Examining the Impact of Liquor Loss on Effluent Toxicity

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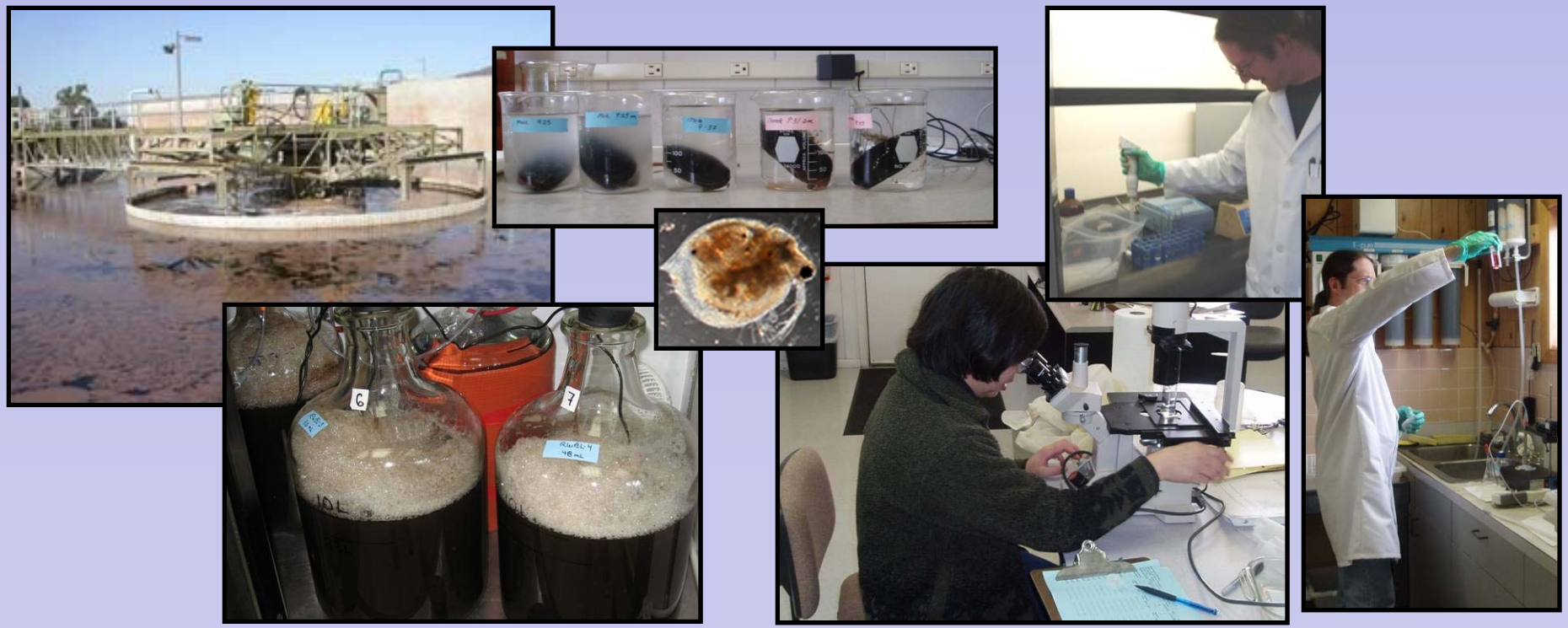


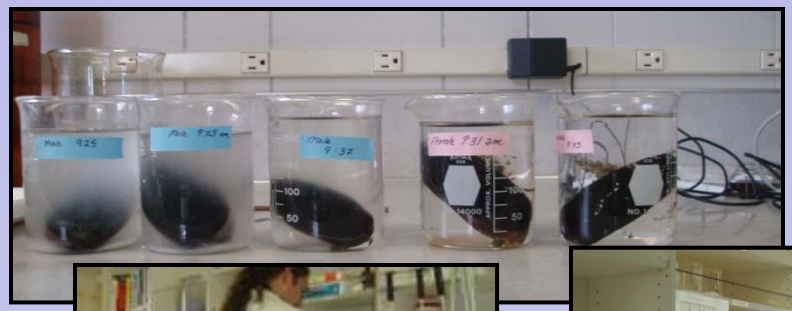
•Systemic losses of weak black liquor (WBL) from pulp mill and recovery systems occur via pulp washers, evaporators, knotting and screening systems and other processes.

