Environmental Toxicology and Chemical Risks

Environmental Impacts of the pulp and paper industry - 2
pp 446-451, 370-376; Wright and Welbourn

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St. Maurice R. White Suckers: chemical exposure and metabolism

St. Maurice R. White Suckers: male serum sex hormones
Upstream/downstream comparison of white suckers in the St. Maurice R.

<table>
<thead>
<tr>
<th></th>
<th>+++</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tissue chlorophenols, dioxins &amp; furans</td>
<td></td>
</tr>
<tr>
<td>Chemical Metabolism (increased CYP1A activity)</td>
<td>+++</td>
</tr>
<tr>
<td>Growth</td>
<td>+++</td>
</tr>
<tr>
<td>Age at Maturity</td>
<td>+</td>
</tr>
<tr>
<td>Size at maturity</td>
<td>++</td>
</tr>
<tr>
<td>Fecundity-age relationship</td>
<td>Disrupted</td>
</tr>
<tr>
<td>Hormone regulation – males, females</td>
<td>Disrupted</td>
</tr>
<tr>
<td>Gonad Size – males</td>
<td>+</td>
</tr>
<tr>
<td>Gonad Size - females</td>
<td>-</td>
</tr>
</tbody>
</table>

• Canadian Studies – 1988-1995
  - Were the Swedish Studies Unique? **NO!**
  - What was the significance of reproductive impairment of fish?*
  - Were chlorinated organic compounds the cause?
  - Is effluent treatment the answer?

* Effects relatively small and evident mostly at the physiological level – No dead bodies in the street!
Theory of River Continuum:
With increasing distance downstream,
- Nutrients will accumulate
- Larger fish (faster growth)
- Increased investment in reproduction
- Earlier maturation
- Larger relative gonad size
- Greater fecundity

River Comparison

<table>
<thead>
<tr>
<th>Site 1</th>
<th>Site 2</th>
<th>Site 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>St. Maurice</td>
<td>Gatineau</td>
<td>Reservoir</td>
</tr>
<tr>
<td>Distance from dam</td>
<td>-10 km</td>
<td>2 km</td>
</tr>
<tr>
<td>Log Drive</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Municipal waste</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Pulp Mill</td>
<td>Yes</td>
<td>No</td>
</tr>
</tbody>
</table>

A comparison of white sucker populations, St. Maurice River vs Gatineau River

**ST. MAURICE – pulp mill**
- Increased tissue dioxin and chlorophenols
- CYP1A induction
- Increased growth
- Constant age to maturity
- Greater size at maturity
- Disrupted fecundity-weight relationship

**GATINEAU – no pulp mill**
- Background tissue chlorophenols
- No CYP1A induction
- Increased growth
- Decreased age to maturity
- Smaller size at maturity
- No change in fecundity-weight relationship
Conclusions

- Fish exposed to pulp mill effluents failed to increase their reproductive capacity despite greater nutrient availability
  - Effluent impact was expressed in a reduced investment in reproduction
- Changes in fish populations in pulp mill contaminated rivers are subtle and difficult to detect
  - Effects not obvious in simple upstream-downstream study
  - Effects evident only by comparison with responses of fish from an uncontaminated river

Are Chlorine and Chlorinated Compounds the Problem?

- Multi-mill study: effects on fish at ALL mills - with and without bleaching
- In-mill studies: greatest source of CYP1A inducers was pulping and effluent treatment (Flavones, stilbenes, retene), not bleaching (AOX)
- Reproductive studies: most likely endocrine disruptor was β-sitosterol (plant sterol)

The Good News – it’s not the chlorine
The Bad News – it’s the wood!

Anaerobic metabolism of abietic acid to retene (Wakeham et al. 1980)

<table>
<thead>
<tr>
<th></th>
<th>Abietic acid</th>
<th>Retene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Log Kow</td>
<td>&gt; 1.74</td>
<td>6.4</td>
</tr>
<tr>
<td>Water Solubility (µg/L)</td>
<td>&gt;1000</td>
<td>16</td>
</tr>
<tr>
<td>LC50 (µg/L)</td>
<td>1000</td>
<td>8</td>
</tr>
<tr>
<td>CYP1A Inducer</td>
<td>No</td>
<td>Yes</td>
</tr>
</tbody>
</table>
Chemicals that may influence reproduction - Structure-Activity Relationships in Action

