Supplemental Materials

Hydrology and soil manipulations of iron-rich ditch mesocosms provide little evidence for phosphorus capture within the profile


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9 pages including cover sheet
Supplemental Materials regarding Materials and Methods

Mesocosm Construction

Despite the attempt to scout a ditch reach without a restricting layer, a restricting layer was found in the C horizons of many ‘Undredged’ mesocosms, and therefore the C horizons of Undredged mesocosms were removed. The shortened mesocosms contained only O and A materials and extended between 18 and 40 cm in depth.

Unlike mesocosms gathered before dredging, Dredged mesocosms almost exclusively contained ditch C material (Ruppert et al., 2014). To avoid the restricting layer found in the C material of Undredged mesocosms, Dredged mesocosms were extracted 160 m upstream within the same ditch. Handling of Dredged mesocosms after extraction was identical to Undredged mesocosms except that Dredged mesocosms contained no restricting layer and were not shortened. In the analysis of whole mesocosm Fe$_{ox}$, Al$_{ox}$ and P$_{ox}$ content different mesocosm mass was controlled for using mesocosm mass as a covariate.

Categorization of soil horizons

C horizons were distinguished from A and O horizons due to a lack of organic matter pigment and pedogenic structure. A and Ag and mucky A horizons were distinguished from O horizons using the formula: $\text{Organic C} (%) = 12 + \text{clay} \times 0.1$, where ‘clay’ = the percent clay present (Soil Survey Staff, 2014). Soils lying above this line were designated as ‘O’ horizons (Soil Survey Staff, 2014). Mucky A horizons were distinguished as lying below the above line and above the following line: $\text{Organic C} (%) = 5 + \text{clay} \times 0.1$. Soils lying below this latter line, with value 4 or more and chroma 2 or less according to the Munsell system, were designated as ‘gleyed’ A or C horizons (‘Ag’ and ‘Cg’ respectively) since their lack of brightness, or gleying, was considered ‘strong’ (Schoeneberger et al., 2002) and was assumed to be due to Fe-reducing
conditions predominating from time to time in ditch soil environments. Soils that were not C
horizons or in any of the other above categories were designated as A horizons. Soil was
pulverized to fine powder using an agate pestle and analyzed for carbon content (LECO CHN-

**Oxalate extractions and analysis**

Oxalate extractions (0.5-g soil:20-mL 0.2 M ammonium oxalate acidified with oxalic
acid to pH=3; similar to Sah and Mikkelsen, 1986) were performed in the dark on material from
individual horizons. Supernatants were analyzed for 1) oxalate-extractable P (P_{ox}) by modified
molybdenum blue method (of Kryskalla et al., 2003) and 2) oxalate-extractable Fe and Al (Fe_{ox}
and Al_{ox}, respectively) on an atomic absorption flame spectrophotometer (AAnalyst 200, Perkin-
Elmer Corp., Waltham, Massachusetts).

**Linear Spine versus simple linear models**

Change point models were developed according to the ‘linear spline’ model of
Fitzmaurice et al. (2004) using the SAS MIXED procedure. Minimization of Akaike’s 2\textsuperscript{nd} order
Information Criterion (AICc; Burnham and Anderson, 2002) was used to determine optimal
change points. AICc is a standard output of the SAS MIXED procedure. When optimal change
points were determined the AICc was used to compare linear spline to simple linear models. If
the AICc of the linear spline model was at least 20 units less than that of the simple linear model
the linear spline model was preferred. Differences in AICc greater than 15-20 indicate that the
model with the higher AICc is not to be preferred (Anderson, 2008).

**Analyzing a change in correlation between DPS and Fe_{ox}**

Similar to piecewise regression, the full dataset was successively partitioned into two
subsets (subset 1 = \text{Fe}_{ox} < k, subset 2 = \text{Fe}_{ox} > k, k=5 to 150 mmol kg\textsuperscript{-1}). Each pair of subsets was
analyzed with a simple linear regression of DPS on $\text{Fe}_{\text{ox}}$ and the $R^2$ was computed for each linear regression. We chose as the optimal analysis the value of $k$ for which the difference in $R^2$ was greatest.

**Supplemental Materials regarding Results**

Characteristics of mesocosm soil materials are provided in Table S4, taken from Ruppert et al. (2014).
Supplemental Figure S1. Mesocosm use and construction. (a) Mesocosms were attached to Marriotte bottles such that supplied water moved upward through the mesocosm. A 40-cm hydraulic head occurred between the air-tube of the Marriotte bottle and the outlet port of the mesocosm. (b) A subset of mesocosms was instrumented with redox electrodes and pore water samplers. Mesocosms were not packed but contained the horizonation and structure of the micro site from which they were gathered. (c) Redox measurements were made with a platinum-tipped and calomel reference electrodes, a multimeter and an additional device to provide stable measurements by creating greater resistance than supplied by the multimeter itself.
Supplemental Table S1. Constituents of simulated groundwater used as input water during upwellings. Based on average groundwater concentrations at the field site from which mesocosms were taken.

