Toxicity of NaF and uptake of F to willows

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Toxicity of NaF and uptake of F to willows
Trees are lovely. Can’t we make a park and remediate at the same time?

Why this study?

F polluted site at Fredericia, Denmark.

The municipality asked if we knew anything about phytotoxicity of F
Scopes of the study

- Examine the toxicity and uptake of fluoride to willows, when they are exposed through their roots? (lab. study)

- Mass balance model for prediction of F uptake to willows

- Evaluate potential of phytoremediation at Fredericia
The willow tree toxicity test

The philosophy: “Healthy tree transpire more than weak trees” (S. Trapp)

Normalized Relative Transpiration (NRT)

\[
NRT(C, t) \ (\%) = \frac{1}{n} \cdot \sum_{i=1}^{n} \frac{T_i(C,t)}{T_i(C,0)} \cdot \frac{1}{m} \cdot \sum_{j=1}^{m} \frac{T_j(0,t)}{T_j(0,0)} \times 100
\]
The definitive test
Calculating effect concentrations by R

Log-logistic model fit with lower transp. boundary of 0 g/h

<table>
<thead>
<tr>
<th>$EC_X$</th>
<th>Estimate</th>
<th>95% CI</th>
</tr>
</thead>
<tbody>
<tr>
<td>$EC_{10}$</td>
<td>38.0</td>
<td>± 34.2</td>
</tr>
<tr>
<td>$EC_{20}$</td>
<td>59.6</td>
<td>± 40.7</td>
</tr>
<tr>
<td>$EC_{50}$</td>
<td>128.7</td>
<td>± 51.1</td>
</tr>
</tbody>
</table>
Average growth rates with 95% CI
Mass balance calculations

\[
m_{\text{init, sol.}} + m_{\text{init, tree}} = m_{\text{end, sol.}} + m_{\text{end, tree}}
\]

\[
TSCF = \frac{\text{Concentration in transpiration stream}}{\text{Concentration in external solution}}
\]
Modelling the uptake of fluoride

The model was used by Trapp et al. (2008) to describe uptake of slat to willows. It is basically just a mass balance.

The model assumes:

- That fluoride is taken up passively with the transpiration stream.

  - Steady state.

  - That the processes responsible for pumping out fluoride from the roots follows the Michaelis-Menten equation for enzymatic removal.

\[
0 = \frac{K_M Q C_W}{M_R} + \frac{Q C_W C_R}{M_R} - \frac{K_M Q C_R}{M_R K_RW} - \frac{C^2 R Q}{M_R K_RW} - K_M k_R C_R - k_R C^2 R - v_{\text{max}} C_R
\]

Solving this for \( C_R \) gives...

Michaelis-Menten equation

\[
v = \frac{v_{\text{max}} C_W}{K_M + C_W} M_R
\]

where \( v \) is the removal (mg/d), \( v_{\text{max}} \) is the maximal removal (mg/(kg plant and d)), \( C_W \) is the concentration in the external solution (mg/L), \( K_M \) is the half-saturation constant, \( M_R \) is the mass of the roots (kg), \( Q \) is the transp. (L/d), \( K_RW \) is the partitioning coefficient between root and water, \( k_R \) is the growth rate of the roots (1/d) and \( C_R \) is the conc. in the roots (mg/kg)
A quadratic equation of the general form: \[ aC^2 + bC + C = 0 \]

With two solutions

\[ C_R = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \]

However only one realistic solution

where

\[ a = -k_R \frac{Q}{MRK_{RW}} \]

\[ b = C_WQ \frac{1}{MR} - K_MQ \frac{1}{MRK_{RW}} - k_RK_M - v_{max} \]

\[ c = C_WK_MQ \frac{1}{MR} \]

where vmax is the maximal removal (mg/(kg plant and d)), \( C_W \) is the concentration in the external solution (mg/L), \( KM \) is the half-saturation constant, \( MR \) is the mass of the roots (kg), \( Q \) is the transp. (L/d), \( K_{RW} \) is the partitioning coefficient between root and water, \( k_R \) is the growth rate of the roots (1/d) and \( C_R \) is the conc. in the roots (mg/kg)
Model results

\[ v_{\text{max}} = C_{W_0} \frac{Q}{M_R} \]

On molar basis = 0.5 mole/(kg d)
The same obtained by Trapp et al. (2008) for salt

