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Comparison of ozonation and reclamation pond biodegradation as treatments to eliminate oil sands process-affected water toxicity in *Chironomus dilutus*

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Overview

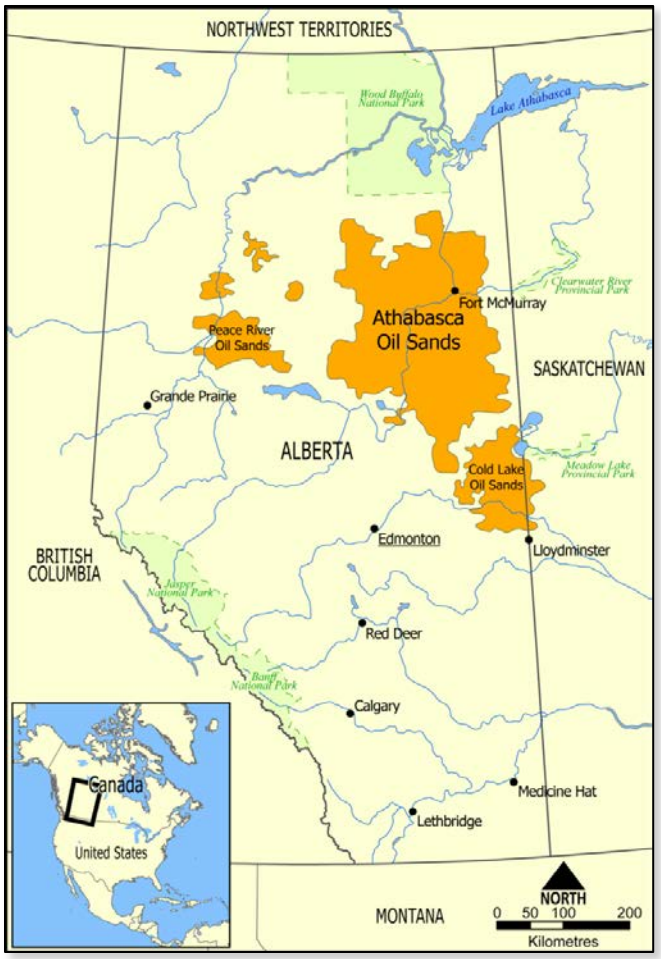
- **Background**
  - Alberta oil sands
  - Oil sands process-affected water
  - Biodegradation
  - Ozonation
- **Study objectives**
- **Methods**
- **Results**
- **Discussion**
- **Future work**

Background

- **Alberta oil sands**

  -Represented over 50% of Canadian crude oil production in 2010 (CAPP, 2011)

  -1.5 million barrels of bitumen produced per day in 2009 (Government of Alberta, 2011)

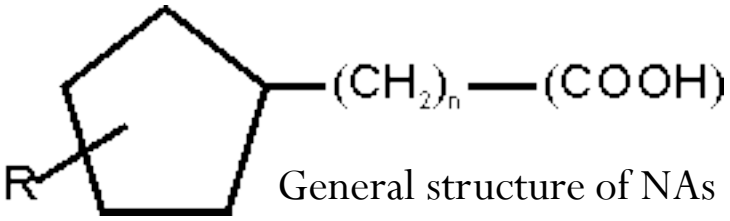


- **Oil sands process-affected water (OSPW)**

  -Produced during extraction of bitumen from oil sands

  → ~ 1 billion m^3 currently in active settling basins (Han *et al.*, 2008)

Background



General structure of NAs

- **Oil sands process-affected water**
  - Major constituents:
    - Salts
    - Metals – Al, As, Cu, Fe, Ni, Pb, V, Zn, others
    - Ammonia
    - Naphthenic acids (NAs) – complex mixture of carboxylic acids found at elevated levels in OSPW
- **NAs**
  - Naturally occur in bitumen; solubilized and concentrated by extraction process and water recycling
  - Believed to be responsible for majority of OSPW toxicity to aquatic organisms → **targets for treatment efforts**

Background

- **Biodegradation of OSPW**
  - Indigenous microbial populations have the ability to degrade NAs to some extent
  - Method currently in use while OSPW is stored in active settling basins
  - Toxicity of OSPW shown to persist following aging
    - Impaired reproduction in fathead minnows (Kavanagh *et al.*, 2011)

