Characterizing the Influence of Clay Pads on Toluene Biogenesis in Peatlands

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Overview

- Introduction
- Methodology
- Results
- Discussion
- Conclusions
- Recommendations/Best Practices

Toluene Biogenesis in Peatlands

- Elevated toluene levels beneath the clay pad of abandoned well-sites
- Evidence of biogenic production
  - Anoxic hypolimnion of lakes in Germany (Juttner and Henatsch 1986; Juttner 1991)
  - Microbe responsible identified (Fischer-Romero et al. 1996)
- Preliminary study found that toluene levels were higher and occurred at greater depths under well pads (capped) versus surrounding uncapped locations

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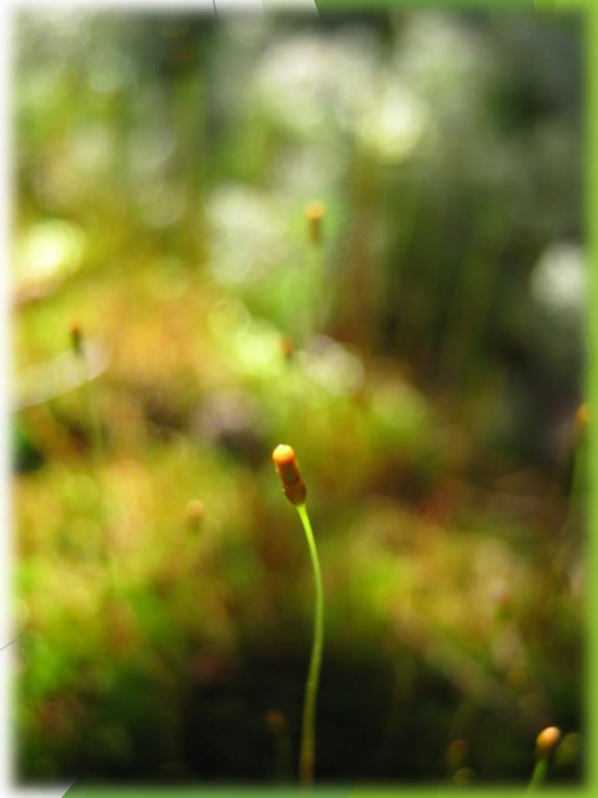
Toluene Toxicity

- Adverse Health Effects
  - rainbow trout (*Oncorhynchus mykiss*) @ 0.02 mg/L.
  - leopard frog (*Rana pipiens*) and the northwestern salamander (*Ambystoma gracile*) @ 0.39 mg/L
  - freshwater invertebrates like *Daphnia magna* LC50 @ 3.75 mg/L
  - freshwater algae (*Selenastrum capricornutum*) @ 12.5 mg/L (CCME 1999, 2004)

Research Objectives

1. Determine if the results from the preliminary analysis are supported by the larger data set.
2. Investigate the influence of sulphate on toluene generation.
3. Investigate the influence of other measured chemicals on toluene generation.
4. Determine if a background toluene benchmark can be determined from the data.
5. Describe the management implications of the results.