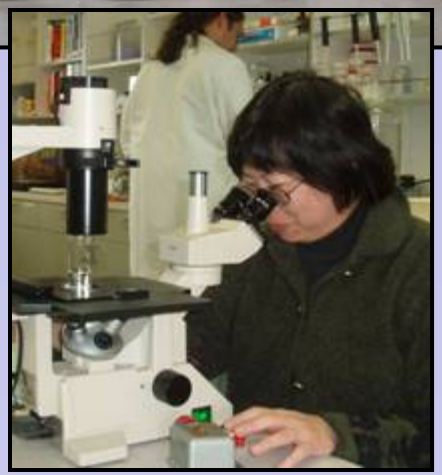
•Upset conditions may result in additional WBL losses, although most mills have collection systems in place that are designed to capture and recover concentrated spilled black liquor

•Best management practices for controlling systemic WBL losses have been effective at reducing WBL from entering the effluent treatment system, but is unclear at what level WBL may contribute to increased toxicity, or whether specific chemical compounds found in WBL may be responsible.

- WBL has been implicated in bioassay responses, but few controlled studies have been conducted to investigate this.
- Environment Canada's EEM Cycle 5 study examined the response of exposure to untreated WBL-spiked effluent on reproduction in five species of fish:
  - Variable, species-specific responses ranging from minimal response to cessation of egg production
  - Confirmed the potential contribution of black liquor in causing final mill effluent-related effects on fish reproduction
- However, in a real-world scenario WBL would be routed to effluent treatment system so organisms are not likely to be exposed to untreated WBL

- Objectives of this study was to evaluate, under controlled conditions:
  - the contribution systemic WBL losses in biologically-treated kraft mill effluents to effluent toxicity
  - effluent parameters that may correlate with biological responses





Methods

- Wastewater and WBL collected from 7 Bleached Kraft mills, WBL added to untreated wastewater from each mill, and treated batchwise in benchtop aerobic reactors.

- Highest concentration was chosen at a level that would result in an approximate doubling of the COD concentration of the control reactor, with lower concentrations 20%, 40%, 60%, and 80% of maximum.