<table>
<thead>
<tr>
<th>Constituent</th>
<th>mg L⁻¹</th>
<th>mmol L⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₄-S</td>
<td>261.5</td>
<td>2.72</td>
</tr>
<tr>
<td>Cl</td>
<td>19.1</td>
<td>0.53</td>
</tr>
<tr>
<td>NO₃-N</td>
<td>16.4</td>
<td>0.26</td>
</tr>
<tr>
<td>PO₄-P</td>
<td>0.48</td>
<td>0.005</td>
</tr>
<tr>
<td>Na</td>
<td>35.7</td>
<td>1.55</td>
</tr>
<tr>
<td>Mg</td>
<td>34.5</td>
<td>1.42</td>
</tr>
<tr>
<td>Ca</td>
<td>34.8</td>
<td>0.87</td>
</tr>
<tr>
<td>K</td>
<td>4.8</td>
<td>0.12</td>
</tr>
</tbody>
</table>
### Supplemental Table S2. Treatment structure of experiment and replication.

<table>
<thead>
<tr>
<th>Soil Treatments†</th>
<th>Hydraulic Treatments‡</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Drained</td>
</tr>
<tr>
<td><strong>Un-Dredged</strong></td>
<td></td>
</tr>
<tr>
<td>Control</td>
<td>6(2)§</td>
</tr>
<tr>
<td>O-Addition</td>
<td>6(2)</td>
</tr>
<tr>
<td>Surf. Removal</td>
<td>6(2)</td>
</tr>
<tr>
<td>Dredged</td>
<td>2(1)</td>
</tr>
</tbody>
</table>

† 'Undredged' ditch mesocosms were gathered before dredging; ‘O-Addition’ mesocosms had 100 g Organic materials surficially added; ‘Surf. Removal’ mesocosms had 2-cm of surficial materials surficially removed; ‘Dredged’ mesocosms were gathered from the same ditch after dredging.

‡ ‘Saturated’ mesocosms were saturated between upwellings of simulated groundwater; ‘Drained’ mesocosms were maintained at field capacity between upwellings of simulated groundwater; ‘Alternating’ mesocosms were held at field capacity after odd numbered simulated groundwater rise events.

§ Number not in parentheses gives number of experimental units allocated to the indicated treatment. Numbers in parentheses give the number of replicates of that treatment instrumented with platinum-tipped electrodes (for Eh) and pore water samplers (for pH).
Supplemental Table S3. Experimental timeline of static hydrologic periods and ‘upwellings’ of simulated groundwater rise in which mesocosm effluent was gathered for analysis.

<table>
<thead>
<tr>
<th>Overall Hydraulic Treatment†</th>
<th>Pre-experiment‡</th>
<th>Interim period§</th>
<th>Interim period</th>
<th>Interim period</th>
<th>Interim period</th>
<th>Interim period</th>
<th>Interim period</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drained</td>
<td>Temporary state#</td>
<td>Drained</td>
<td>Drain.</td>
<td>Temp. state</td>
<td>Drain.</td>
<td>Temp. state</td>
<td>Drain.</td>
</tr>
<tr>
<td>Saturated</td>
<td>Drain.</td>
<td>Temp. state</td>
<td>Sat.</td>
<td>Temp. state</td>
<td>Sat.</td>
<td>Temp. state</td>
<td>Sat.</td>
</tr>
<tr>
<td>Alternating</td>
<td>Drain.</td>
<td>Temp. state</td>
<td>Sat.</td>
<td>Temp. state</td>
<td>Sat.</td>
<td>Temp. state</td>
<td>Sat.</td>
</tr>
</tbody>
</table>

† ‘Drained’ mesocosms were drained following each ‘upwelling event’; ‘Saturated’ mesocosms were held saturated throughout the experiment; ‘Alternating’ mesocosm were drained or remained saturated after an upwelling in a cyclic fashion.

‡ Before the first upwelling all mesocosms were at field capacity, but unsaturated.

§ Upwellings occurred when simulated groundwater (Table 1) was added to the bottom of each mesocosm (1 L mesocosm day⁻¹) and effluent was collected from the top for analysis.

¶ Between upwellings, interim periods occurred in which a mesocosm was held either in a drained or saturated ‘temporary state’.