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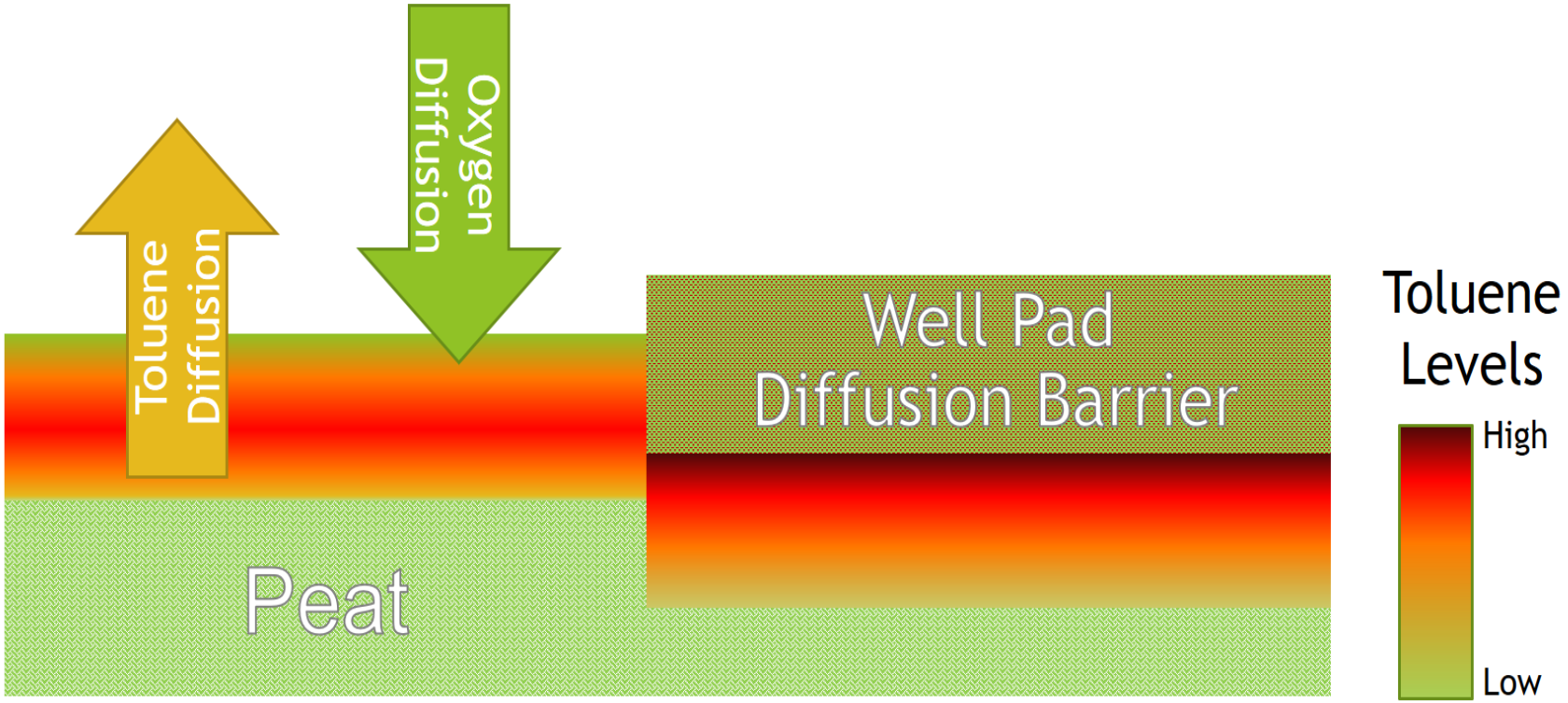
Hypothesis



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Methodology

- 6518 samples total
- Toluene data: 2049 samples
- Petrogenic impact: 413 samples
- Mineral soil: 1220 samples
- N=413 remaining samples, 249 with detailed salt data

- Statistical methods
  - Non-normal
  - Detection limits
  - Imbalance of capped and uncapped data sites

- Differences between two groups: Mann Whitney U
- Correlation Analysis: Kendall's Tau
- Multivariate: Maximum Likelihood Estimation (MLE) Censored Regression Analysis