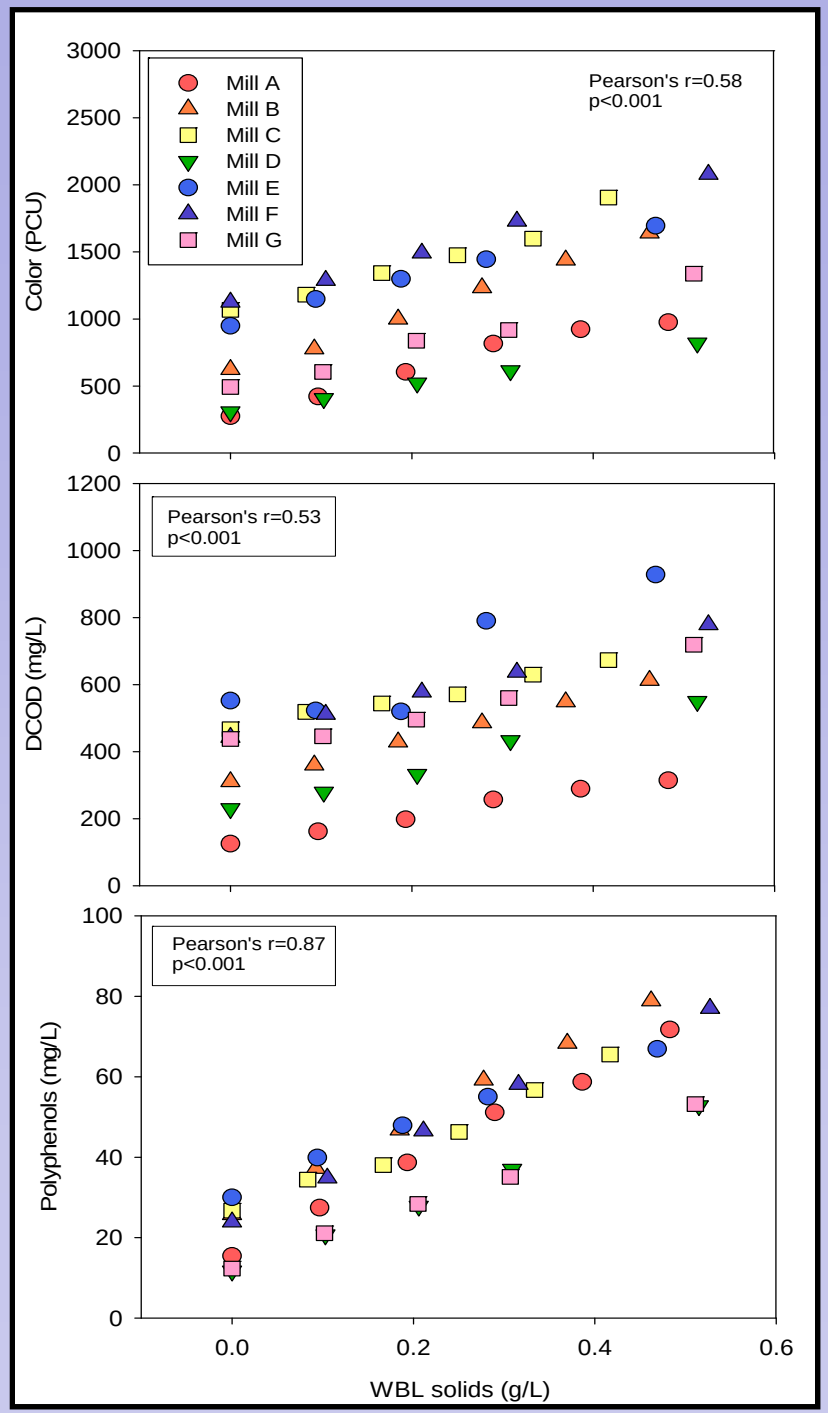
Treatment	Average Incremental COD from WBL Treatment		Equivalent WBL (16.4% BLS) Loss to Sewer	
	mg/L	Equivalent kg/day in 95,771 m^3/D	m^3/day	Litres/minute
Control	0	0	0	0
Low	98	9,389	52.2	36.3
Med. Low	195	18,643	104.5	72.6
Medium	293	28,032	157.1	109.1
Med. High	391	37,421	209.3	145.4
High	488	46,720	261.6	181.6

•Following biotreatment, chronic toxicity of the mill- and lab-treated effluents were evaluated using standardized WET tests:

- •marine mussel (*Mytilus*) larval development—all effluents
- •7-d *Ceriodaphnia* growth and reproduction—subset of effluents

- All effluents were characterized for:

- • pH
- •Colour
- •Conductivity
- •Turbidity
- •TSS
- •Polyphenols
- •Hardness
- •Alkalinity
- •Salinity
- •BOD
- •DCOD
- •DOC
- •Phytosterols
- •Resin acids