# ‘Temporary state’ gives the hydrology that mesocosms experience at any particular time. ‘D’ indicates a drained state (held near field capacity); ‘S’ indicates a saturated state in which mesocosms were inundated with water such that 10 cm of free water persisted above the soil surface.
Supplemental Table S4. Properties of mesocosm horizons harvested at the end of the experiment.

<table>
<thead>
<tr>
<th>Horizon properties</th>
<th>Mucky A</th>
<th>A</th>
<th>Ag</th>
<th>C</th>
<th>Cg</th>
</tr>
</thead>
<tbody>
<tr>
<td>thickness (cm)</td>
<td>0.0</td>
<td>9.7</td>
<td>7.7</td>
<td>0.12</td>
<td>0.14</td>
</tr>
<tr>
<td>Organic Carbon (%)</td>
<td>15.4±3.1</td>
<td>2.0±0.2</td>
<td>1.4±0.1</td>
<td>0.12±0.12</td>
<td>0.14±0.04</td>
</tr>
<tr>
<td>Fe$_{ox}$ (mmol kg$^{-1}$)</td>
<td>382±98</td>
<td>57±5b</td>
<td>31±4c</td>
<td>1.4±0.5d</td>
<td>2.4±0.3d</td>
</tr>
<tr>
<td>P$_{ox}$ (mmol kg$^{-1}$)</td>
<td>300±42a</td>
<td>27±3b</td>
<td>13±2c</td>
<td>1.4±0.5d</td>
<td>2.4±0.3d</td>
</tr>
<tr>
<td>matrix hue (Munsell)</td>
<td>(10.00±0.67)YR</td>
<td>(9.71±0.14)Y</td>
<td>(9.90±0.17)Y</td>
<td>(10±0.67)Y</td>
<td>(10±0.42)Y</td>
</tr>
<tr>
<td>matrix value (Munsell)</td>
<td>2.0±0.4a</td>
<td>1.8±0.1a</td>
<td>1.8±0.1a</td>
<td>1.6±0.1a</td>
<td>4.6±0.3b</td>
</tr>
<tr>
<td>matrix chroma (Munsell)</td>
<td>4.4±0.1a</td>
<td>4.9±0.1b</td>
<td>5.2±0.1cd</td>
<td>5.3±0.1c</td>
<td>4.7±0.2ab</td>
</tr>
<tr>
<td>pH</td>
<td>4.4±0.1a</td>
<td>5.2±0.1cd</td>
<td>5.3±0.1c</td>
<td>4.7±0.2ab</td>
<td>4.8±0.1ab</td>
</tr>
<tr>
<td>bulk density (g cm$^{-3}$)</td>
<td>0.16±0.09a</td>
<td>0.98±0.04b</td>
<td>1.15±0.05b</td>
<td>1.38±0.21bc</td>
<td>1.63±0.15c</td>
</tr>
<tr>
<td>clay (%)</td>
<td>5.0±3abc</td>
<td>13±0.4c</td>
<td>13±0.5c</td>
<td>6±4 bc</td>
<td>4±1a</td>
</tr>
<tr>
<td>texture(s)</td>
<td>Oe, SiL, Si</td>
<td>L, SL, L, SiL</td>
<td>SL, L, SiL</td>
<td>S, LS, L</td>
<td>S, LS</td>
</tr>
<tr>
<td>dominant texture</td>
<td>Oe</td>
<td>SiL</td>
<td>L</td>
<td>LS</td>
<td>LS</td>
</tr>
</tbody>
</table>

† ‘Dredged’ mesocosms gathered after dredging; ‘Undredged’ mesocosms gathered before dredging.
‡ Within rows, means followed by the same letter are not significantly different at the 0.05 level according to Tukey-adjusted means comparison tests. Uncertainties are standard error.
§ oxalate extractable iron ‘Fe$_{ox}$’, and phosphorus ‘P$_{ox}$’
¶ 10.00YR=0.
Source: Ruppert et al. (2014)
Supplemental Fig. S1

a) Mariotte bottle

b) O-Addition material

10 cm
10 cm
10 cm

Soil pH
port

Tubing port allowing attachment / detachment of input water tubing to provide input water and maintain saturation or provide drainage

10 cm

Horizon 1
Horizon 2
Horizon 3

3 Redox electrodes per horizon

Geotextile
Gravel
Geotextile
Mesh

Effluent Outlet port

Device providing increased internal resistance beyond multimeter

40 cm

Effluent Collection bottle

Calomel Reference electrode

Redox electrode

Multimeter
Supplemental Material References