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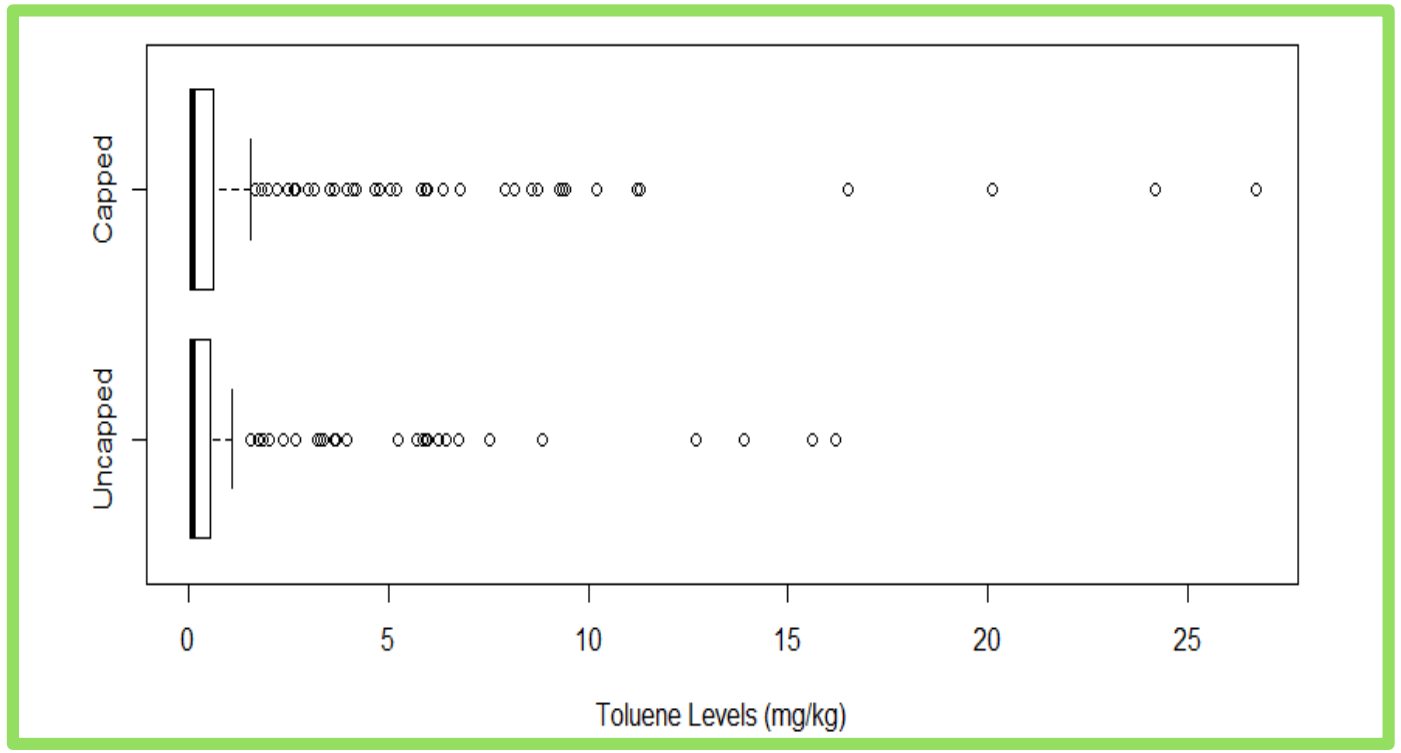
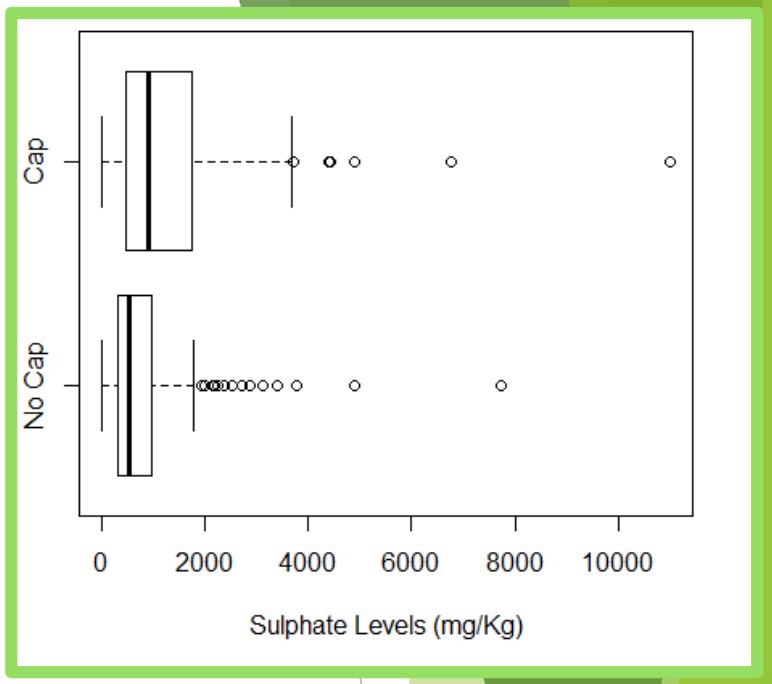
