Microbes in the Papermachine Environment

Linda Robertson

TAPPI Monograph: Microorganisms in Papermaking

Chapter 1

www.iMicrobial.com
Independent consulting for industry

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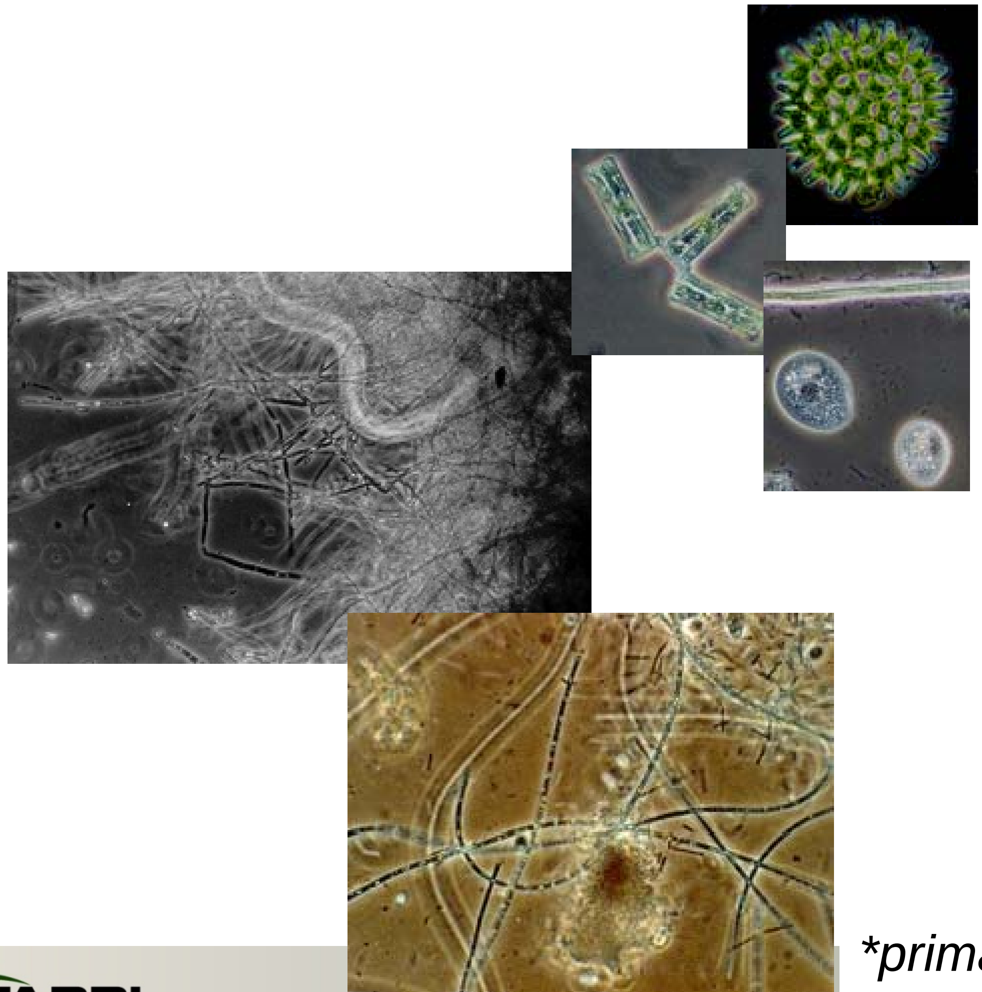
Microbes in Paper System



- Bacteria: filamentous* & single-cell
- Fungi
- Protozoa*
- Ameba*
- Rotifers *
- Worms*
- Algae*

*primarily enter via inadequately treated water

Why do they grow?

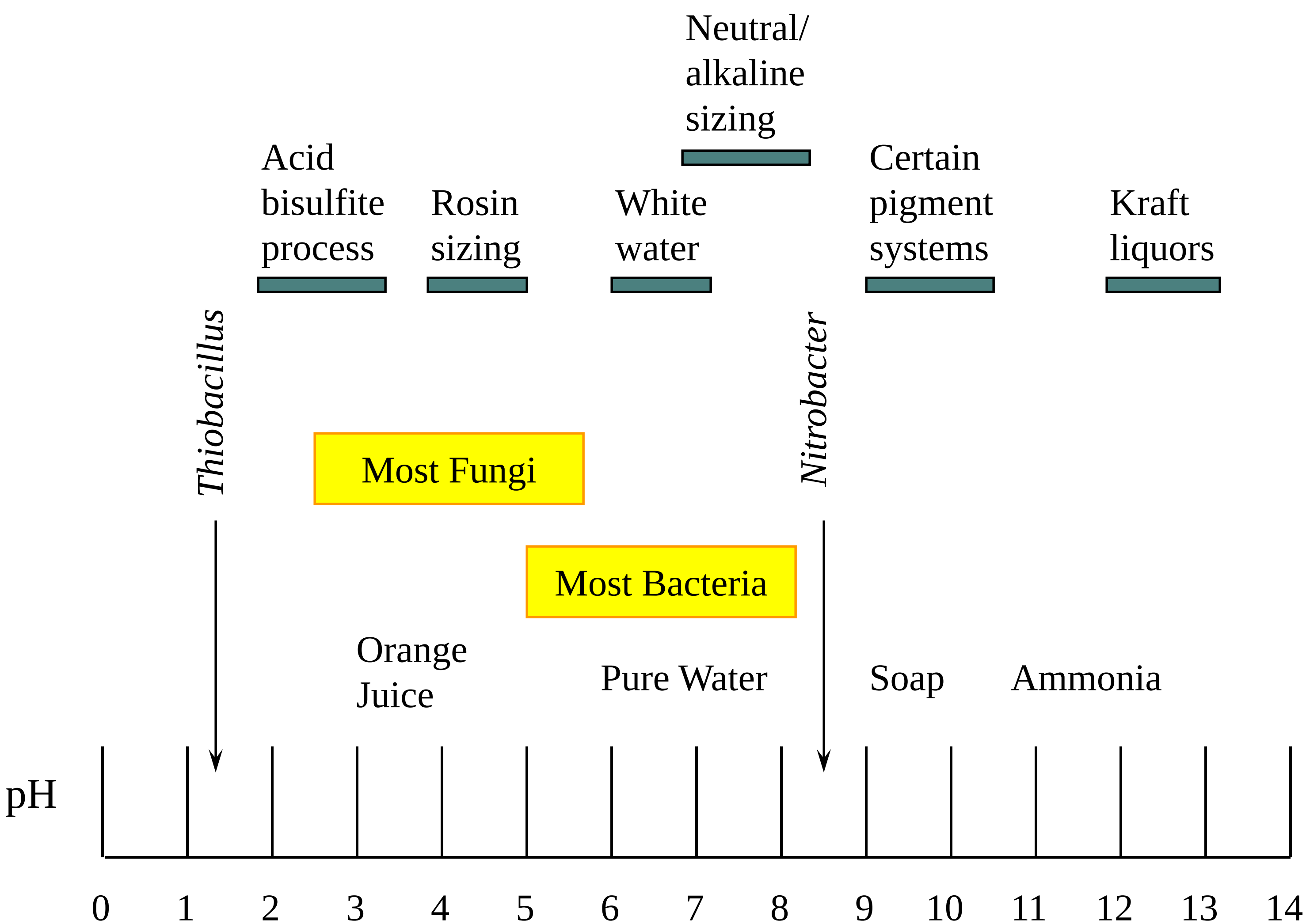
pH

Temperature

Oxygen Levels

Nutrients

pH Preference of Microorganisms

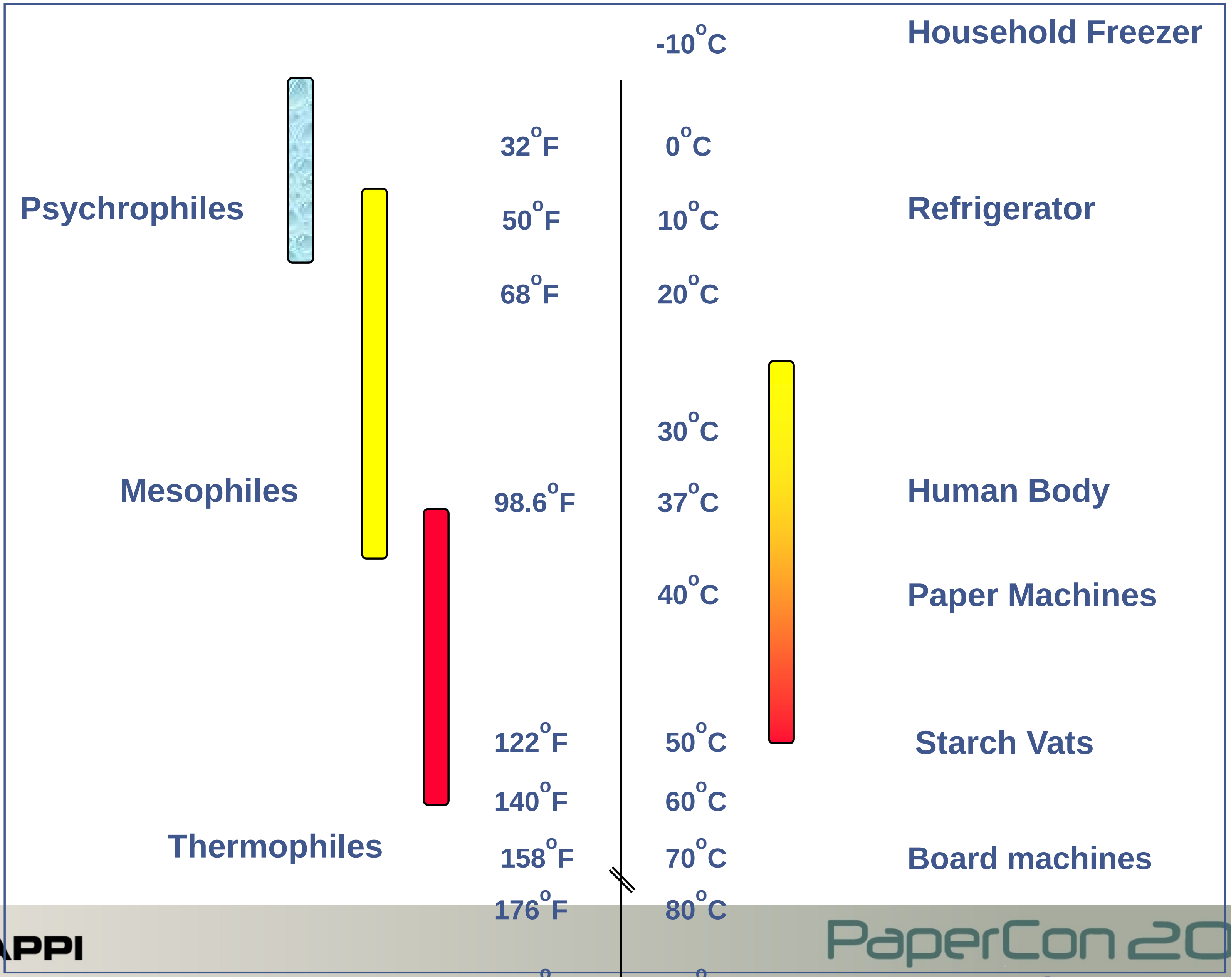


Alkaline Vs. Acid

Affect of pH on microbial growth

	Acid	Alkaline
Typical bacteria	fungi	filamentous
Predominant bacteria	single cell bacteria	single cell
Organisms		
Typical	filamentous bacteria	fungi
Minor	protozoa	protozoa
Organisms	algae	algae
Biocide Needs	1 X	2 - 4 X

Temperature Growth Ranges of Bacteria



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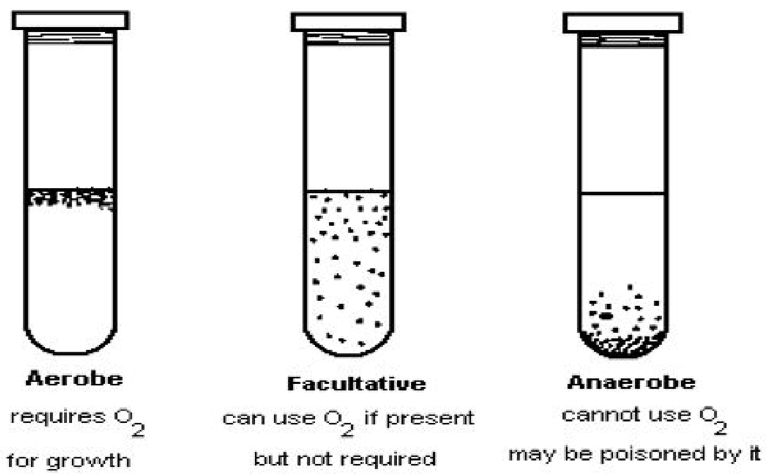
Oxygen Requirements of Microorganisms



Deposit scraped from machine & sheet defect

Deposit from foil pan containing fungi & bacteria

Sheet defect and hole

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Impact of microbes

- Reduced paper quality
  - Rejected paper
  - Loss of customers
- Machine downtime
- Decreased profitability
  - $14,000/hour loss due to downtime on high speed machine based on $700/ton paper price

Why do microbes grow?