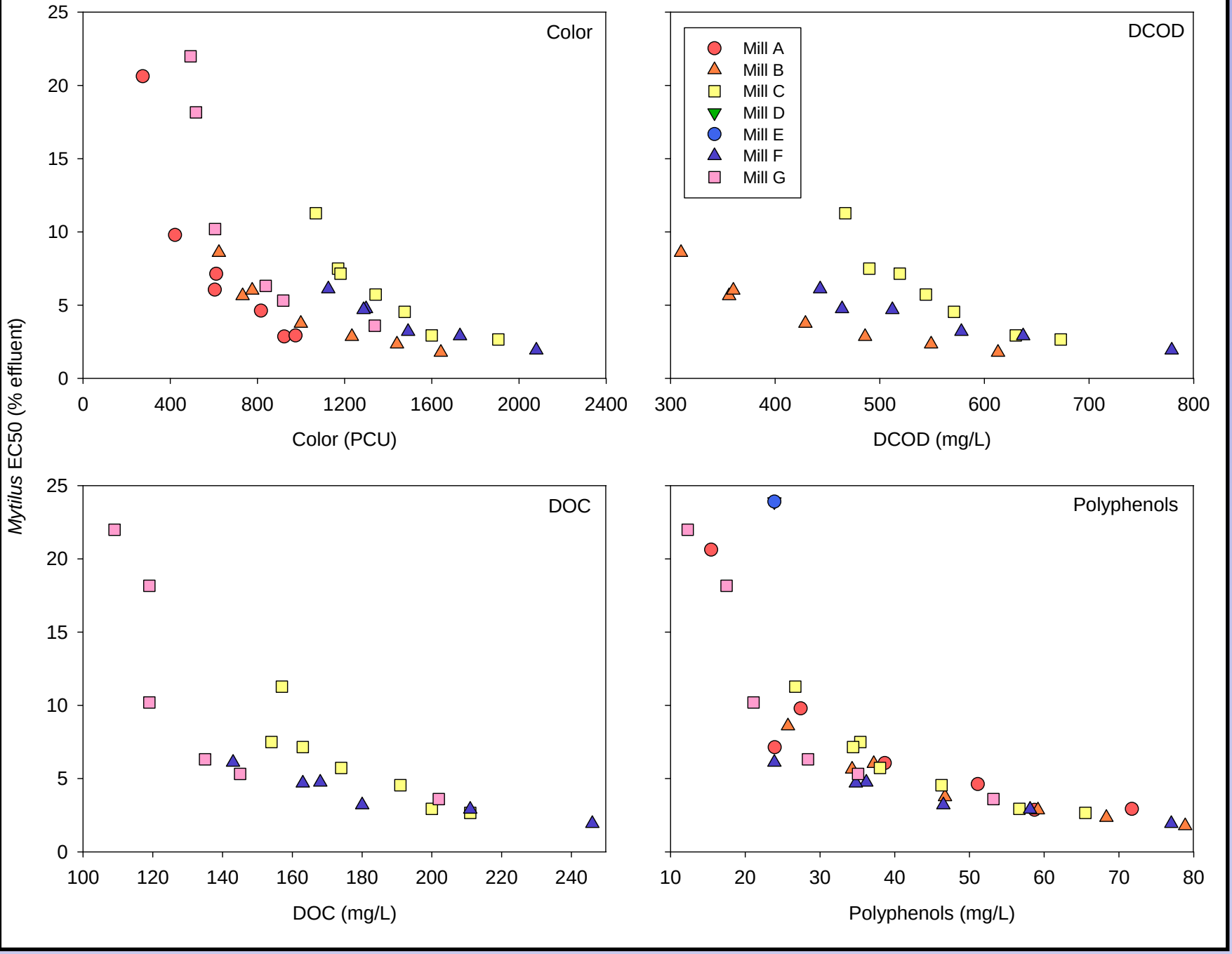


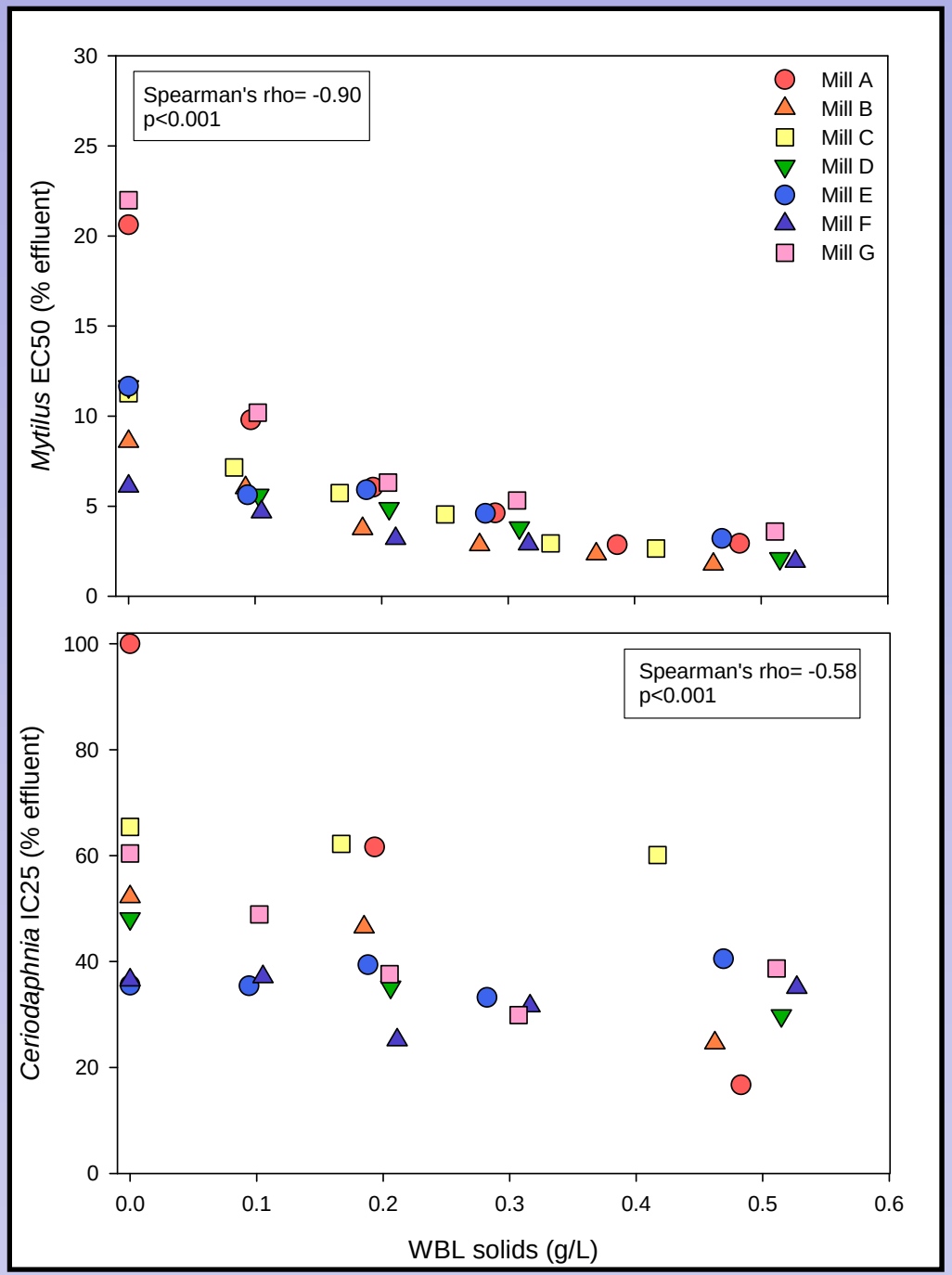
Results

- Some measured parameters increased with increasing WBL solids.
- Weaker WBL-associated increases (Pearson's $r<0.47$) also seen with:
  - β-sitosterol
  - Palustric acid
  - Abietic acid
  - Neoabietic acid

- Significant relationship seen between some effluent constituents and *Mytilus* larval development
- Relationships differed with mill