- sitosterol
- cholesterol
- estradiol
- genistein

**β-sitosterol – evidence for endocrine disruption**

* Receptor Interactions
  - Binds to rat cytosolic estrogen receptors
  - Estrogenic in a T-47D cell line, but not MCF-7 cells

* Interactions with estrogen synthesis or metabolism
  - Inhibits estrogen-specific 17β-hydroxysteroid oxidoreductase type I enzyme
  - Reduces uptake of cholesterol from the gut (decreased plasma cholesterol) and by cells
  - Reduces activity of Cytochrome P450sc (side chain cleavage) enzyme (first step in conversion of cholesterol)

* Estrogenic Functions
  - Stimulates uterine growth in some mammals

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**Model of Pulp mill effluent effects on fish reproduction**

- Effluent Discharge
- Nutrient Enrichment
- Increased food availability

- Accumulation of Sitosterol
- Block cholesterol uptake
- Reduced plasma sex steroids (T, 11-KT, E₂, preg)
- Reduced oogenesis, spermiogenesis
- Molecular/cellular

- Altered 2nd sexual Characteristics, delayed maturation
- Reduced gonad size, egg size, fecundity
- Greater age at maturity, size at maturity
- Individual

- Reduced reproductive success
- Weak year classes
- Biomass decreases?
- Biomass increases?

- Increased growth rates
- Population
Revised Pulp and Paper Mill Effluent Regulations in Canada - 1992

- Limited BOD, TSS, pH, chlorinated dioxins and furans
- Included toxicity tests – trout and/or *Daphnia magna*
  - 100% survival in 100% effluent for 96 h (fish) or 48 h (*Daphnia*)
- Global First: Environmental Effects Monitoring Program
- Applied to all mills

Pulp Mill Environmental Impacts –1990’s

**Mills** - Larger, more efficient, mostly Kraft and TMP
**Output** - 1000 - 1500 ADMT/d

**Impacts**

- **Physical** - smaller ‘footprint’
  - greater reliance on recycled fibre (US laws)
  - water use – reduced from 140 to <40 m³/ADMT
- **Chemical** - reduced concentrations of all constituents
  - dioxins & furans eliminated
- **Biological/Ecological** - less sublethal toxicity
  - new issue - eutrophication due to nutrient enrichment

- **Effluent Treatment** - 1° universal, 2° almost universal, 3° rare

The Great Pulp Mill Effluent Onion

- Organic Enrichment: BOD, COD, pH, Anoxia
- Acute Lethality: Resin and Fatty Acids
- Mercury Contamination
- Chlorinated Compounds
- Phosphate Esters

Nutrients again

If effluent is not clean enough to re-use in the mill, why is it clean enough to discharge?
Is Effluent Treatment the Answer?

“We are in the business of making pulp and paper, not of treating effluents”

- Industry spokesperson, 2nd International Conference on the Environmental Fate and Effects Bleached Kraft Mill Effluents, Vancouver, 1994

**Solutions:**
- Increase carbon recovery in pulping
- Computer process control
- Increase oxygen delignification, reduced bleaching
- Increase water re-use and recycling
- Increase energy recovery
- Identify problem waste streams and focus control

**Ultimate Goal:** zero discharge, closed loop mill

**Challenges:** remove chemicals from the effluent without creating toxic solid waste or air pollution

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**ENSC 201 - Pulp and Paper -2**

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**ALCELL PULPING PROCESS**

**WOOD CHIPS**

**ETHANOL**

HIGH PRESSURE & TEMPERATURE

**WOOD PULP**

**ETHANOL FURFURAL LIGNIN**

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**Kraft Pulping**

**Wash water**

**Bleach water**

**Wastewater**

**VOLATILES**

**BIOSOLIDS**

Particulates
- Wood fibre
- Grit
- Particulates
- Degraders
- Wood fibre

**1° Treatment**

**2° Treatment**

**Receiving Environment**
Canada’s First (and only) closed-loop mill, Meadow Lake, Saskatchewan

Lessons Learned

• Complex effluents are like layers of an onion. As you peel back one layer of effects, you reveal another
• Toxicity testing is as important as chemical testing of effluents
  - too many compounds to identify, measure, and to conduct ecological risk assessment
• Impacts are best understood by studying the receiving water ecosystem
• Reproductive impacts may be hard to detect, but can eliminate fish populations as effectively as acute mortality
• End-of-pipe solutions are more expensive than process control
  - the key is to increase efficiency of conversion of feed stocks to product
  - carbon lost to effluent treatment is a wasted resource and an environmental problem