- Machines contain:
  - Fluids
  - Diverse microflora
  - Wood fibers, fines, sugars
  - Fillers
  - Various additives

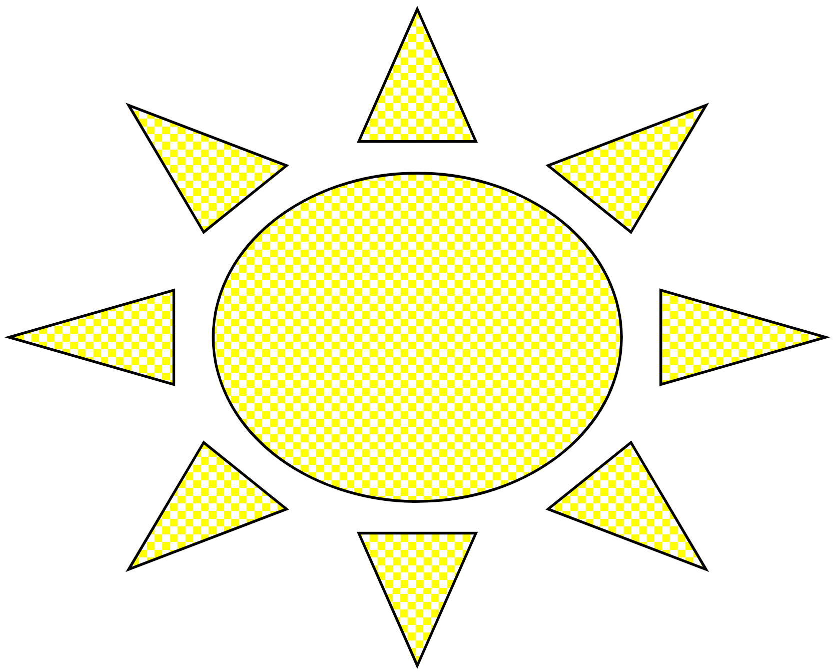
suitable pH ranges

nutrients

surfaces

varied oxygen levels

Nutrients



- Sunlight
- Sugars
- Contaminants
- Cellulose
- Lignin
- Other microbes
- Minerals
- ***Dilute biocides***

i.e. machines contain:

Multiple & ideal niches for growth

&

Food!

Industry changes resulting in increased microbial problems:

- High speed machines
  - Increased surface area at wet end/high misting
- Alkaline pH
- Increased filler levels
- Increased recycle pulp
- Water system closure
- Lighter weight grades
- Boilout interval changes

Detrimental microbial activity

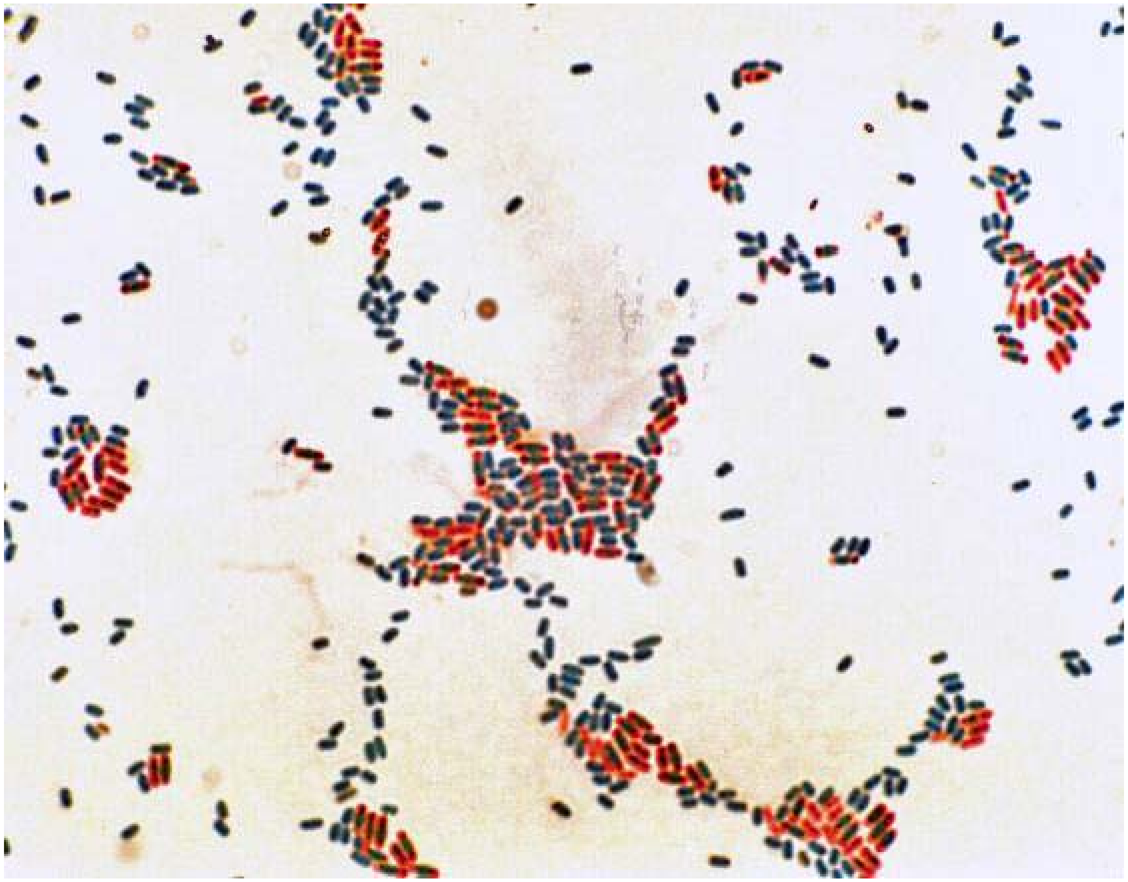
- Deposits
  - Biofilm formation
  - Sheet defects

- Spoilage
  - Less visible often overlooked
  - Frequently occurs in:
    - Chests
    - Additives

Microscopy of deposits

- Brightfield
- Stains
- Phase contrast

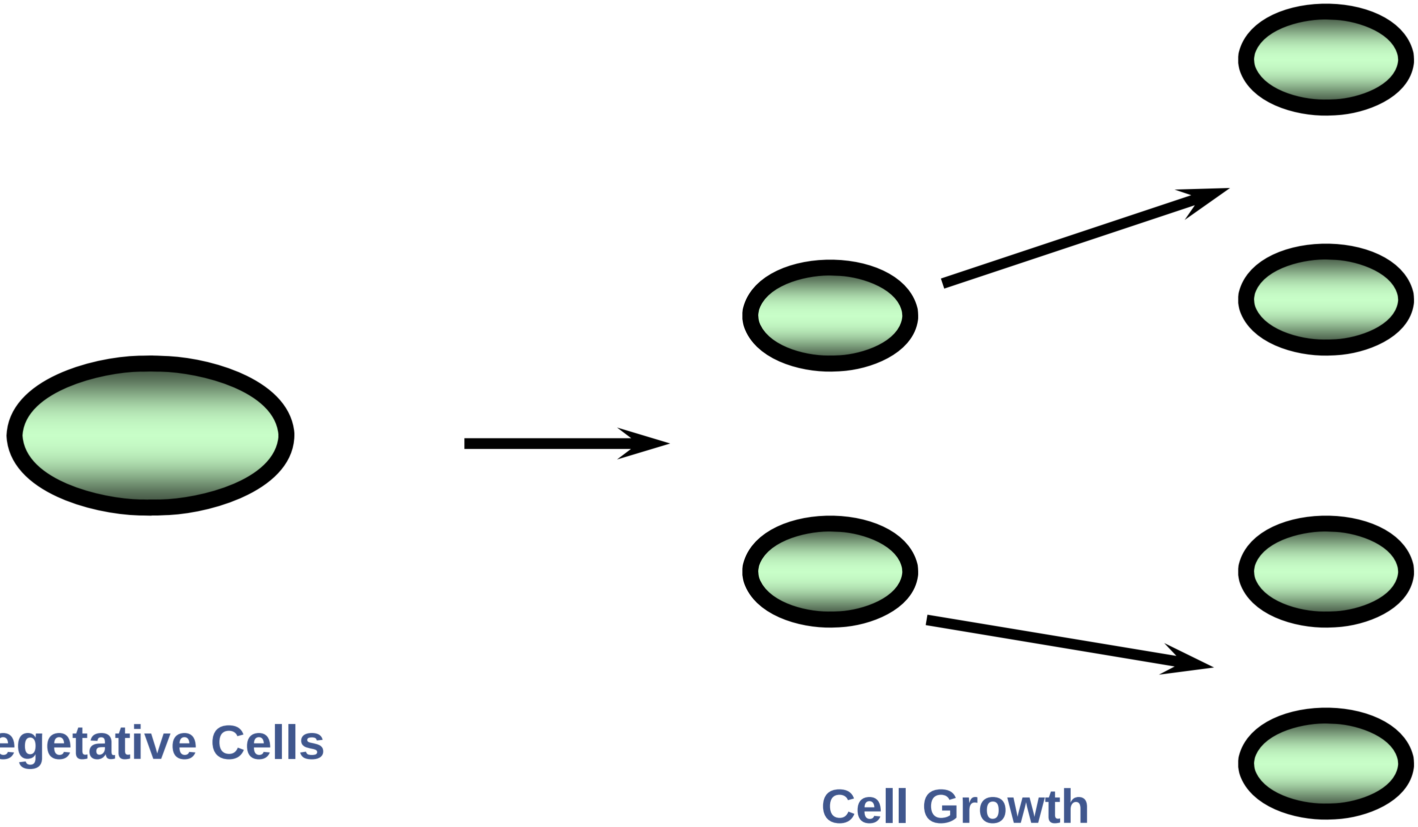
Unicellular bacteria



- Endospore stain of *Bacillus* colony
- Cells rod shaped
- Endospores green (malachite)
- Vegetative cells red (safranin counter stain)

Spores brightfield stained 1000x

Bacterial Growth

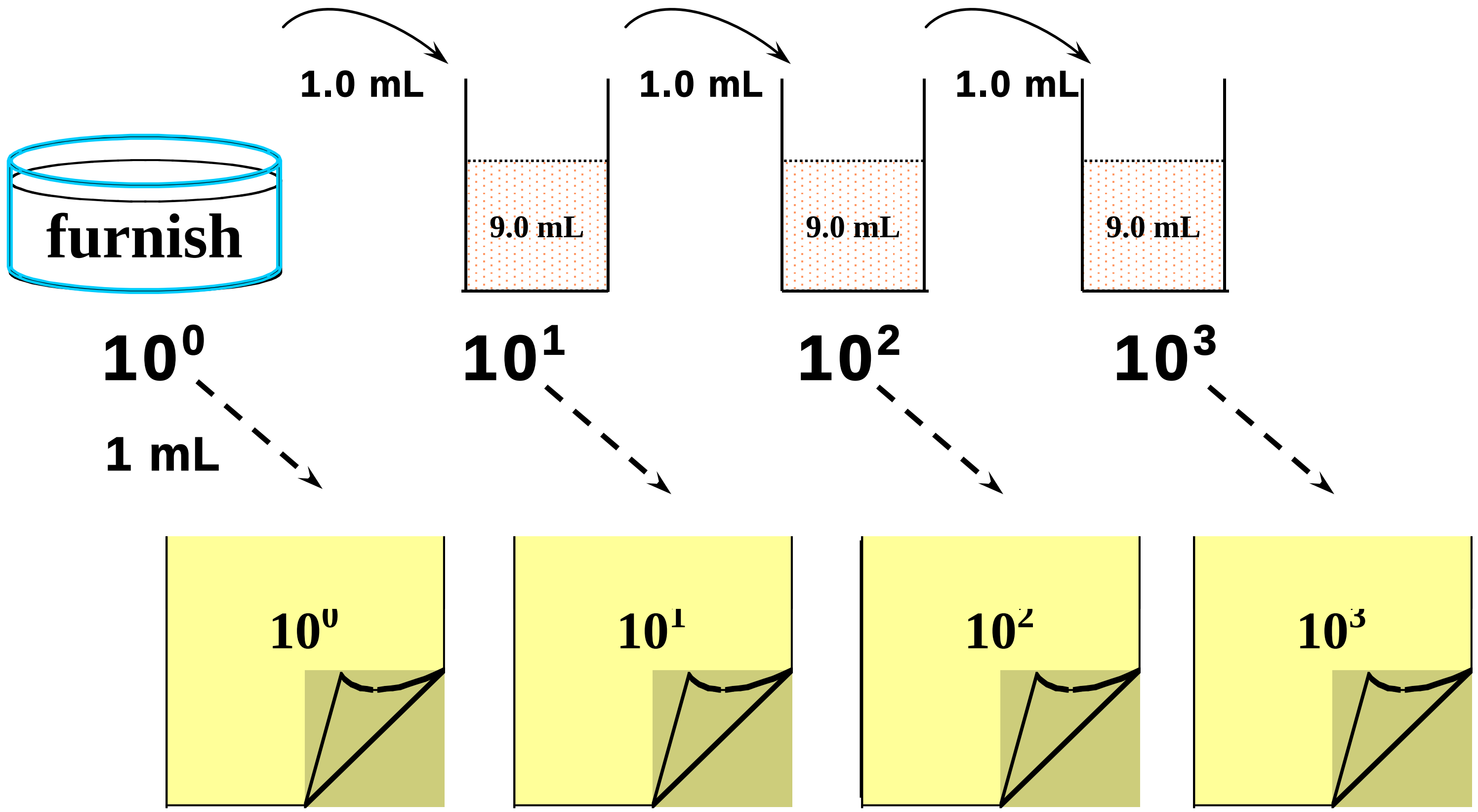


MYTH

- If counts go up from 2 million to 1 million
- YOU ARE IN terrible SHAPE!!!