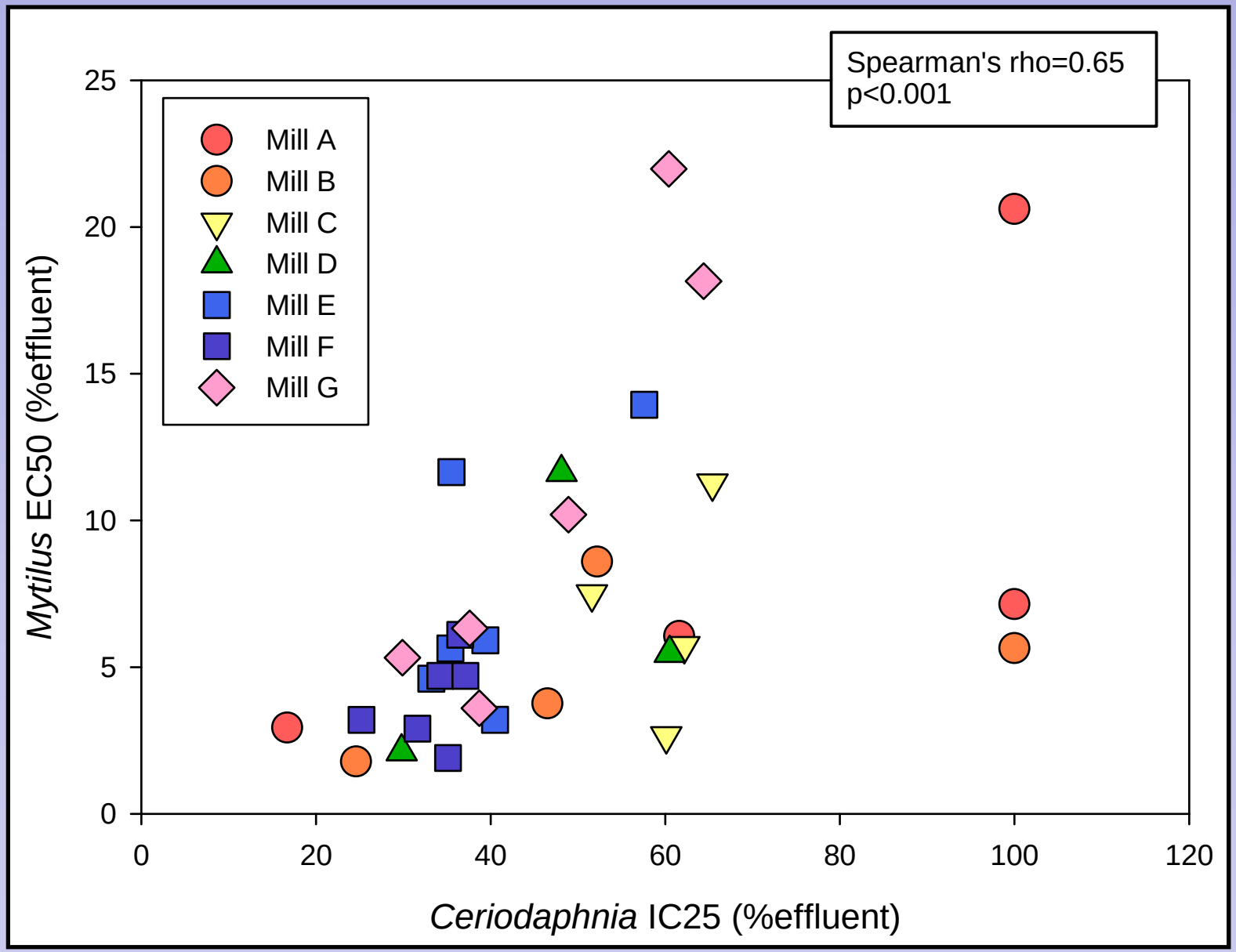
Parameter	Mill A	Mill B	Mill C	Mill D	Mill E	Mill F	Mill G
Color	✓	✓	✓			✓	✓
Conductivity		✓					
Polyphenols	✓	✓	✓			✓	✓
Hardness					✓		
DCOD		✓	✓			✓	
DOC			✓			✓	✓
Abietic acid	✓						