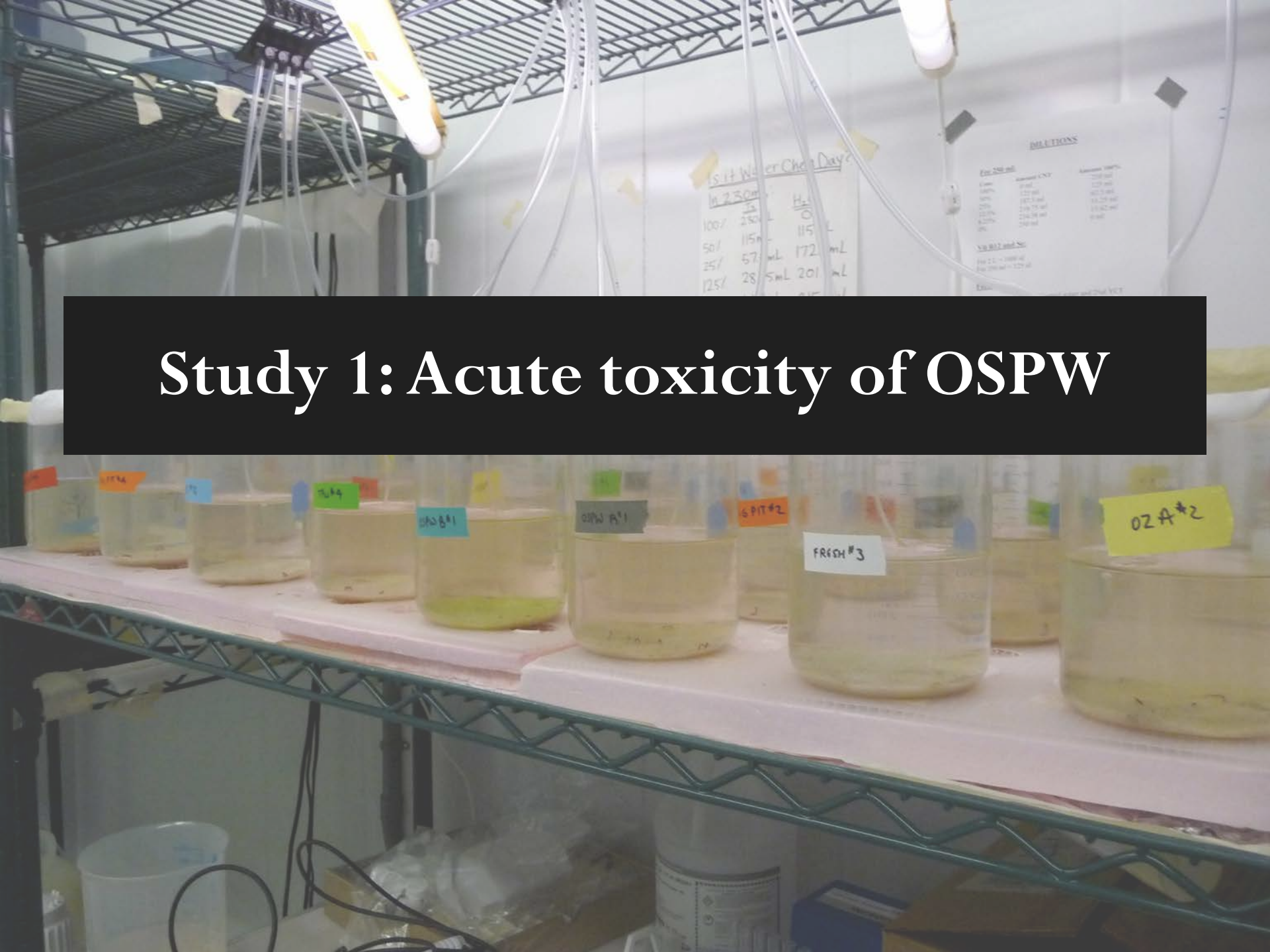
Background

- **Ozonation**
  - Popular for water treatment – disinfecting properties, precipitation of heavy metals/metal complexes, oxidizes ammonia, eliminates toxic organics
  - OSPW found to be non-toxic (using Microtox ®) after 50 minutes and 70% NA reduction (to 20mg/L) (Scott *et al.*, 2008; Gamal El-Din *et al.*, 2011)
  - Greater MW NAs removed by ozonation – targets persistent NA fractions → increases microbial degradation (Martin *et al.*, 2010; Gamal El-Din *et al.*, 2011; Perez-Estrada *et al.*, 2011)