- Unlike Enron or your bank account there is no statistical significance between 1 million and 2 million

PLATE COUNT



Petrifilm

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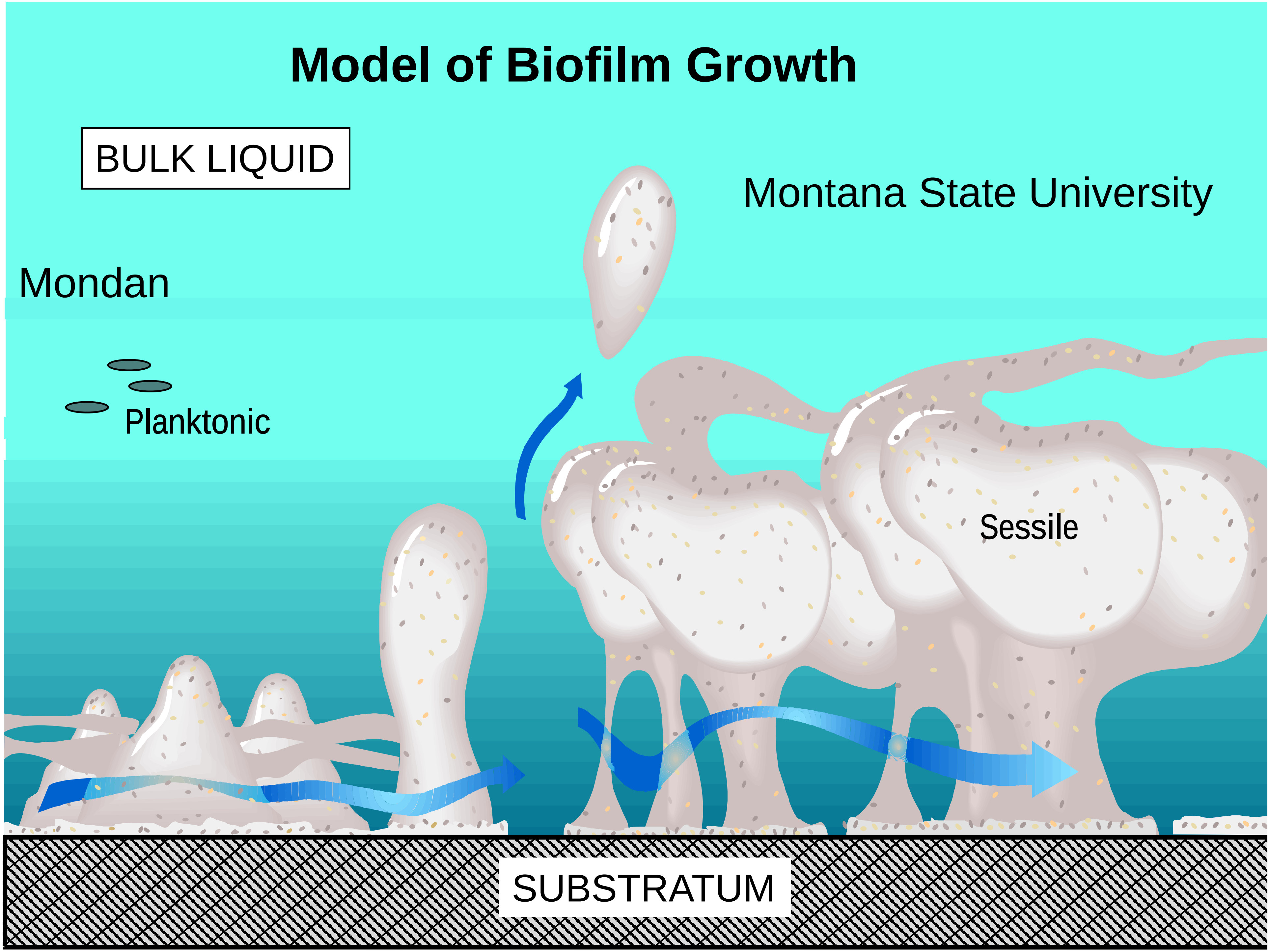
Myth

- With a “total” count you can identify and count all of the microbes in the system

- Not likely
  - many will not grow on the media you use
  - many will not grow in the standard incubation time period
  - many have probably never been identified!


Model of Biofilm Growth
BULK LIQUID
Montana State University
Mondan
Planktonic
Sessile
SUBSTRATUM

Filaments

- Many species
- Form long stringers
- Alkaline to neutral machines

Phase-contrast 400x

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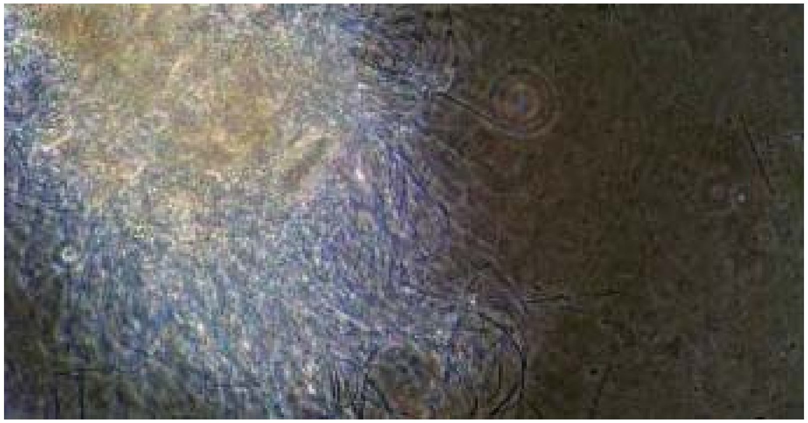
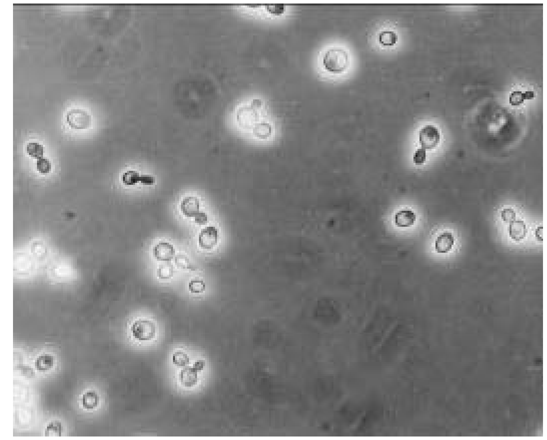
Filamentous bacteria

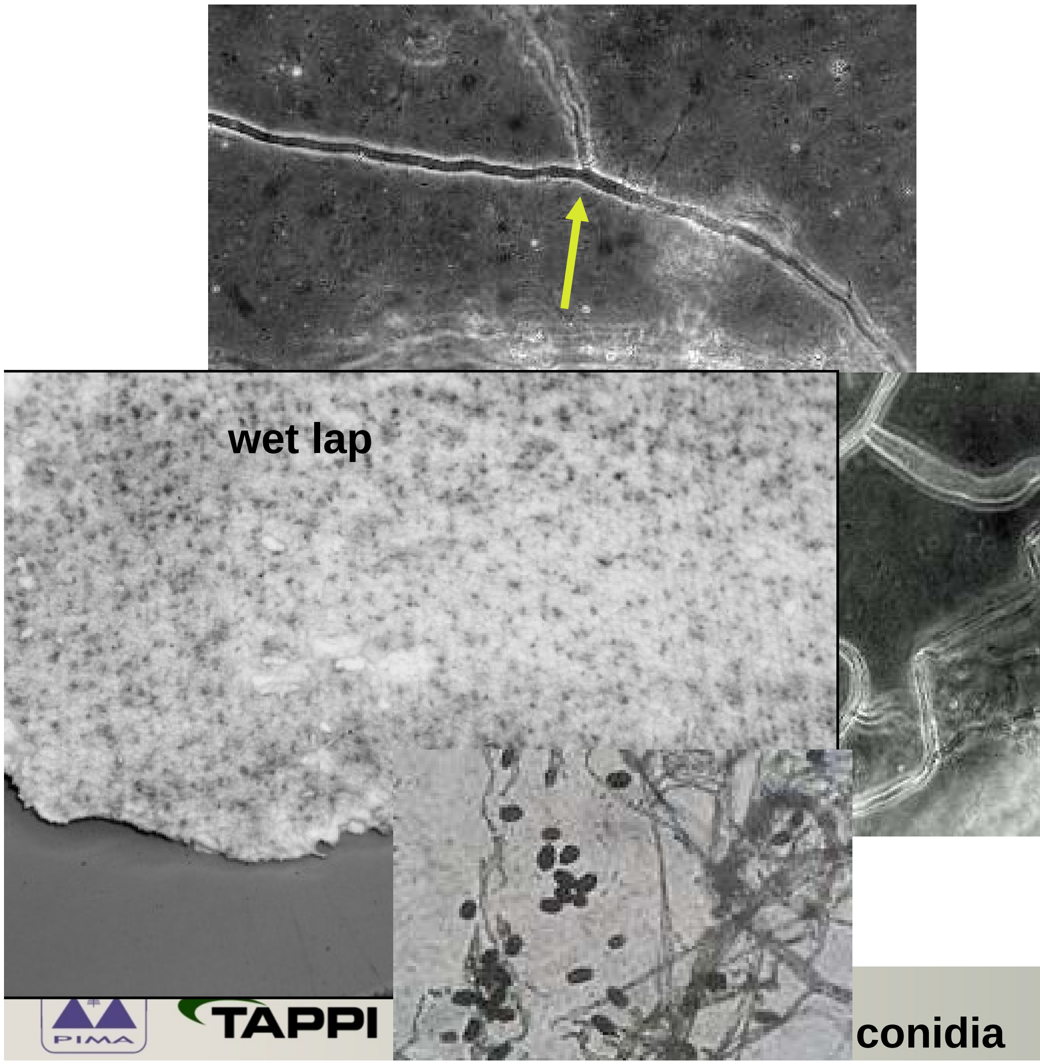


Although “normal” bacteria they form long filaments that mat & trap materials.
Many types have sheath structures that make them difficult to kill

Fungi

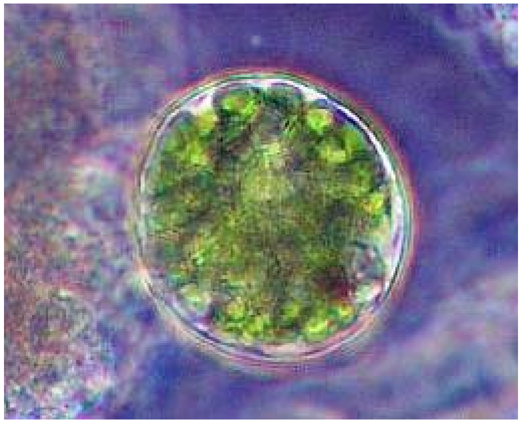
Fungi *AKA mold, yeast*



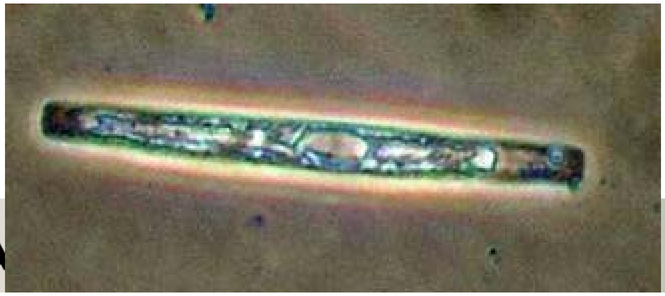


conidia

- Form tough rubbery mats
  - Different from bacteria genetically, respond to different biocides
- Seen in wet lap, recycle pulp, additives, acid machines, or alkaline using biocides with no anti-fungal activity
  - End use product issue
    - Mold-proofing



- Algae enter the mill via inadequately treated water
  - Fresh
  - Run off
  - Out door clarifier
- They need light to grow
  - Produce chlorophyll
- Found around light sources
- Green spots on paper
- Safety hazards



