klebsiella spp, E. coli, Enterobacter spp.

4.5 - 8.0

Obrigado!
Thank you!