Overall objectives

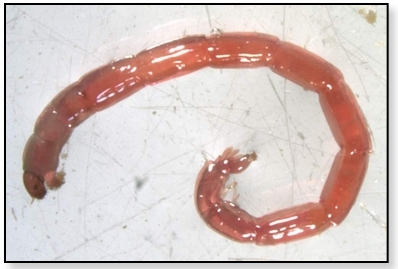
- 1. To characterize the effects of exposure to untreated OSPW in a benthic invertebrate model, *Chironomus dilutus*
  - "Fresh" OSPW from West In-Pit settling basin

- *2.* To determine whether treatment of OSPW using ozonation or biodegradation ("aging") effectively reduces its toxicity to *C. dilutus* larvae



Study 1: Acute toxicity of OSPW

Study objectives



- 1. To characterize the effects of short-term (10 d) exposure to OSPW in *Chironomus dilutus* larvae

- *2.* To determine whether treatment of OSPW using aging or ozonation effectively reduces its toxicity to *C. dilutus*
  - Assessed in terms of survival and growth (as fresh mass)

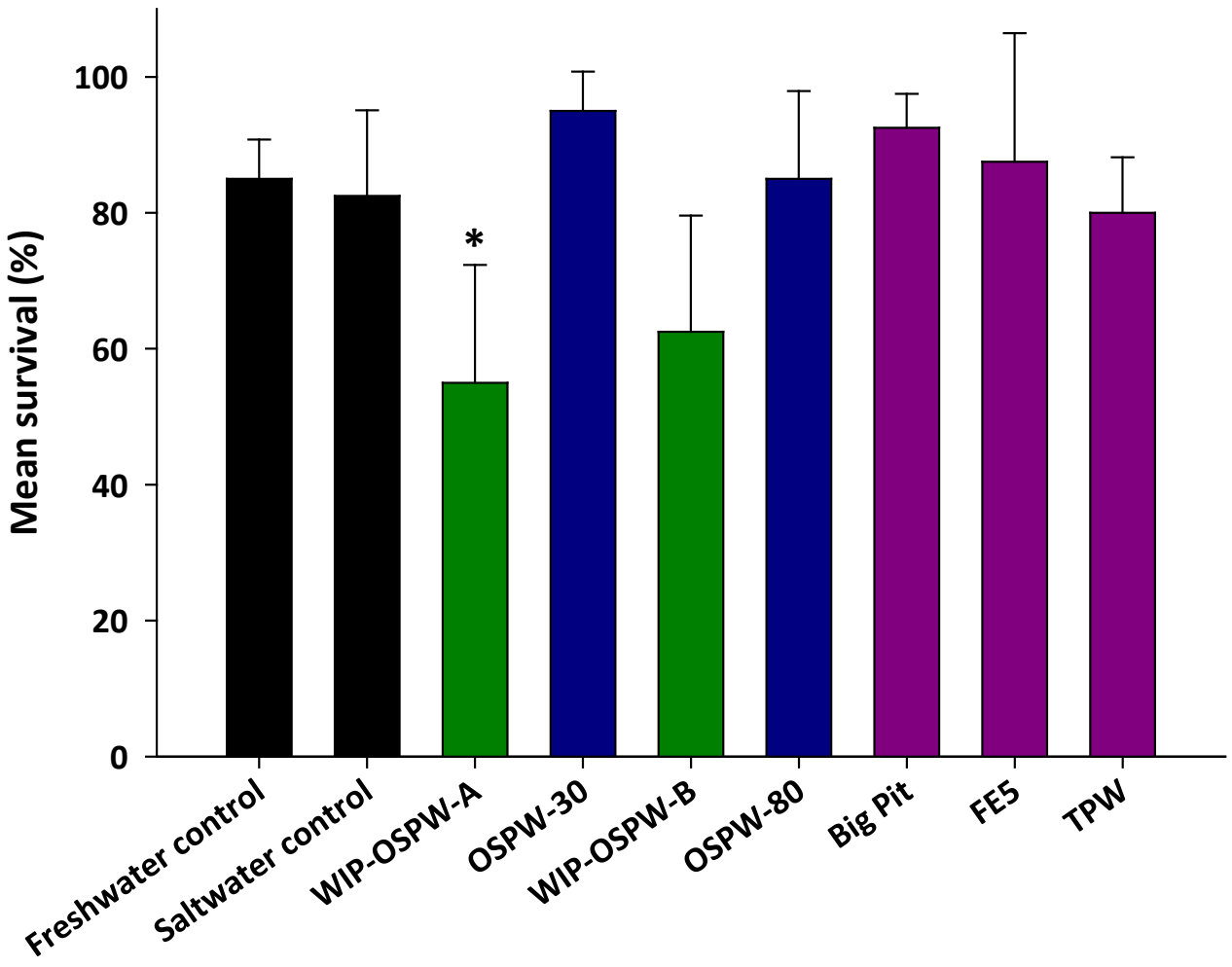
Methods

- *Chironomus dilutus* larvae – 8-9 days old
- 10-day exposure - survival and measurement of mean fresh mass
- Daily feeding and 50% water change on alternating days
- Waters: Freshwater control, saltwater control, untreated OSPW, ozonated OSPW, aged OSPW
  - OSPW collected from Syncrude West In-Pit settling pond in (A) 2009 or (B) 2010
  - Aged water from Big Pit, FE5, and TPW
- 2 degrees of ozonation – (A) 30 mg/L or (B) 80 mg/L applied to WIP-OSPW

Treatment waters

- WIP-OSPW:
  - Total [NAs] –70-72 mg/L in both WIP-OSPW-A and WIP-OSPW-B (as measured by FTIR)
- Ozonated-OSPW:
  - Total [NAs] – 16 mg/L in OSPW-80
- Aged waters:
  - Big Pit – mature fine tailings capped with freshwater in 1993; [NAs] – 23 mg/L
  - FE5 – mature fine tailings capped with OSPW in 1989; [NAs] – 13 mg/L
  - TPW- OSPW aging since 1993; [NAs] – 35 mg/L