“higher” life forms

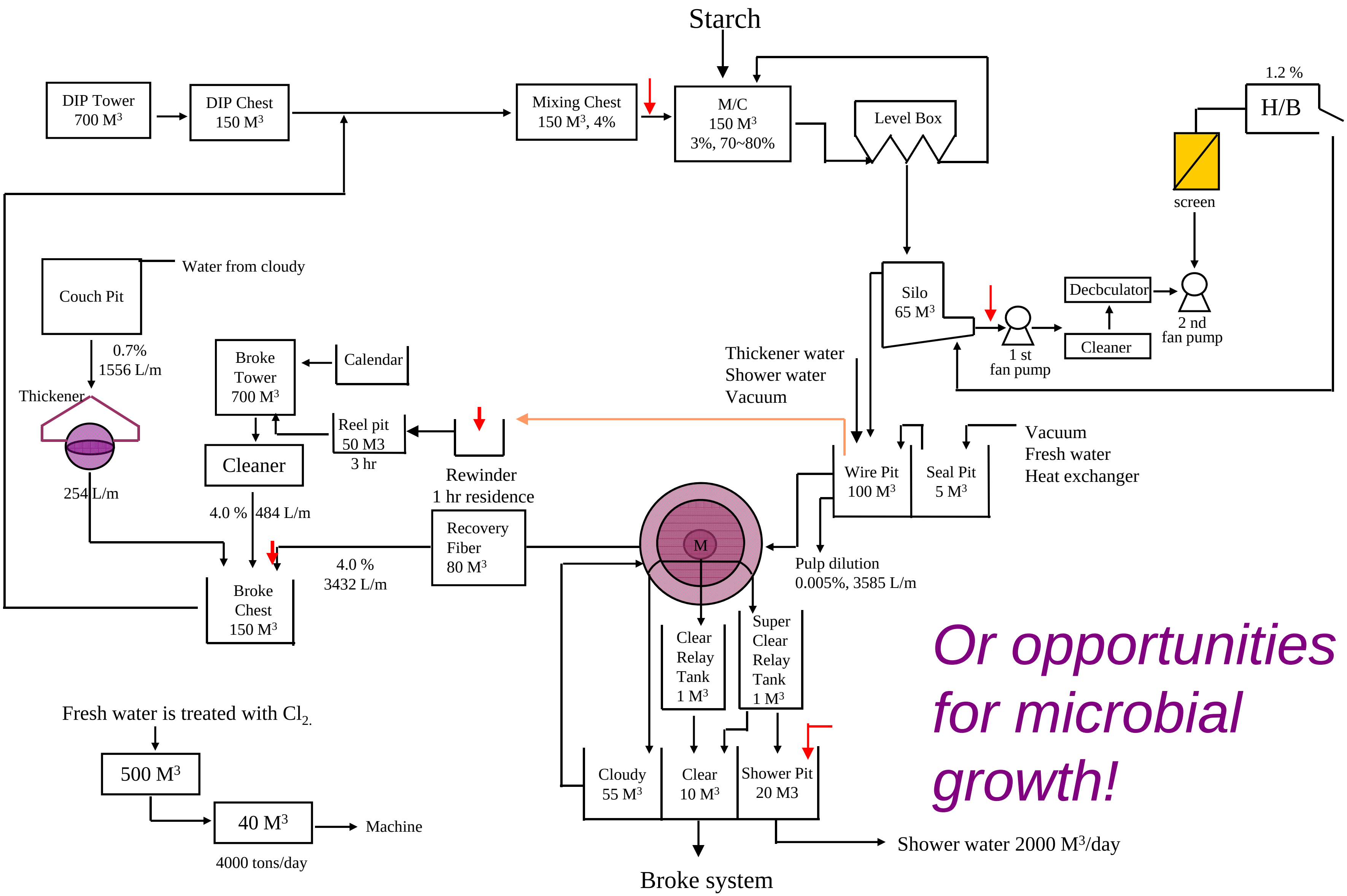
Microbes indicative of inadequate freshwater treatment. Excellent in wastewater treatment not on machine. Highly motile

Videos on request……

Non-microbial deposits

- In addition to wood fibers, fibrils, fines and fillers other materials deposit
- Mimic microbes:
  - Strength additives
  - Uncooked starch granules

Generic machine diagram



Or opportunities for microbial growth!

Fresh water

- All types of microbes enter mill via this route
- Filamentous bacteria, algae, protozoa, worms are so called “fresh water contaminates”
- Critical to control of machine

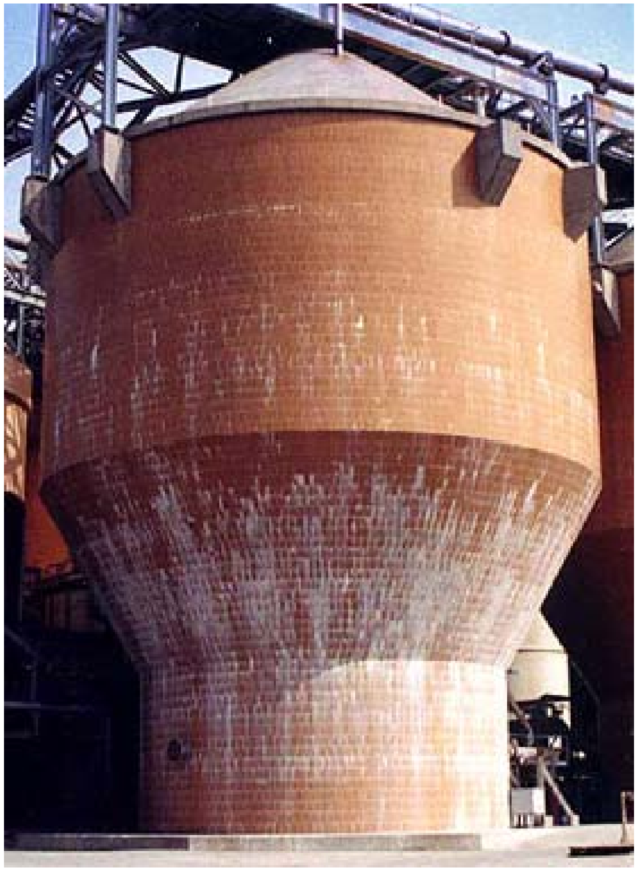
White water system

- Water is recovered and reused on machine
- Water filtered through saveall
- Issue covered in Chapter 5

kidneys of machine

Fiber-Virgin

- Can be sterile if bleached with harsh chemistries
- Then the microbes present come from dilution water
- “Gentler” bleaching chemistries allow organisms to survive and/or thrive
- Recycle water used for dilution can be heavily contaminated

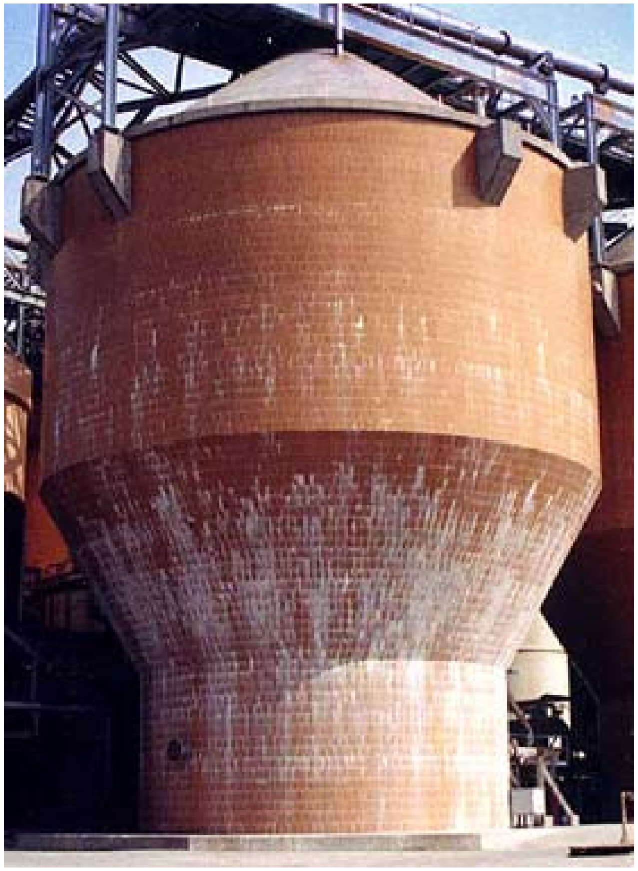


Fiber-Broke Towers

Frequently heavily contaminated

Coated broke is loaded with nutrients to increase microbial activity

Anaerobic spoilage serious problem with pH depression, ORP reduction, fiber strength loss during storage



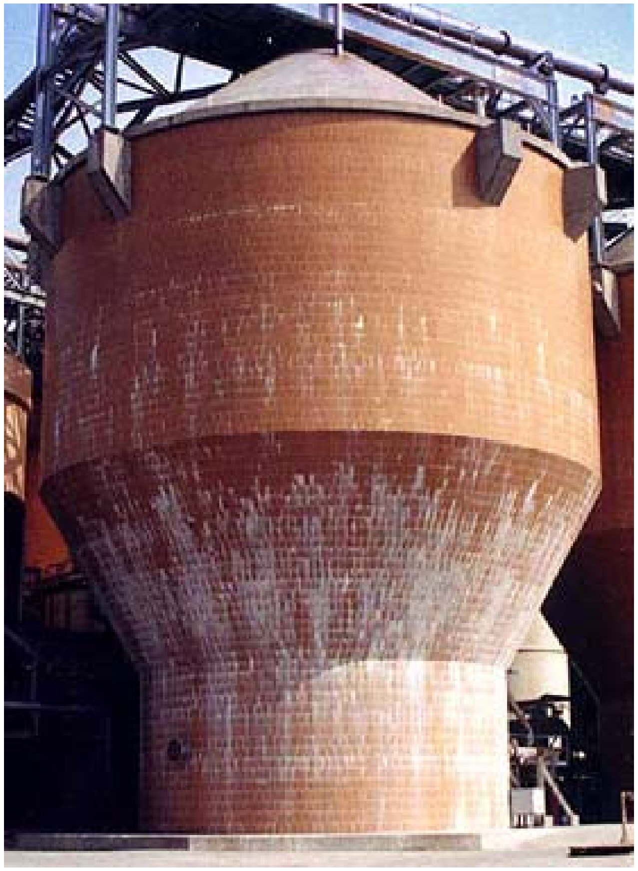
Fiber-Recycle

Often heavily contaminated

Peroxide bleaching may select for bacteria that produce catalase and consume the bleaching chemical

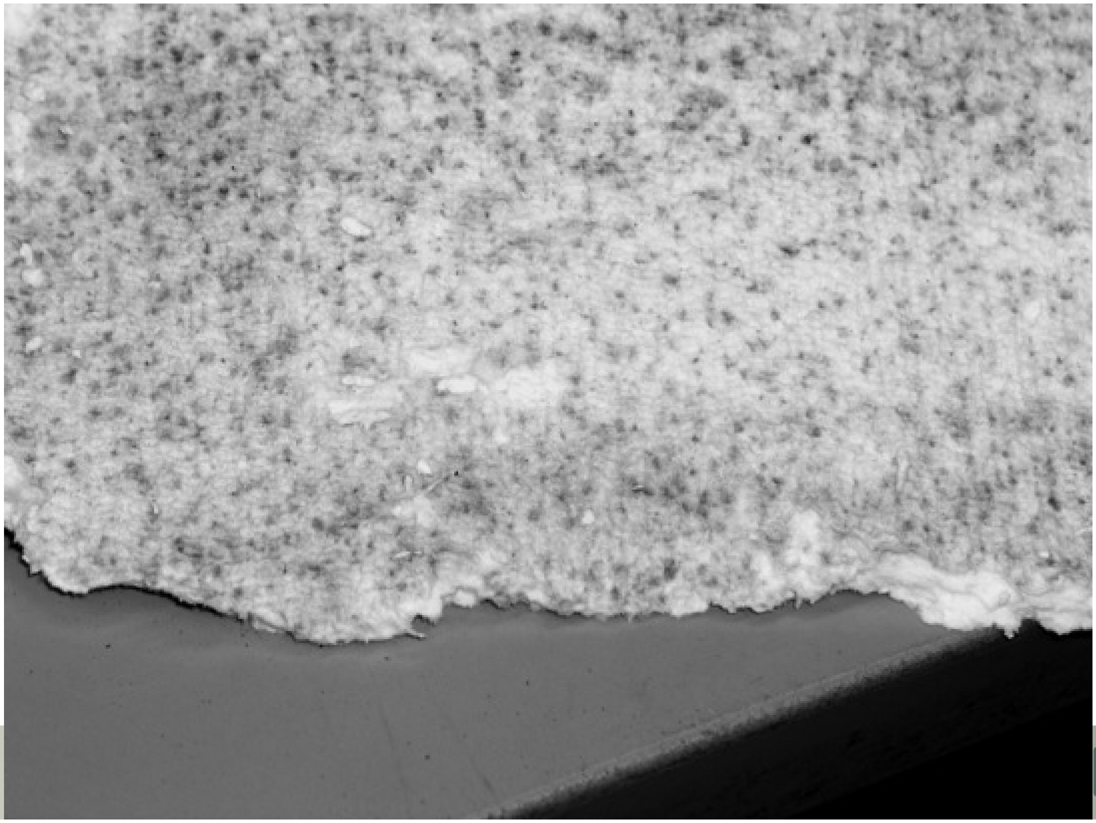
Reductive bleaching chemicals can inactivate common biocides

Long storage times lead to anaerobic bacterial activity



Fiber

- Dry lap
- Wet lap
  - Moisture allows growth



Machine surfaces

- Headbox
- Approach piping
- Frame

- Microbes prefer to attach to surfaces
- Prevention of adhesion critical to deposit control and reduction of sheet defects