Break through point = 209.5 mg/L

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
<th>Origin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration in solution, ( C_{W_0} )</td>
<td>0-400</td>
<td>mg/L</td>
<td>Measured</td>
</tr>
<tr>
<td>Root mass, ( m_R )</td>
<td>0.001</td>
<td>kg</td>
<td>Estimated</td>
</tr>
<tr>
<td>Transpiration stream, ( Q )</td>
<td>0.04</td>
<td>L/d</td>
<td>Measured average</td>
</tr>
<tr>
<td>Half-saturation constant, ( K_M )</td>
<td>2</td>
<td>g/L</td>
<td>Fitted</td>
</tr>
<tr>
<td>Maximum enzymatic removal rate, ( v_{\text{max}} )</td>
<td>8.992</td>
<td>g/kg/d</td>
<td>Fitted</td>
</tr>
<tr>
<td>Root growth rate, ( k_R )</td>
<td>0</td>
<td>d(^{-1})</td>
<td>Estimated</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Equation</th>
<th>Valid conc.</th>
<th>( R^2 )</th>
<th>n</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regression 1</td>
<td>( y = 0.128x - 5.186 )</td>
<td>C &lt; 209.5 mg/L</td>
<td>0.764</td>
<td>16</td>
</tr>
<tr>
<td>Regression 2</td>
<td>( y = 1.005x - 210.5 )</td>
<td>C &gt; 209.5 mg/L</td>
<td>0.790</td>
<td>8</td>
</tr>
</tbody>
</table>
Potential for phytoremediation

Assuming:
A = 1 ha, pollution depth = 2 m, \( C_{\text{soil}} = 200 \text{ mg F/kg} \), soil density = 2 kg/L, 100 L of water in order to produce 1 kg of plant (Larcher, 2003), \( C_{\text{water}} = 50 \text{ mg F/L} \) and a production of plant mass per square meter per year of 2 kg.

Total mass of fluoride = 8000 kg.

TSCF at 50 mg F/L is approximately 0.1.

Total removal time is then approximately 800 years.
Conclusions

• The phytotoxicity of fluoride has been assessed through the willow tree toxicity test. EC10: 38.0±34.2 EC20: 59.6±40.7 and EC50:128.7±51.1 (mg F/l)

• Uptake of fluoride to willows could be described by a non-linear mathematical mass balance model indicating a break through point at 209.5 mg F/L and with a maximum enzymatic removal rate of 8992 mg/kg/d

• The mechanisms responsible for pumping out F from plant cells are most likely the same responsible for pumping Cl out

• Phytoremediation at Fredericia takes approx. 800 years

Questions
Transpiration of the controls

Table 5.2: Transpiration rates (g/h) of the control trees during the different time intervals of the preliminary willow tree toxicity test.

<table>
<thead>
<tr>
<th>Category</th>
<th>Tree no.</th>
<th>0-16.75h</th>
<th>16.75-41h</th>
<th>41-72h</th>
<th>72-92.5h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>3</td>
<td>1.654</td>
<td>1.674</td>
<td>1.594</td>
<td>1.634</td>
</tr>
<tr>
<td>Control</td>
<td>6</td>
<td>1.200</td>
<td>1.225</td>
<td>1.181</td>
<td>1.210</td>
</tr>
<tr>
<td>Control</td>
<td>13</td>
<td>0.985</td>
<td>0.990</td>
<td>0.942</td>
<td>0.922</td>
</tr>
<tr>
<td>Control</td>
<td>16</td>
<td>0.991</td>
<td>1.035</td>
<td>1.065</td>
<td>1.132</td>
</tr>
<tr>
<td>Control</td>
<td>20</td>
<td>1.313</td>
<td>1.344</td>
<td>1.319</td>
<td>1.346</td>
</tr>
</tbody>
</table>
Table 5.3: Ratios of fluoride concentration in external solution before and after the preliminary and definitive test \( \frac{C_{\text{end}}}{C_{\text{Init}}} \). Concentrations were measured by conductivity meter.

<table>
<thead>
<tr>
<th>Conc. (mg F/L)</th>
<th>1</th>
<th>10</th>
<th>50</th>
<th>100</th>
<th>200</th>
<th>400</th>
<th>1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Preliminary test</td>
<td>1.56</td>
<td>1.24</td>
<td>-</td>
<td>1.21</td>
<td>-</td>
<td>-</td>
<td>0.99</td>
</tr>
<tr>
<td>Definitive test</td>
<td>-</td>
<td>-</td>
<td>1.46</td>
<td>1.35</td>
<td>1.18</td>
<td>1.01</td>
<td>-</td>
</tr>
</tbody>
</table>
pH and dissociation

\[ C_{\text{non-dissociated acid}} = \frac{1}{1 + 10^{(pH - pK_a)}} \]

where \( pK_a \) is the acid dissociation constant.

\( pK_a \) (HF) = 3.17 \( \Rightarrow \) 0.1 % non-dissociated HF at pH 6.

app. 1 % non-dissociated HF at pH 5.