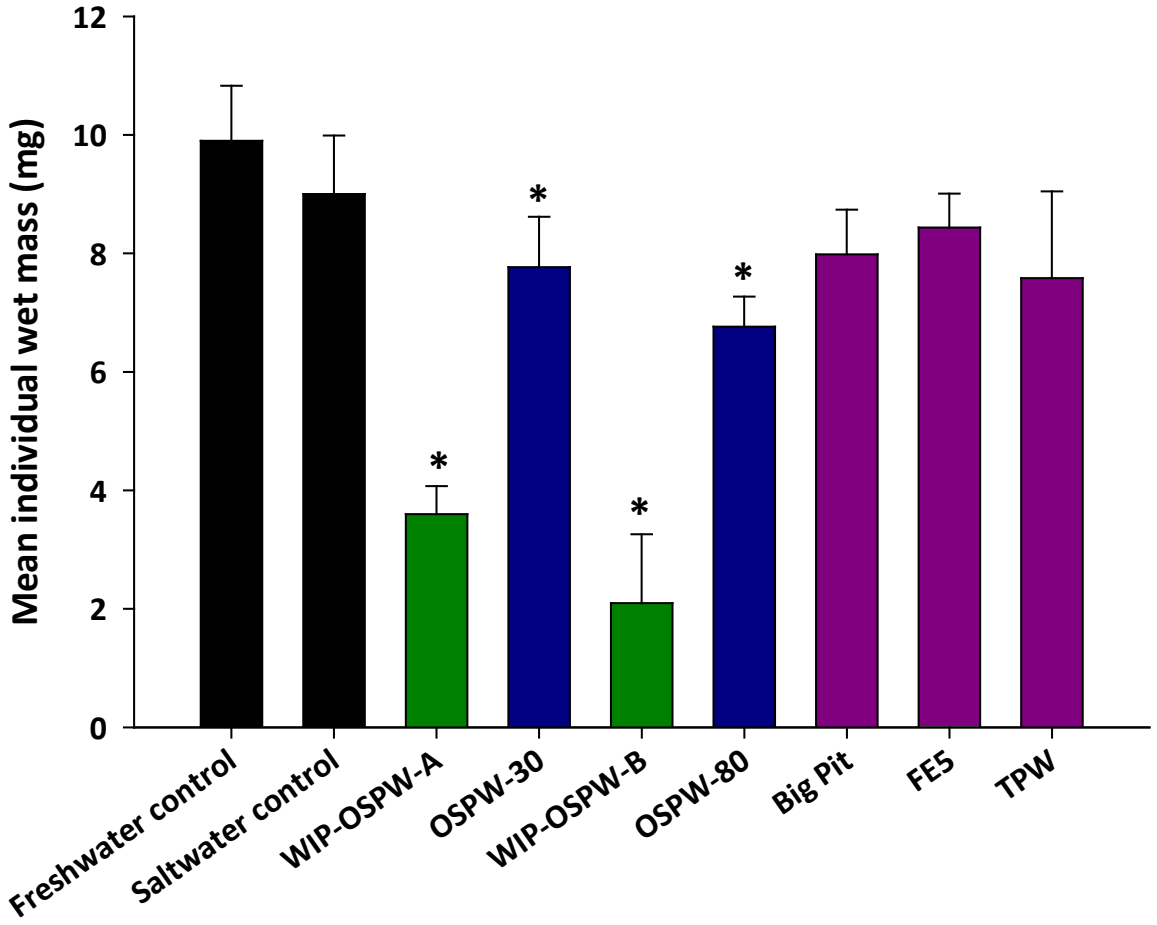
Results -Survival



Significant differences from the freshwater control were determined using a one-way ANOVA followed by Tukey's HSD post-hoc test (n=4, $\alpha = 0.05$).

- Significantly less survival in WIP-OSPW-A ($p<0.05$)
- Less survival in WIP-OSPW-B (non- significant trend)
- No differences among ozonated or aged OSPW and controls

Results - Growth



Significant differences from the freshwater control were determined by one-way ANOVA followed by Tukey's HSD post-hoc test (n=4, α =0.05).