Microbes and stickies from a closed machine

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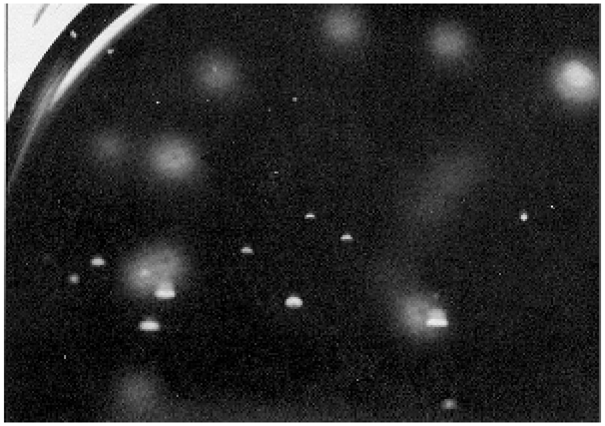
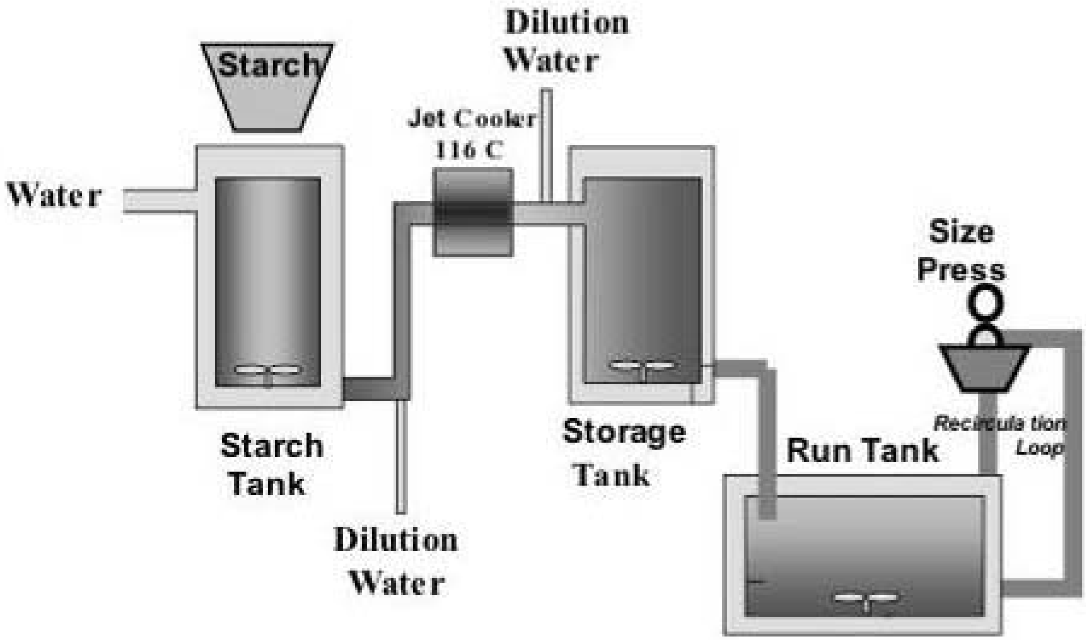
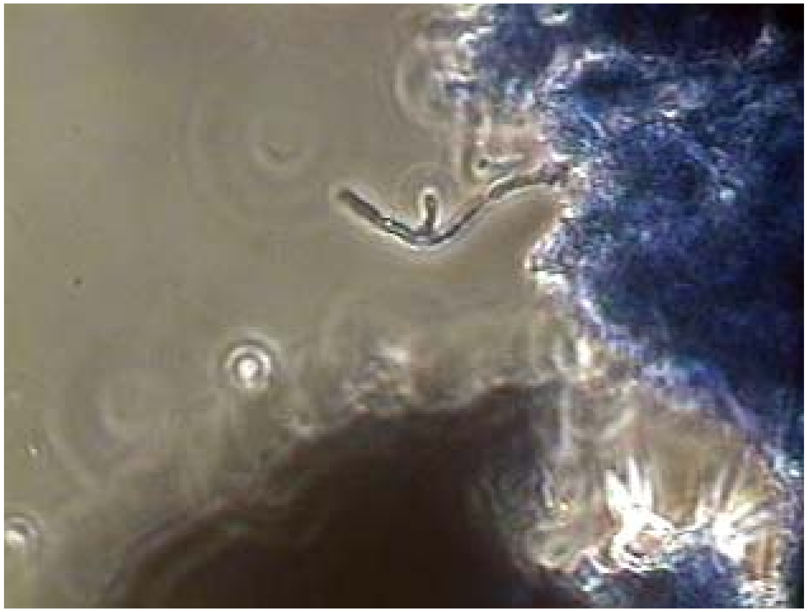
Additives



- Nutrients for microbial growth
- Microbes destroy properties critical for functional properties
- Directly added/Indirectly in system via broke



Additives



- Dyes
- Polymers
- Fillers
  - Clay
  - TiO_2
  - Carbonate
- Protein
- Latex

Summary Chapter 1

- Microbial colonization of machines increases downtime and decreases profitability.
- Understanding the papermaking process and basic microbial physiology is essential in diagnosing and solving problems.
- Biofilms form deposits that lead to sheet defects.
- Microbial spoilage of additives and fibers can alter pH, cause odors, and reduce sheet strength and quality.

Building Leadership Excellence

Chapter 3: Control of Microorganisms in Papermaking Systems: Development of Treatment Strategies

Authors: Lynda Kiefer & Tod Stoner

Presented by: Janet H. Woodward

Buckman

Commitment makes the best chemistry.

May 1-4

PaperCon 2011

Northern Kentucky Convention Center

RETHINK PAPER: Lean and Green

Introduction

- Microbial contamination can cause numerous issues
  - Holes
  - Defects
  - Off-spec paper (e.g. liquid packaging)
- Typical deposits seen in a paper machine are a combination of organics, inorganics, and microorganisms

Key Elements of a Successful Microbial Control Program

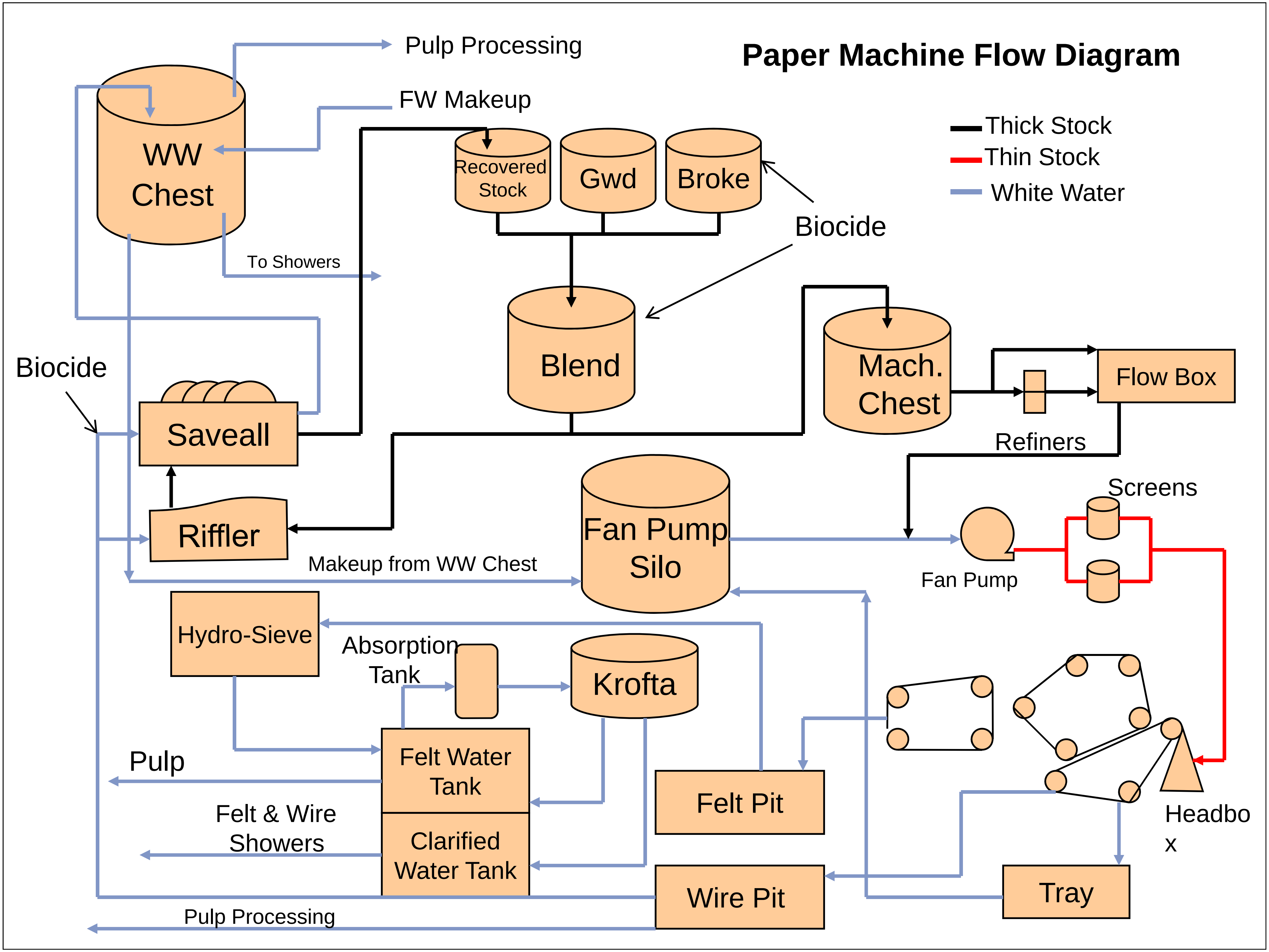
- Engineering survey
- Microbiological survey
- Product selection
- Implementation / Follow-up
- Housekeeping

Engineering Surveys

- Three major systems of concern
  - Water
  - Stock
  - Additives
- Tank/Chests
  - Volumes / capacity / flows
  - Agitation
  - Sampling points

Engineering Surveys, Con't

- Recycle lines / Dead legs
- Freshwater / Dilution water sources
- Temperature and pH
- Process additives
- Current biocide program
- Grades produced



Paper Machine Flow Diagram
Thick Stock
Thin Stock
White Water
Pulp Processing
FW Makeup
WW Chest
To Showers
Recovered Stock
Gwd
Broke
Biocide
Blend
Mach. Chest
Flow Box
Refiners
Biocide
Saveall
Riffler
Makeup from WW Chest
Fan Pump Silo
Fan Pump
Screens
Hydro-Sieve
Absorption Tank
Krofta
Felt Water Tank
Clarified Water Tank
Pulp
Felt & Wire Showers
Felt Pit
Wire Pit
Tray
Headbox
Pulp Processing

Microbiological Survey

- General microbiological survey of machines
  - Visual observations, odors, collecting deposits, gathering production data
- Deposit analysis
  - Microbiological analysis of deposits
    - Can include wet mounts, simple stains, differential stains
    - Looking for type of organism(s) and quantity
  - Chemical analysis (inorganic salts, organics)

Microbiological Survey, Con't

- Micro audit of process waters, additives, stock chests
  - pH and temperature should be noted
  - Plating for aerobic/anaerobic bacteria, fungi, other problem-causing organisms

Paper Machine Deposit Analysis

Inorganics	Organics	Biological
Calcium	Fatty acids	Bacteria
Aluminum	Rosin acids	Fungi
Silica	Machine oils	Algae
Iron	Cellulose	Protozoa
Barium	Lignin	Nematodes
Clay	Dyes	
	Polymers (size)	

Product Selection

- Microbiocides
  - Biocide (slimicide; quick killer)
    - Kills microorganisms
    - Used for wet-end applications
  - Biostat (preservative)
    - Inhibits reproduction; doesn’t necessarily kill
    - Used for stock, broke, and additive preservation
  - For an effective biocide program, have to consider:
    - Product
    - Contact time
    - Concentration

Product Selection

- Regulatory requirements
  - Environmental Protection Agency: All microbiocides must be registered
  - Food and Drug Administration: Four allowances that affect microbiocides used in the production of paper/board that may contact food
    - 21 CFR § 176.300: Wet-end applications
    - 21 CFR § 176.170: Dry-end applications where paper/board may contact aqueous or fatty food (strictest regulation)
    - 21 CFR § 176.180: Dry-end where paper/board may contact dry food (e.g. cereal boxes)
    - 21 CFR § 170.105: Adhesive applications