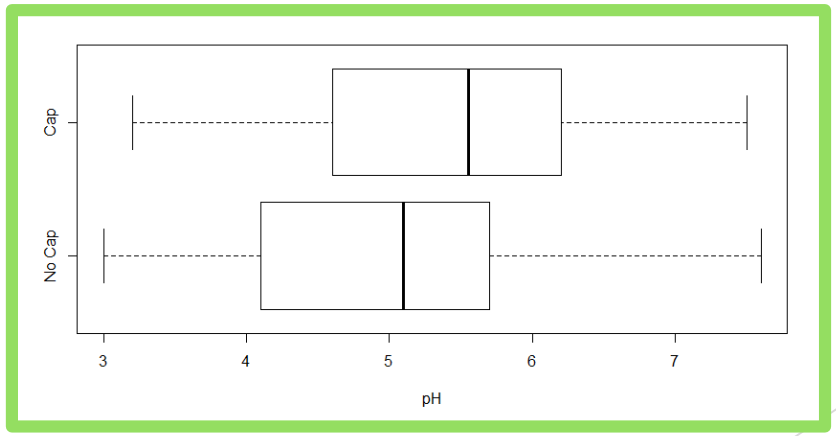
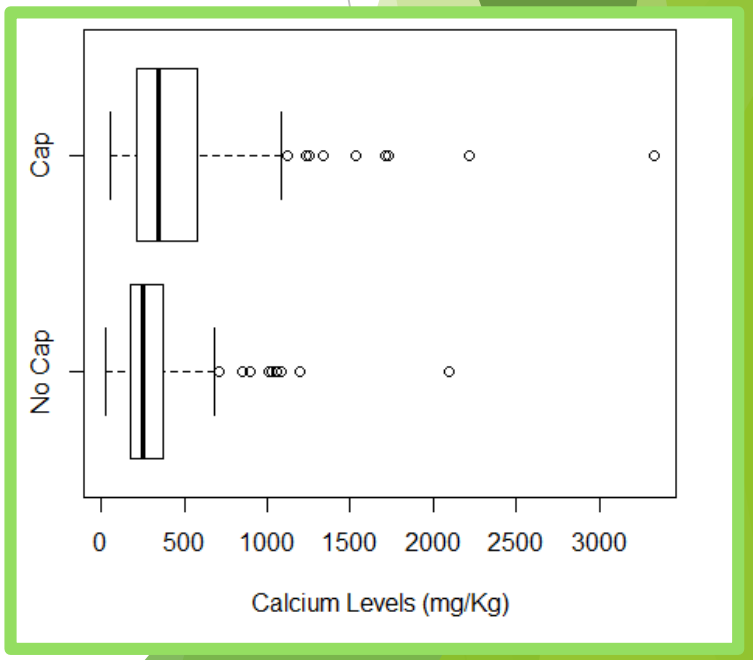
Site Differences