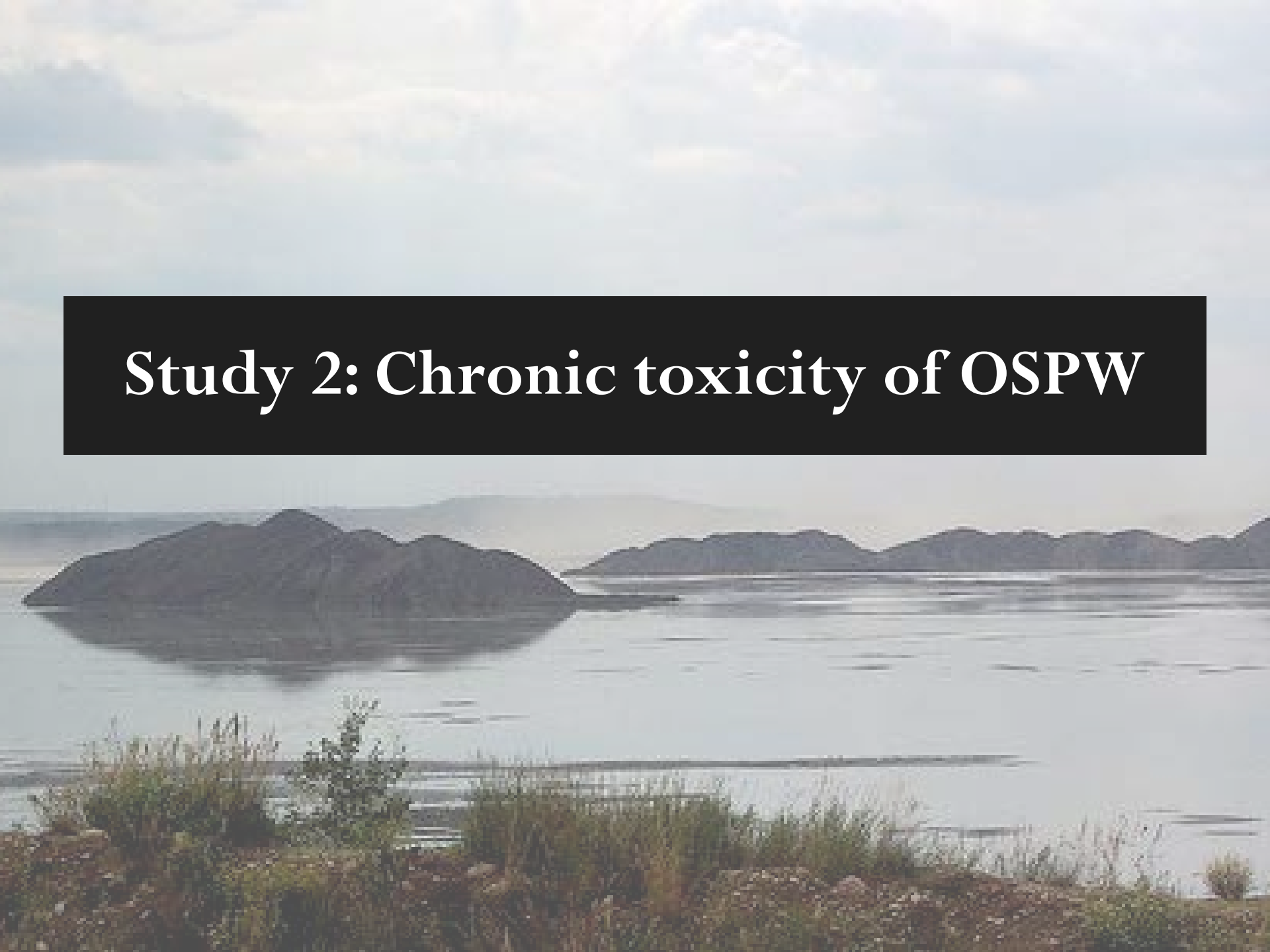
- WIP-OSPW-A-exposed larvae had 64% less fresh mass than freshwater controls

- WIP-OSPW-B-exposed larvae had 79% less fresh mass than freshwater controls

- Exposure to ozonated OSPW – significantly attenuated growth inhibition effects, but lesser masses than controls (22% and 32% less mass)

- No effects on fresh mass following aging of OSPW

Study 2: Chronic toxicity of OSPW



Study Objectives

- 1. To characterize the effects of long-term exposure to OSPW in *Chironomus dilutus* larvae

- *2.* To determine whether treatment of OSPW using aging or ozonation effectively reduces its toxicity to *C. dilutus*

  - Assessed in terms of pupation, emergence, sex ratio

Methods

- Followed same exposure methodology as previous study, except activated charcoal-treated FE5 and WIP-OSPW-A