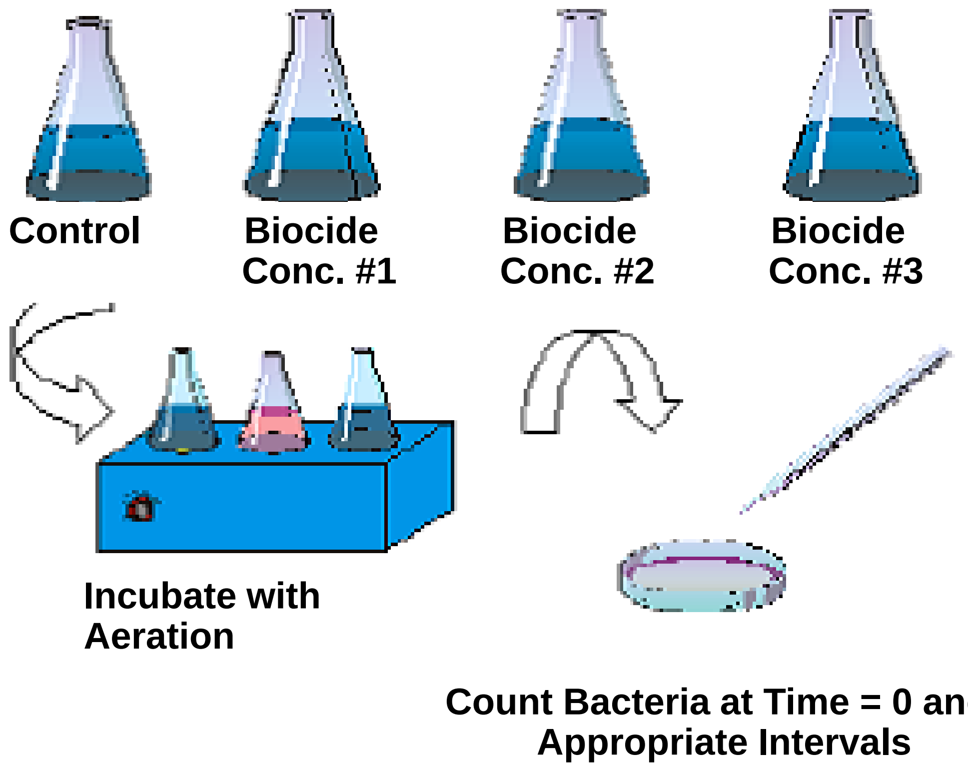
Product Selection

- Regulatory requirements
  - Parallel regulations in Canada and Europe
- Safety / Environmental
  - MSDS
  - Discharge permits

Product Selection

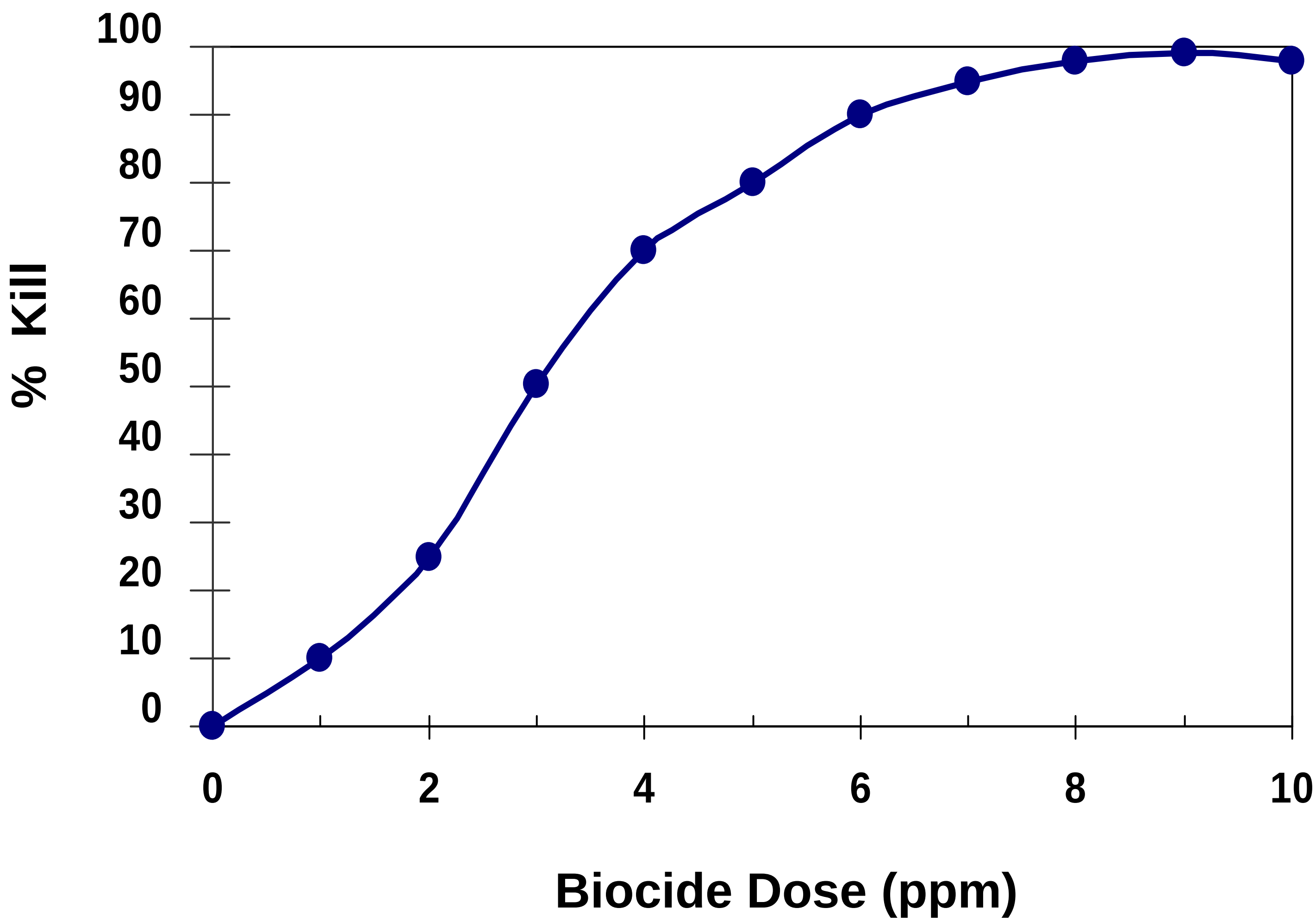
- Oxidizing biocides
  - Hypochlorous acid, hypobromous acid, chlorine dioxide, chloramine chemistries
  - May be “stabilized”; e.g. hydantoins
  - Typically applied on a continuous basis
- Organic biocides
  - Organosulfurs, organobromines, cationics, isothi azolones, and aldehydes
  - Typically applied on an intermittent dosing
- Non-biocidal technology
  - Enzymes, biodispersants, and adjuvants

Lab-Based Bioassay Screening
(Biocide Dose Response Study)



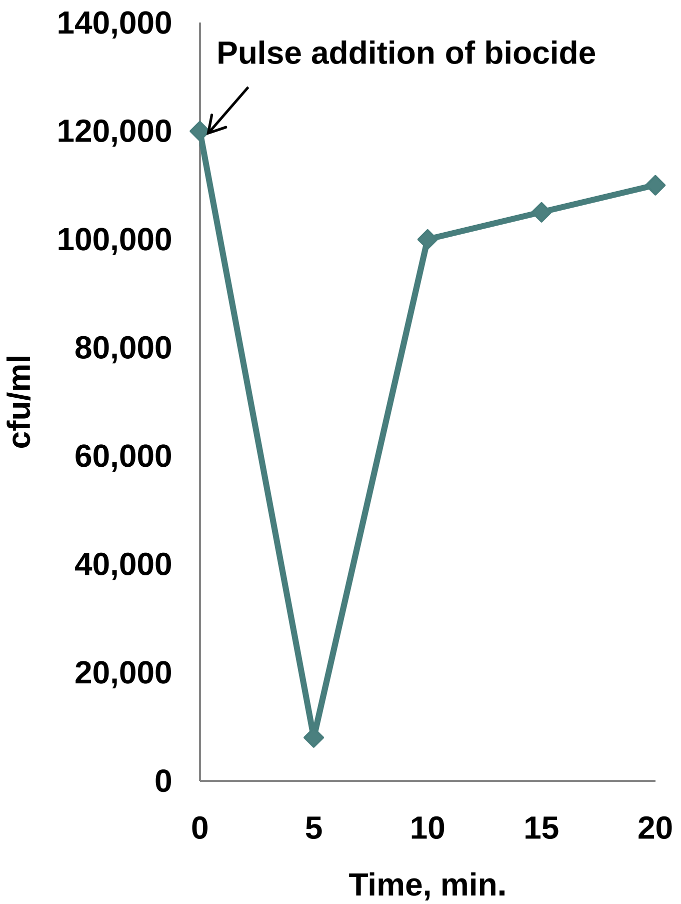
$$\% \text{ Kill} = 1 - \frac{\text{Treated Count}}{\text{Control Count}} \times 100$$

Biocide Dose Response Curve



Field Evaluation of Biocides
(Biocide Pulse Test)

1. Biocide is pulse-fed (slug dosed) to a tank to achieve target dose immediately
2. Bacterial counts taken over time with no further biocide added
3. See effect of dilution



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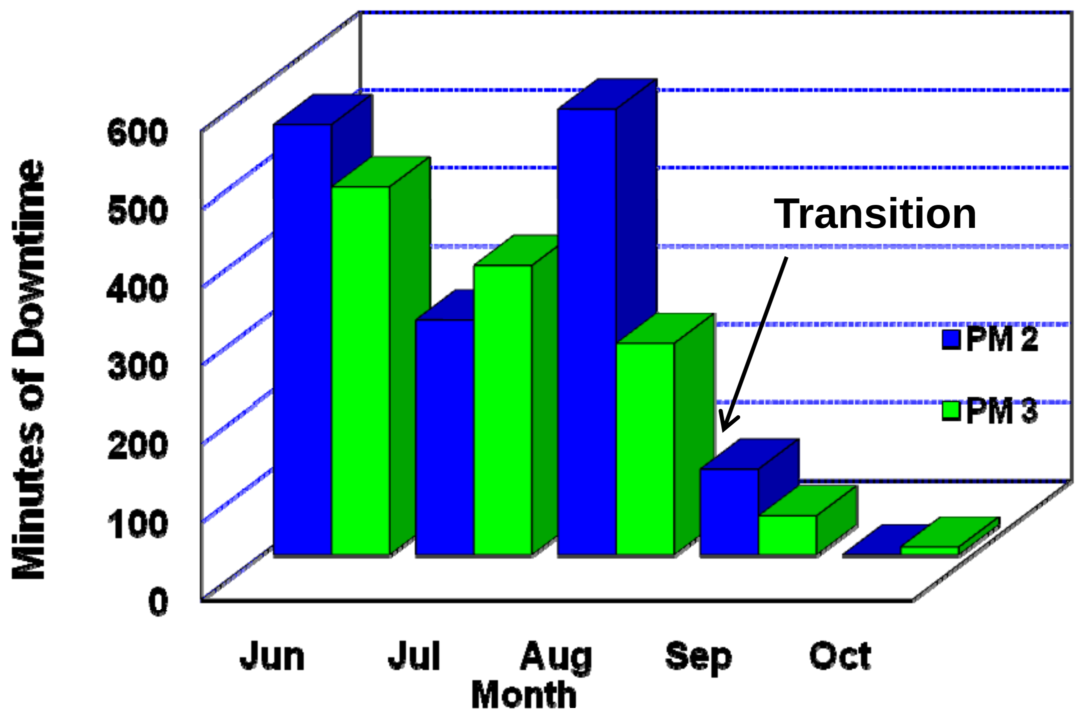
Monitoring and Follow Up

- Perform routine monitoring
  - Machine runnability, quality, defects, deposits, etc
- Compare new program to old one

Machine Downtime Due to Wash-ups



Summary

- Monitor microbiological contaminants throughout the process
  - Utilize chemical analyses as needed
- Define biocide treatment with lab studies and confirm with field testing
  - Evaluate best options
- Follow biocide manufacturers recommended dosing and safety information
- Follow up with routine monitoring
  - Do not allow microbiological problems to get established; they are easier to prevent than to remove

Effect of Water Recovery & Reuse on Microbial Activity

Linda Robertson

TAPPI Monograph: Microorganisms in Papermaking

Chapter 5

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Independent consulting for industry

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Water

- 21st Century severe competition for planet's resources
- Historically mills sited near abundant water
- Water critical:
  - Pulping,
  - Chemical dilution
  - Process makeup, etc.
- Treatment of incoming and exiting water expensive

Costs of an Open System

- water treatment
- chemicals loss
- fines loss
- **energy**

Optimizing Water

- Conservation
  - Example: minimize water loss by shutting off continuously running hoses
- Water Reuse
  - Reclaim water from one source and use it in another without making changes to water quality
- Water recycling
  - Improve the water quality before reuse
  - Becomes more expensive

Degree of closure

- Difficult to define
  - zero effluent
  - tons or gallons of fresh water/ton of paper
- Grade specific
  - fine vs. board mill
  - many board mills zero effluent
- Water use
  - 1993 Panchapakesan
    - <19 m^3/t good
    - 19-30 m^3/t average
    - >30 poor
  - 2005 fine papermachines
    - 12-15 m^3/t common
    - 9-11 m^3/t frequent
    - China reports 5-6 m^3/t