	Toluene
Ca	-0.33***
Cl	-0.10
EC	-0.17**
K	0.05
Na	0.13
pH	-0.38***
SO_4	-0.28***





Multivariate Analysis

Explanatory Variable	Coefficient	Standard Error	P-value
Intercept	4.89	1.48	**0.0009**
Cap	5.33	1.91	**0.005**
pH	-0.66	0.26	**0.01**
Cap*pH	-0.87	0.36	**0.02**
Depth Interval	-0.62	0.23	**0.007**
Frozen	-1.00	0.92	0.28
Bog	0.56	0.63	0.38

$$\text{Toluene}(mg/kg) = 4.89 + 5.33(\text{cap}) - 0.66\ (\text{pH}) - 0.87\ (\text{cap*pH}) - 0.62(\text{Depth Interval}) - 1(\text{frozen}) + 0.56(\text{bog})$$

$$\Delta Toluene_{\left(\frac{mg}{kg}\right)} \Big/ _{\Delta Cap} = 5.33 - 0.87 \times (pH)$$

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Multivariate Analysis

	Toluene Prediction by Median Site Conditions	
Explanatory Variable	Capped	Uncapped
Intercept	4.89	4.89
Cap	5.33 x 1 = 5.33	5.33 x 0 = 0
pH	-0.66 x 5.6 = -3.70	-0.66 x 5.1 = -3.37
Cap*pH	-0.87 x 1 x 5.6 = -4.87	-0.87 x 0 x 5.1 = 0
Depth Interval	-0.62 x 1.1 = -0.68	-0.62 x 1.25 = -0.78
Frozen	-1.00 x 0 = 0	-1.00 x 0 = 0
Bog	0.56 x 1 = 0.56	0.56 x 1 = 0.56
Total Toluene (mg/kg)	1.53 mg/kg	1.30 mg/kg