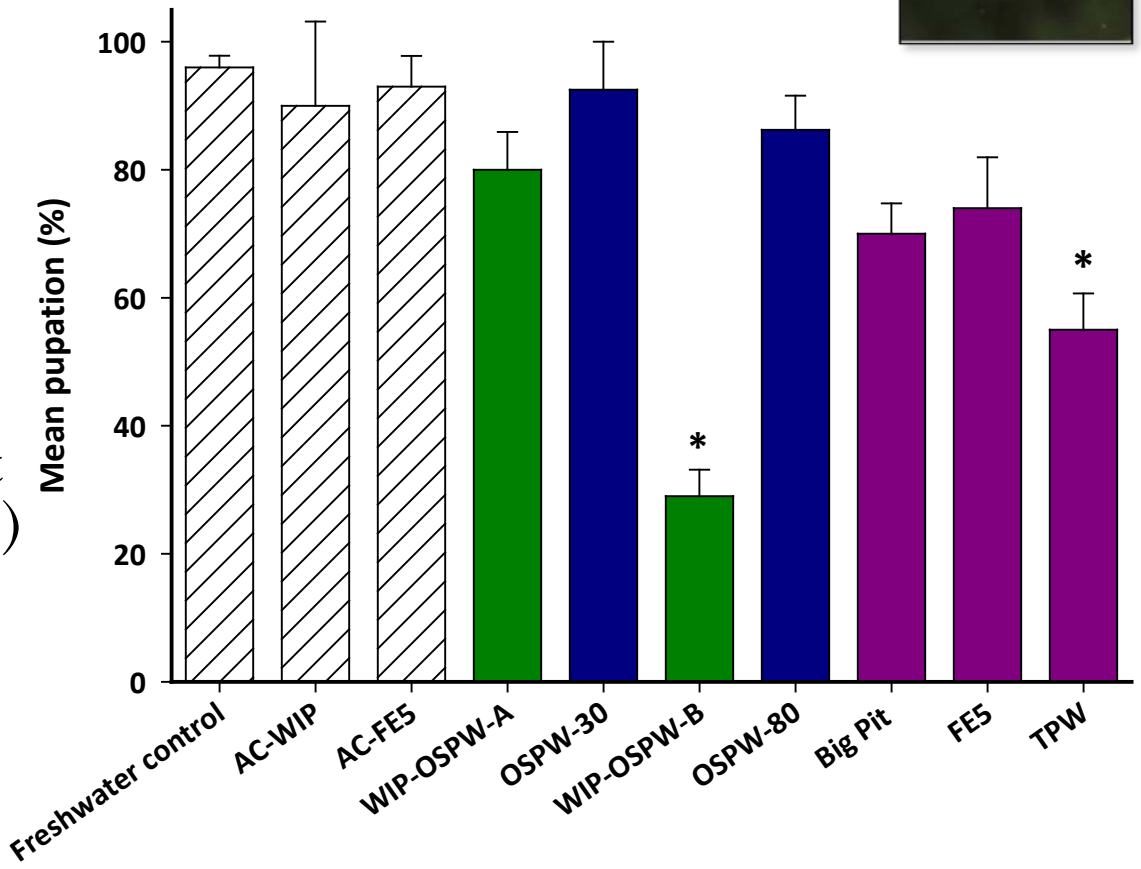
- Collected adults and recorded sex and day of emergence

- Noted larval and pupal deaths and recorded time to pupation

- Allowed all individuals from beaker to emerge or die before takedown

Results – Pupation