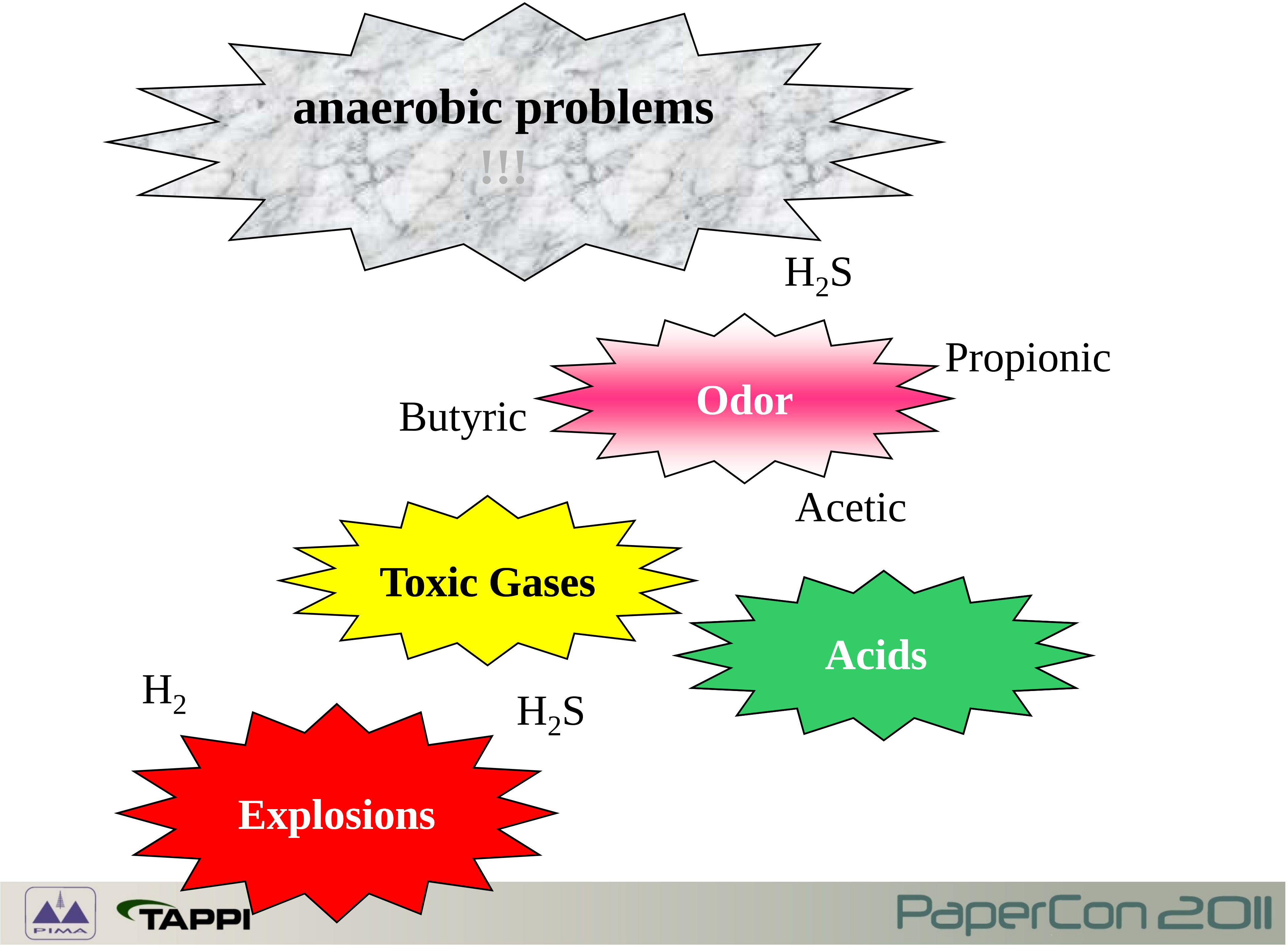
Changes in operational practices increase microbial problems:

- Water system closure
  - Noxious chemical cycle up
  - Nutrients cycle up
  - Stagnant chests
- Neutral to alkaline conditions allow anaerobes to thrive
- Increased use of recycle fiber
  - Coatings on paper
  - “Extra” nutrients and contaminants
  - “Poorer’ quality recycle fiber
- Large chests constructed with long dwell times
- Reduced biocide programs due to cost constraints

Freeze dried/cycled up water

Water Analysis	In ppm:	
Inductively Coupled Plasma Argon Analysis:		
Sodium	81	900
Calcium	46	440
Magnesium	5.4	58
Aluminum	1.5	15
Iron	< 0.1	0.3
Potassium	2.5	28
Manganese	< 0.1	0.5
Phosphorus	< 0.1	0.5
Sulfur	43	470
Ion Chromatography:		
Chloride	53	550
Nitrite (NO_2)	< 2.9	< 2.9
Nitrate (NO_3)	< 2.9	< 2.9
Sulfate (SO_4)	120	1200
COD (Filtered)	430	4100

As received | Concentrated


anaerobic problems
!!!
H_2S
Propionic
Butyric
Odor
Acetic
Toxic Gases
Acids
H_2
H_2S
Explosions
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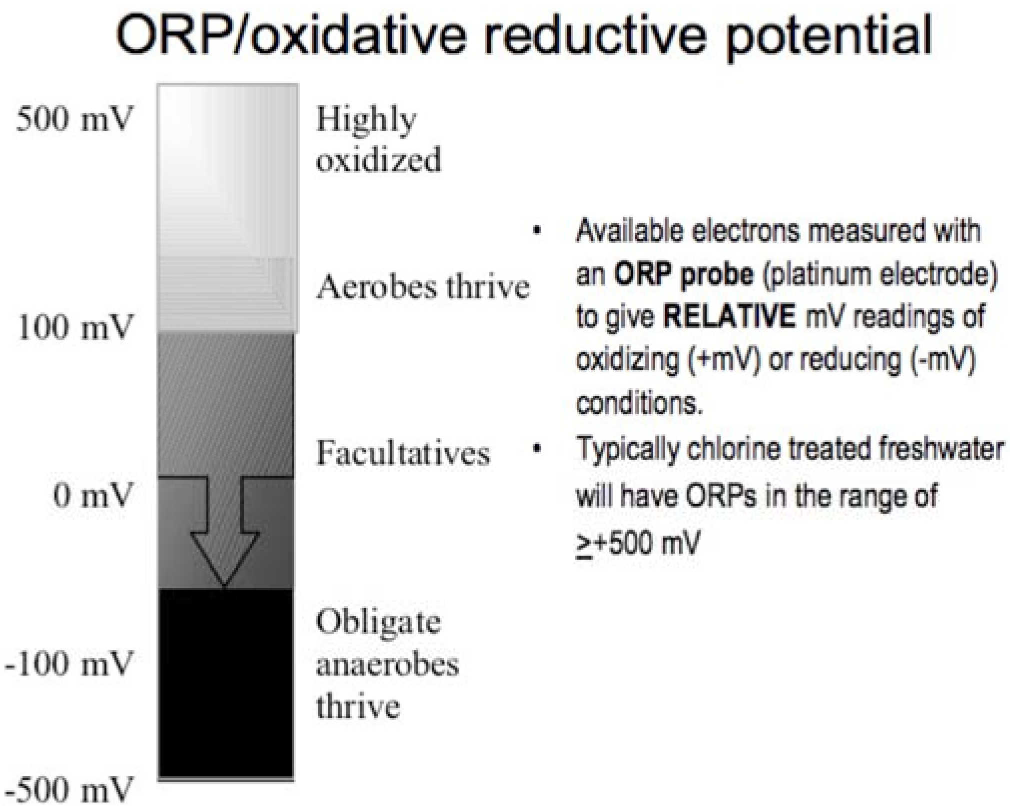
Mill Safety Issues

- H_2S & H_2 have caused deaths of workers in industry
  - Known problem
  - More serious in recycle systems
- Hydrogen Sulfide
  - Detected by the human nose at 0.1 ppm
  - 3 ppm the odor is objectionable
  - 10 ppm health affects are noticeable (headaches)
  - 100 ppm people lose their ability to smell.
  - By 300 ppm life threatening.
  - 1000 ppm the person goes into irreversible respiratory failure
  - Found at 55 ppm in gypsum mill
  - Linerboard 45-300 ppm over walk space & chests

ORP/oxidative reductive potential

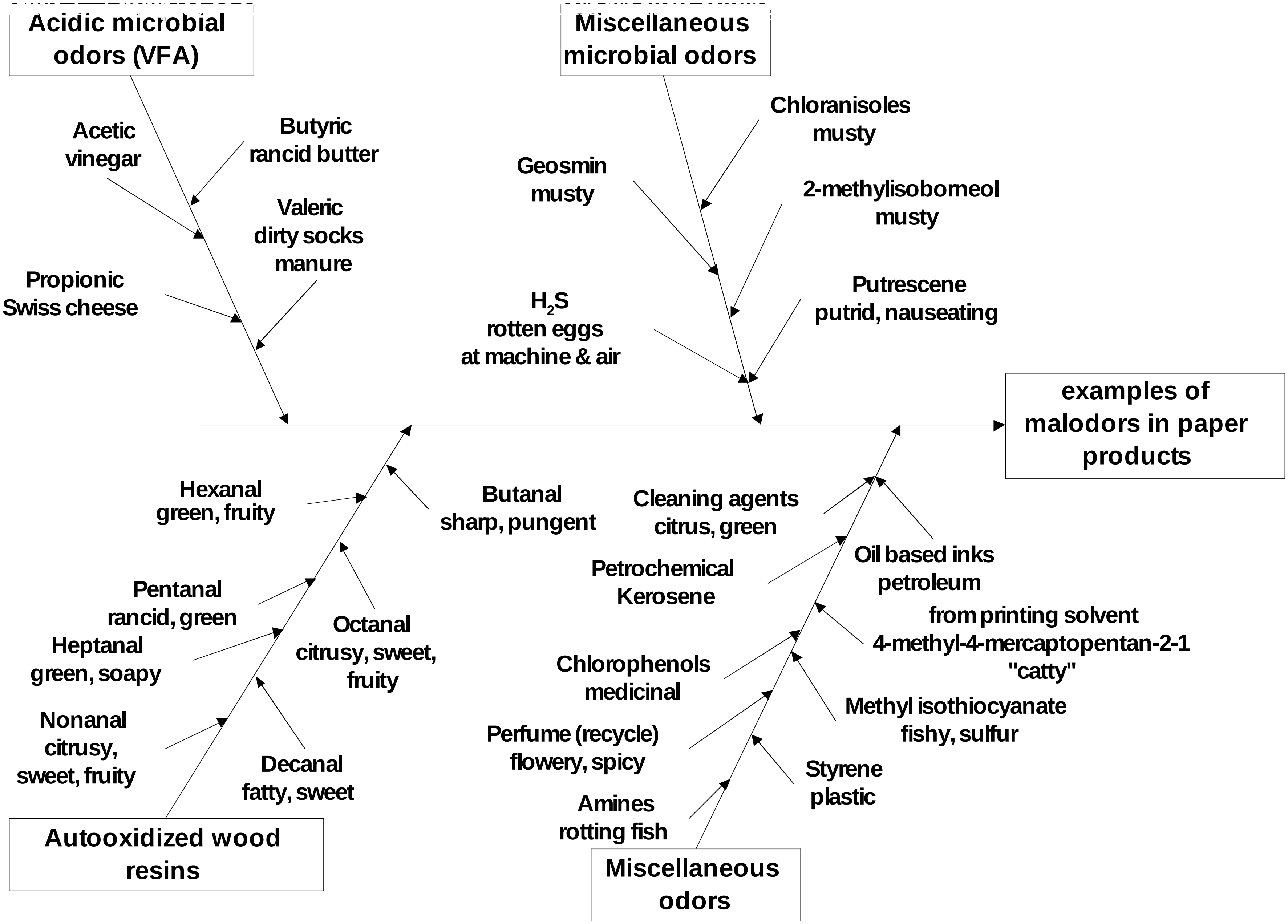


- Available electrons measured with an **ORP probe** (platinum electrode) to give **RELATIVE** mV readings of oxidizing (+mV) or reducing (-mV) conditions.
- Typically a fine paper **oxidizing program** will have ORPs in the headbox in the range of +200 to +300 mV
- Closed reductive systems will be lower

RPTA & IPST
Survey of board mills

- Corrosion
  - *Not as severe as predicted*
- Presence of corrosion elements
  - *didn't correlate to:*
    - extent of corrosion
    - degree of closure

- Minimize Problems by:
  - *Treating Recycled water*
  - *Upgrading construction materials*


Acidic microbial odors (VFA)
Acetic vinegar
Butyric rancid butter
Valeric dirty socks manure
Propionic Swiss cheese
Miscellaneous microbial odors
Chloranisoles musty
Geosmin musty
2-methylisoborneol musty
Putrescene putrid, nauseating
H_2S rotten eggs at machine & air
examples of malodors in paper products
Hexanal green, fruity
Butanal sharp, pungent
Pentanal rancid, green
Octanal citrusy, sweet, fruity
Heptanal green, soapy
Nonanal citrusy, sweet, fruity
Decanal fatty, sweet
Autooxidized wood resins
Cleaning agents citrus, green
Oil based inks petroleum
Petrochemical Kerosene
from printing solvent 4-methyl-4-mercaptopentan-2-1 "catty"
Chlorophenols medicinal
Methyl isothiocyanate fishy, sulfur
Perfume (recycle) flowery, spicy
Styrene plastic
Amines rotting fish
Miscellaneous odors