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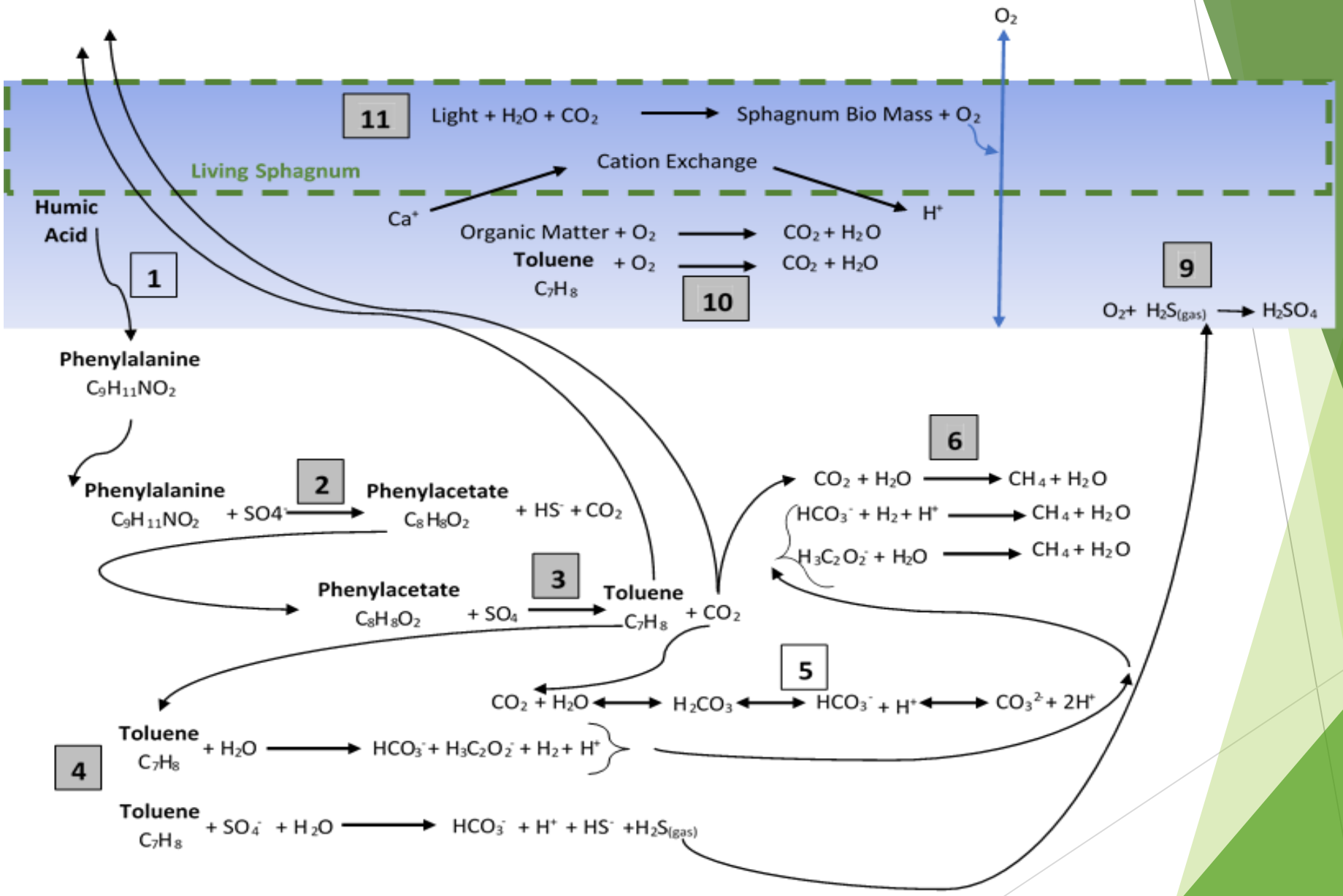
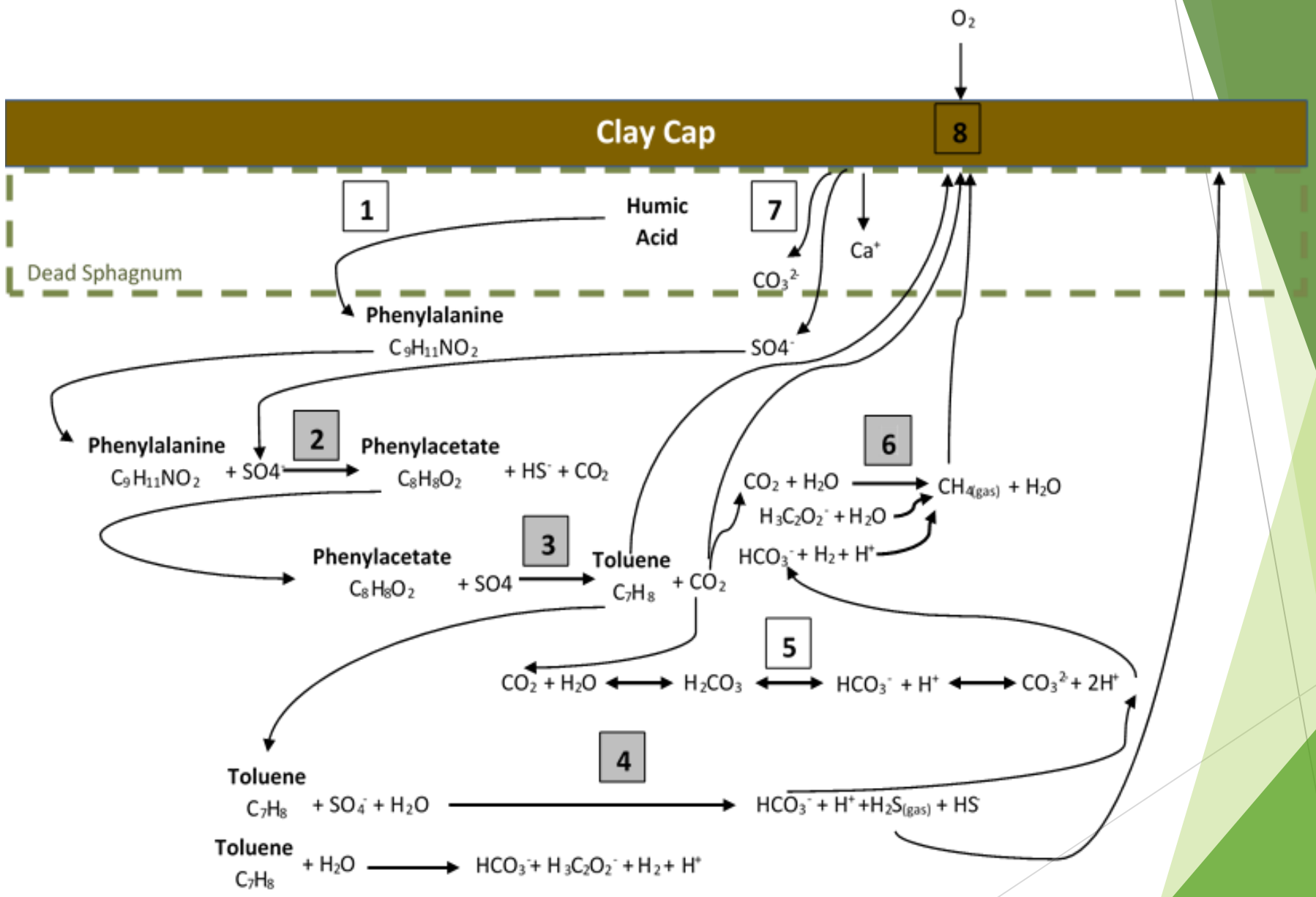