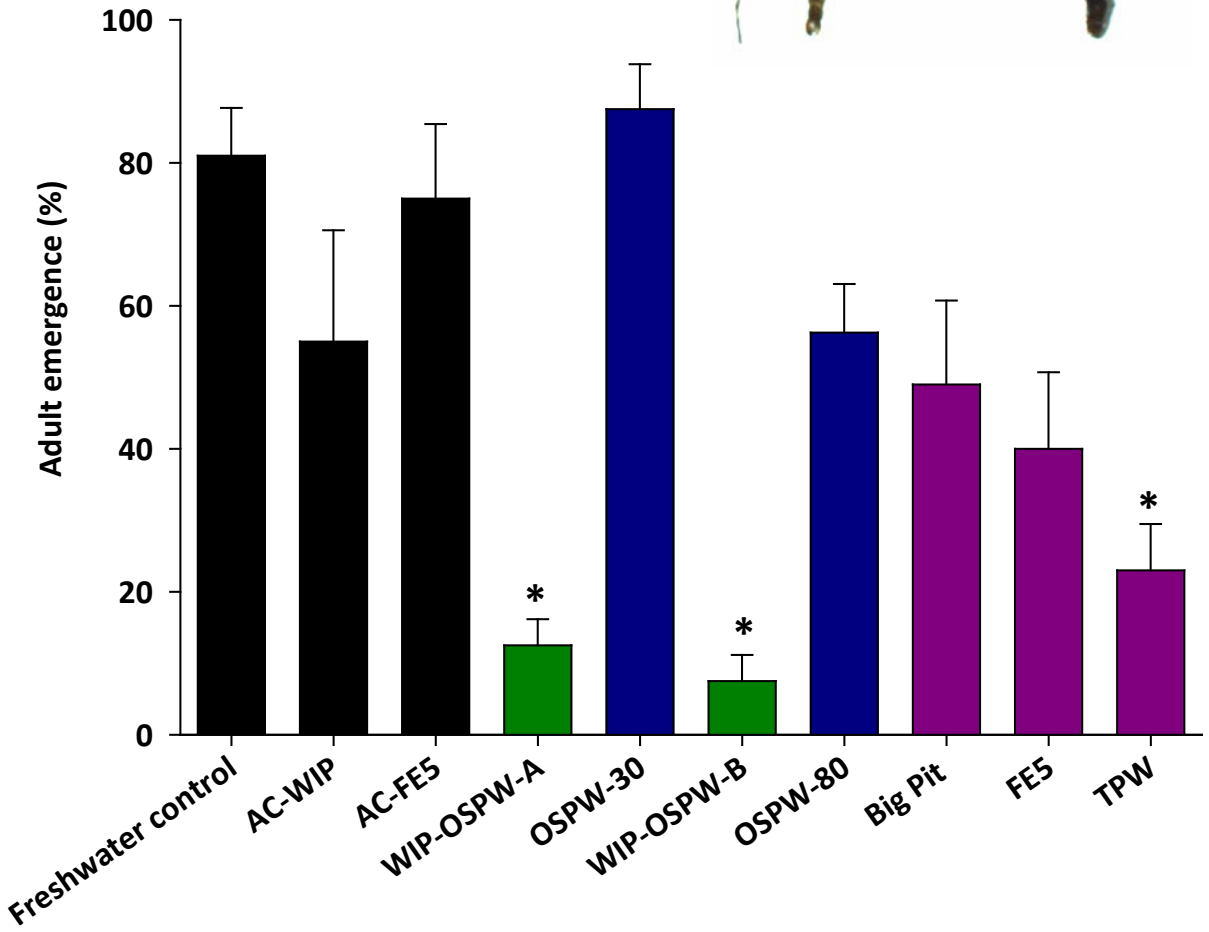
- Significantly less pupation in WIP-OSPW-B vs. freshwater controls ($p<0.05$)
- Significantly less pupation in TPW (but not other aged waters) vs. controls
- Pupation in ozonated-OSPW no different from controls