White water system

- Water is recovered and reused on machine
- Water filtered through saveall

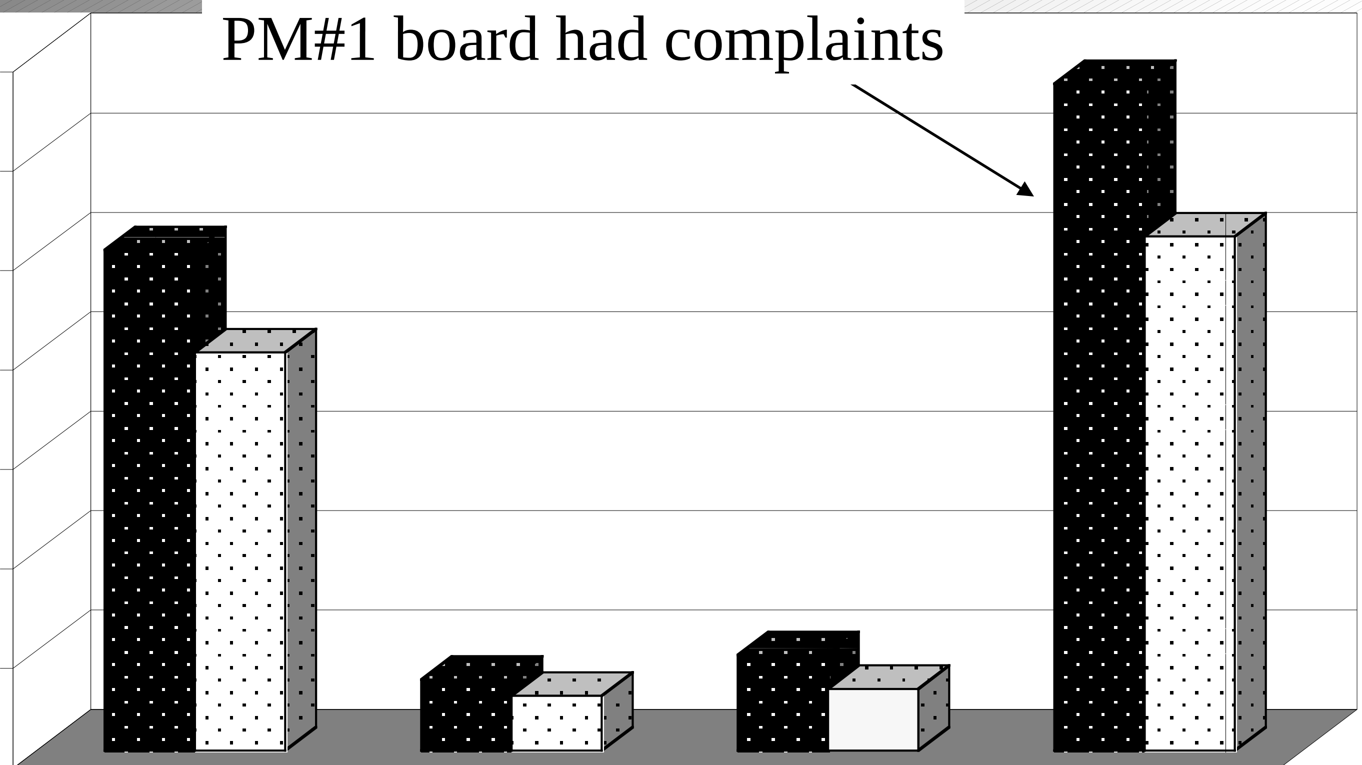
Microbiologically

- Treated whitewater for pulp dilution excellent
- Stagnant recovered water for dilution a serious problem
- Treated whitewater for starch makeup is still a problem due to endospores and amylase producers

Volatile Fatty Acid Odor Case Study

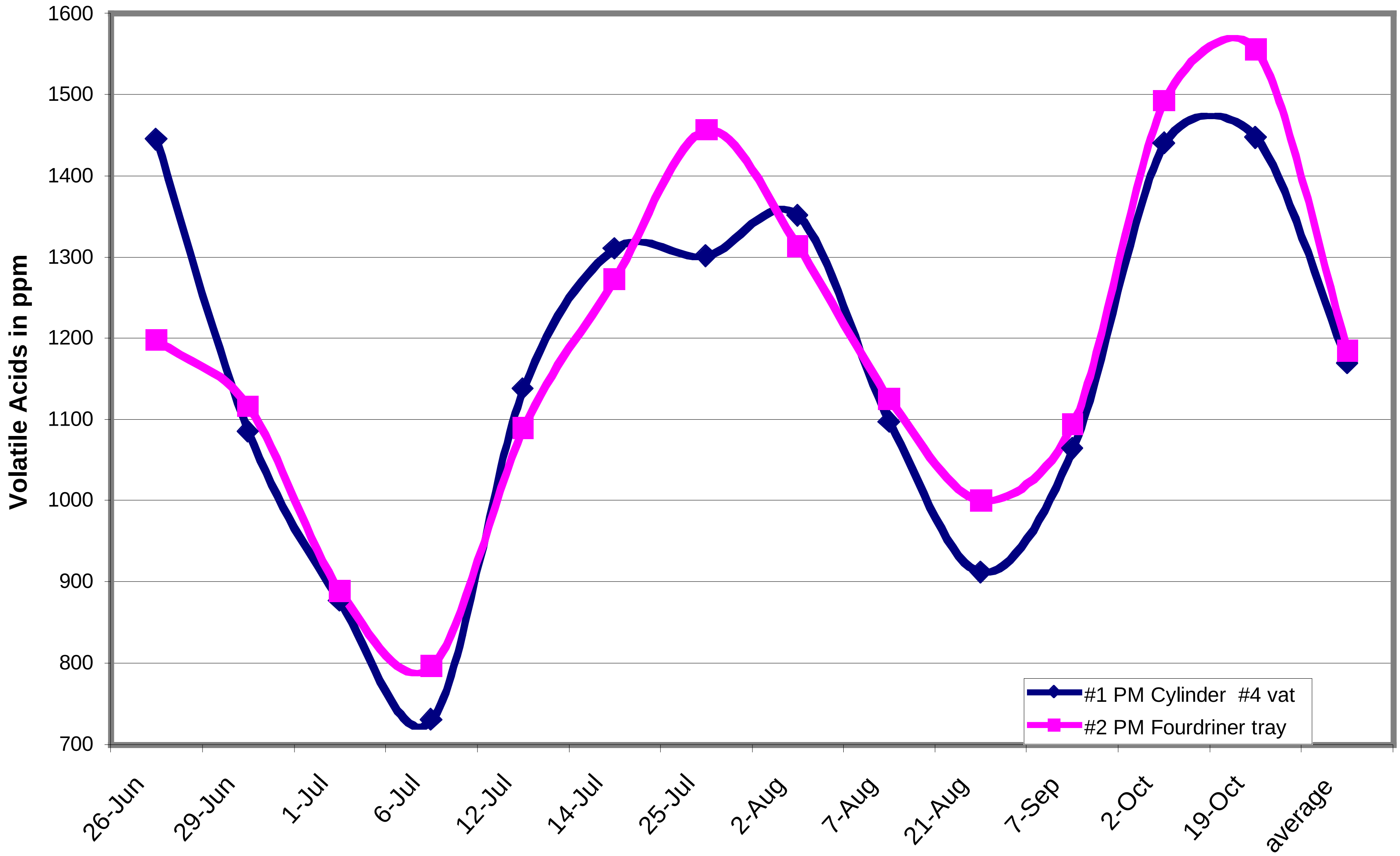
- Recycle mill with 2 machines with same furnish, water and additives
- Odor increased when water discharge decreased from 946 m^3/day to 340 m^3/day
- Paperboard from cylinder machine (#1 PM) had foul aroma
  - heavyweight stock (535 g/m^2) with a moisture content averaging 6%
- Paperboard from Fourdrinier (#2 PM) acceptable
  - lighter weight board (150-g/m^2) had slightly lower moisture content (5%)

VFA levels in finished board made from each machine



	acetic	propionic	butyric	total VFA
PM#1 Board	1006	142	192	1340
PM#2 Board	800	110	124	1034

VA levels in process waters conducted at the mill site for 5



VA & VFA matched set comparison of process fluids and board

	volatile acids*	"total" VFA**	Acetic**	Propionic**	Butyric**
PM#1 vat cylinder water	2025	1895	1400	160	335
PM#2 tray water	2088	1860	1370	160	330
PM#1 Board	no data	2545	1930	175	440
PM#2 Board	no data	1530	1140	130	260
*HACH method		**GC method			

Reported as parts per million

Key Discoveries

- Board formed on #1 machine had higher VFA concentrations and odor complaints
- Both machines had:
  - Similar populations
  - Similar ORP Ranges
  - Similar VFA levels in the fluids
  - Similar biocide programs
- Moisture content:
  - #1 is 6%
  - #2 is 5%
- Less VFA is volatilized during drying in the high odor paperboard

VFA Case Study

- Understanding machine operations, microbial metabolism and how this influenced odor in the finished board led to changes in biocide program
- Lower VFA targets needed on machine producing the heavyweight board due to higher carryover of VFA.
- The problem-solving approaches and program changes used at this mill nearly eliminated odor complaints.

Biocides and closure

- Certain biocides may not function as well under changed ORP conditions
  - Isothiazolins/DBNPA/etc.
- Oxidant demand can increase dramatically
  - Chlorine/bromine/and other oxidants
- Odiferous biocides like carbamate may be more noticeable
- Tolerance or resistance may develop more rapidly
  - Glutaraldehyde/quaternary ammonium compounds/peroxides/isothiazolins/etc.
- Requires knowledge to manage and avoid problems

Water Sources

- Well, reservoir, river
  - Normally easiest to treat and purest
  - Use for chemical dilution---nutrients: protein starch
- Water reused within mill
  - Known quantity
  - Best used for pulp dilution, showers
- Biologically stabilized water
  - Reduces sugars/BOD
  - Reduces VFA odor on machine
  - Purple water in California
- Reverse Osmosis
  - Closest to freshwater

Summary

- Water Reuse is achievable with proper planning
- This avoids
  - Anaerobe problems
  - Odors
  - Hazardous gases
- Biocides
  - may need to change type
  - may need to increase dose

Chapter 6: Boilouts – Chemical Cleaning Programs

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Commitment makes the best chemistry.

PIMA TAPPI PaperCon 2011

Definition - Boilout

- Noun: A chemical cleaning solution composed of alkaline, acid or enzymatic cleaning agents in combination with penetrants, dispersants and water

- Verb: A periodic chemical cleaning of the papermaking system under controlled pH and temperature conditions

Goals of a Boilout

- Remove organic and inorganic build-up in and on process equipment, tanks, lines, filters, chests etc
- Remove deposits that can break loose and cause holes and breaks
- Clean the forming fabric
- Housekeeping = Runnability
  - Regular boilouts combined with simple housekeeping measures can account for *up to 60% of the overall success of a deposit control* program

Benefits of a Boilout

- Prevent premature buildup of microbiological deposition
  - Reduce costs associated with slime control program
- Prevent corrosion pitting
  - Anaerobic activity underneath scale, stock, and biofilm cause microbiologically induced corrosion
- Control/eliminate scale formation
  - Long term scale deposits can restrict flow
- Removal of organic deposits
  - Can cause sheet defects if not removed

Boilout Components

- Caustic (Sodium Hydroxide)
  - 2-5% typical use level
  - Do not exceed pH 13
  - Enables saponification and emulsification of hydrophobic organic components
  - Kills slime forming bacteria and fungi
- Acid (Sulfuric)
  - Use level dictated by consumption during boilout
  - Critical to monitor pH and temp during boilout as potential for corrosion is higher than with caustic boilout
  - Mostly used to dissolve $CaCO_3$

Boilout Components

- Organic penetrants & dispersants
  - 0.1-0.5% typical usage rates
  - Main purpose is to speed up process by softening inorganic deposits
- Inorganic dispersants & chelants
  - Wide variety, tailored to specific types of inorganic deposits
  - Most act through anionic dispersion and crystal modification
- Foaming agents
  - Carry boilout solution to areas not normally reached
- Fiber
  - Scrubbing action

Typical Boilout Procedure

- Pre boilout wash-up
- pH of 12 - 12.5
  - P alkalinity must be maintained between 10,000-15,000 ppm
- pH 2 – 3 for acid
- Temperature of 130° - 145° F
- Re-circulation for 1 to 3 hours
- Post boilout wash-up - *very important!*
- Neutralization of boilout solution during dump to effluent

Alternatives to Traditional Boilouts

- Enzymes
  - 0.1-0.5% typical usage rates
  - Proprietary combinations of dispersants and surfactants such as Buzyme® Boilout Programs
  - Effective in removing MB, starch, cellulosic and protein containing deposits
  - Alternative if high or low pH solutions are problematic
- Neutral pH Boilouts
  - Use of dispersants and penetrants with standard temperature and time
  - No adjustment of pH

Pre-boilout

After enzyme boilout

Summary

- Successful boilouts depend on:
  - Adequate time
  - Proper pH (alkalinity)
  - Correct temperature
  - Solution formulation
  - Proper wash-up after the boilout