O2
11
Light + H2O + CO2
Sphagnum Bio Mass + O2
Living Sphagnum
Cation Exchange
Ca+
H+
Humic Acid
1
Organic Matter + O2
CO2 + H2O
Toluene + O2
C7H8
CO2 + H2O
10
9
O2+ H2S(gas)
H2SO4
Phenylalanine
C9H11NO2
6
Phenylalanine
C9H11NO2
+ SO4-
2
Phenylacetate
C8H8O2
+ HS- + CO2
CO2 + H2O
CH4 + H2O
HCO3- + H2 + H+
CH4 + H2O
H3C2O2- + H2O
CH4 + H2O
Phenylacetate
C8H8O2
+ SO4
3
Toluene
C7H8
+ CO2
5
CO2 + H2O
H2CO3
HCO3- + H+
CO3 2- + 2H+
4
Toluene
C7H8
+ H2O
HCO3- + H3C2O2- + H2 + H+
Toluene
C7H8
+ SO4- + H2O
HCO3- + H+ + HS- + H2S(gas)


O_2
Clay Cap
8
Dead Sphagnum
1
Humic Acid
7
Ca^+
CO_3^{2-}
Phenylalanine
$C_9H_{11}NO_2$
$SO4^-$
Phenylalanine
$C_9H_{11}NO_2$
+ $SO4^-$
2
Phenylacetate
$C_8H_8O_2$
+ HS^- + CO_2
6
$CO_2 + H_2O$
$CH_{4(gas)} + H_2O$
$H_3C_2O_2^- + H_2O$
$HCO_3^- + H_2 + H^+$
Phenylacetate
$C_8H_8O_2$
+ $SO4$
3
Toluene
C_7H_8
+ CO_2
5
$CO_2 + H_2O$ H_2CO_3 $HCO_3^- + H^+$ $CO_3^{2-} + 2H^+$
Toluene
C_7H_8
+ $SO_4^- + H_2O$
4
$HCO_3^- + H^+ + H_2S_{(gas)} + HS^-$
Toluene
C_7H_8
+ H_2O
$HCO_3^- + H_3C_2O_2^- + H_2 + H^+$

Objectives Revisited

- Toluene Level Differences Between Capped and Uncapped Sites (Objective 1)
- Relationship Between Sulphate and Toluene (Objective 1, Objective 2)
- Influence of other Measured Chemicals on Toluene Generation (Objective 3)
  - pH, salt ions
- Toluene Benchmark (Objective 4)
- Describe the management implications of the results (Objective 5)

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Conclusions

- Hypothesis supported
  - clay cap was associated with a significant increase in toluene of 0.46 mg/kg at average pH conditions
- Site conditions are important predictors of toluene levels
  - toluene levels was significantly dependent on site pH level
  - significant correlation between toluene and sample depth
- The results of this study suggest it is possible to detect toluene differences between sites with differing conditions and that remediation criteria might best be established as benchmark comparisons to ‘background’

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Best Practices

- Absence of Peatland based guidelines for remediation
- Frozen sample complications
- Sample location complications

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Recommendations

- Further Study
  - Specifically with factors contributing to biogenesis and biodegradation
    - “Background” conditions
    - Sulphur, other nutrients electron acceptors
    - Possible remediation pathways
    - pH and toluene
- Removal of physical clay pad structure, total or partial
- Revisit construction standards-When are clay pads actually needed?

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Thank you!

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