Significant differences from the freshwater controls were determined by one-way ANOVA followed by Tukey's HSD post-hoc test ($n= 4$ or 8, $\alpha =0.05$).

Results-Emergence

- Significantly less adult emergence in both WIP-OSPW-A and WIP-OSPW-B ($p<0.001$)
- Generally fewer emerging adults in aged-OSPW, statistically fewer in TPW vs. controls
- Ozonation attenuated effects on emergence
- Sex ratios no different from 1:1 in any treatment



Significant differences from the freshwater controls were determined by one-way ANOVA followed by Tukey's HSD post-hoc test (n= 4 or 8, α =0.05).

Discussion

- Based on studies 1 and 2, exposure of *C. dilutus* larvae to untreated OSPW may cause:
  - Some reduced survival
  - **Significant growth inhibition**
  - Reduced pupation
  - **Severely reduced emergence of adults**

Discussion

- Biodegradation of OSPW:
  - Results in **lesser concentrations of NAs** (vs. fresh WIP-OSPW)
  - **Eliminated effects on growth and survival** of larvae
  - Failed to eliminate effects on pupation and emergence – both were less than controls, especially in TPW (greatest concentration of NAs) – **chronic toxicity remains → active treatment required**

Discussion

- Ozonation of OSPW has potential to:
  - **Attenuate growth inhibition** effects
  - Eliminate any reductions in survival
  - **Improve pupation and emergence** success
  - Minimize toxicity on a much shorter time scale than required by biodegradation

Conclusions

- Untreated OSPW resulted in toxicity in a benthic invertebrate model following **both short-term** and **long-term** exposures

- Toxicity manifested mainly as **growth inhibition** and **impaired adult emergence**

- Biodegradation **improved survival and growth**, but did not eliminate impairment of pupation and emergence

- Ozonation of OSPW **attenuated the observed acute and chronic toxicity**

Future work

- Field surveys - Implications of growth and emergence inhibition at the community level
  - Are effects occurring on-site?

- Elucidate mechanism of toxicity
  - Expression of metabolic, endocrine-related, and ribosomal protein genes
  - Any risk of new toxicity from ozonation by-products?

- Improve fractionation abilities to identify specific NAs of interest
  - Bioassays with different fractions since NA profiles varied in current tests

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Thanks for your attention!
Questions?

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