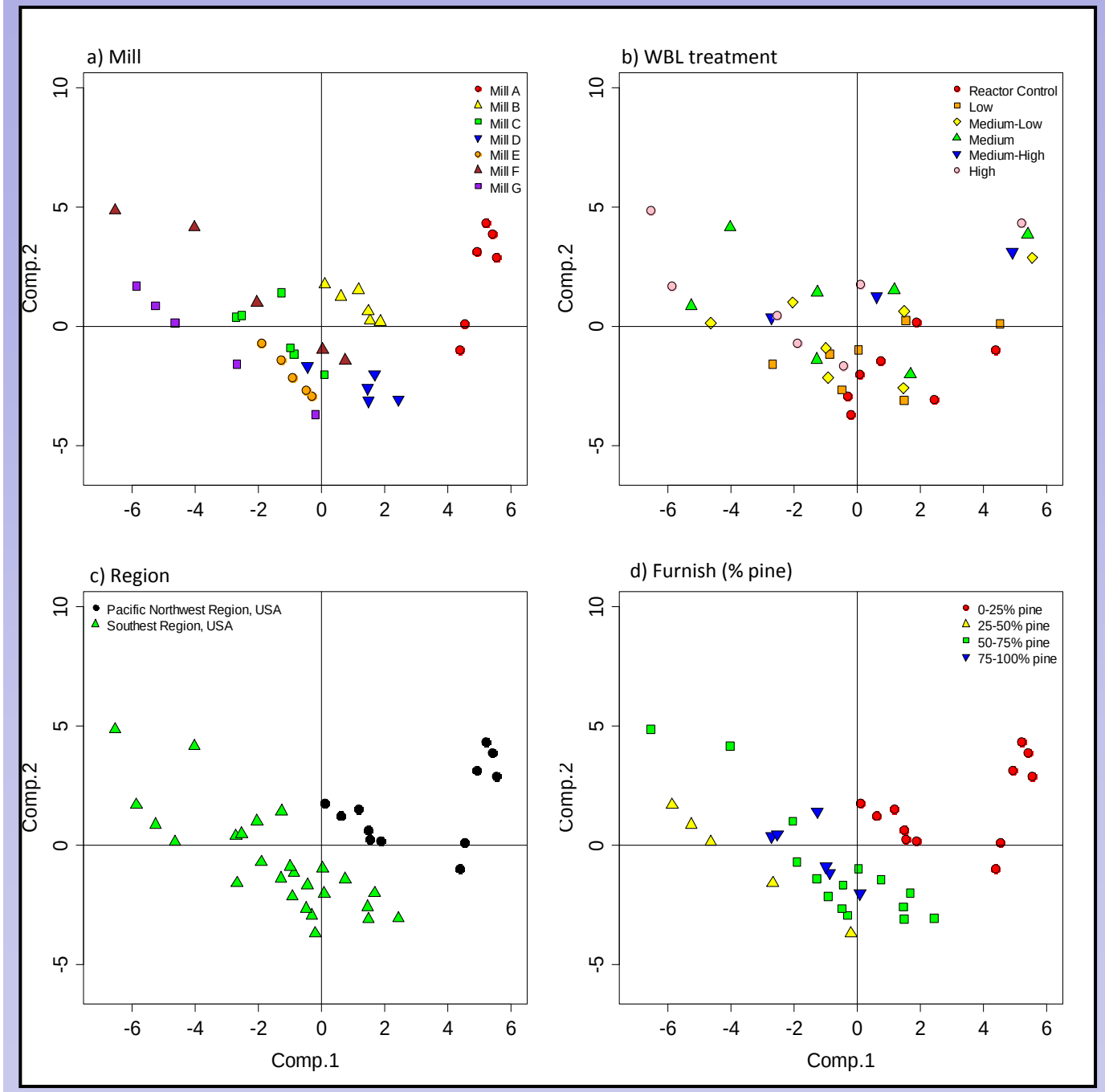

Color
DCOD
DOC
Polyphenols
Mill A
Mill B
Mill C
Mill D
Mill E
Mill F
Mill G
Mytilus EC50 (% effluent)
Color (PCU)
DCOD (mg/L)
DOC (mg/L)
Polyphenols (mg/L)



- As WBL solids increase, *Mytilus* larval development and *Ceriodaphnia* reproduction decreases
- *Mytilus* larval development showed a greater sensitivity to weak black liquor additions than *Ceriodaphnia*

Overall relationship between response of *Mytilus* and *Ceriodaphnia*, but patterns are generally not predictive at the mill level.





- Principal Components Analysis based on effluent constituents showed samples grouped by mill rather than WBL concentration

What does this study show?

- Biotreated Kraft mill wastewaters spiked with WBL showed an increase in some measured constituents, but effluent chemistry generally mill-specific regardless of WBL content
- Biological responses generally increased as WBL spiking levels increased
- Response to WBL exposure was greater for *Mytilus* larvae development than for *Ceriodaphnia* reproduction
- Bioassay response was correlated with certain effluent constituents
- Study findings suggest that ongoing systemic black liquor losses can result in an increased response of organisms commonly used in whole effluent toxicity assays at Canadian mills

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