Biogeochemistry of Inorganic P, Mn, and Fe in Seasonally Reduced Soils of the Willamette Valley, Oregon

By

Rex King

A THESIS

submitted to

Oregon State University

Bioresource Research Major

and

International Degree

In partial fulfillment of
the requirements for the
degree of

Bachelor of Science in Bioresource Research
and
Bachelor of Arts in International Degree

December 1997
Bachelor of Science in Bioresource Research thesis of Rex O King presented on Dec 12, 1997

APPROVED:

[Signature]
Mentor

[Signature]
Secondary advisor

[Signature]
Co-director of the Bioresource Research Major

I understand that my thesis will become part of the permanent collection of Oregon State University, Bioresource Research Program. My signature below authorizes the release of my project to any reader upon request.

[Signature]
(student's name), author
Saturated soils undergo reduced conditions as microorganisms consume oxygen and require other terminal electron accepting processes for the mineralization of soil organic carbon. Currently, the soil redox potential has not been considered as important when sampling these soils for Fe, Mn, and PO$_4$. Since Fe- and Mn-oxides are electron sinks for these reactions, the redox potential should affect their solubility in the soil. Phosphate solubility, should also be closely related to redox potential. Current methods for sampling Fe(II), Mn(II) and PO$_4$ under reduced conditions are inadequate since they do not protect the samples from contamination by O$_2$. The presence of O$_2$ results in oxidation and subsequent precipitation of Fe-phosphate from solution. The co-precipitation of Fe-phosphate lowers the amount of PO$_4$ and Fe(II) in solution leading to the conclusions that the concentration of these elements is less than exists in the natural state.

These reduction and oxidation reactions are occurring in close to 200,000 acres of wetland soils in the southern Willamette Valley. On this scale, the wetlands play an important role in the non-point sources of phosphorus. The cyclic nature of reduced conditions on riparian soils of the Willamette Valley, and its effects on the solubility of Fe, Mn, and PO$_4$ is investigated in the second part of this thesis. Fe and PO$_4$ concentrations under dry conditions, representative of the dry summers, were almost nonexistent. Mn was more soluble under reduced conditions, but still a fair proportion of the total Mn was soluble even under dry conditions.
conditions. Mn and PO₄ each had a relative redox potential in which their solubility decreased when the soil redox potential passed below their respective arbitrary value. This suggesting that at lower redox potentials, these ions formed new insoluble minerals.
# Table of Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>1</td>
</tr>
<tr>
<td>TABLE OF CONTENTS</td>
<td>3</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>4</td>
</tr>
<tr>
<td>LIST OF APPENDICES</td>
<td>5</td>
</tr>
<tr>
<td>INTRODUCTION</td>
<td>6</td>
</tr>
<tr>
<td>METHODS AND MATERIALS</td>
<td>8</td>
</tr>
<tr>
<td>Soils Microcosm Experiment</td>
<td>8</td>
</tr>
<tr>
<td>Field Experiment</td>
<td>9</td>
</tr>
<tr>
<td>RESULTS</td>
<td>11</td>
</tr>
<tr>
<td>Evaluation of Closed-Headspace Well Performance</td>
<td>11</td>
</tr>
<tr>
<td>Field Experiment</td>
<td>17</td>
</tr>
<tr>
<td>Redox potentials</td>
<td>17</td>
</tr>
<tr>
<td>Cumulative Soluble Nutrients</td>
<td>21</td>
</tr>
<tr>
<td>Soil Profiles</td>
<td>25</td>
</tr>
<tr>
<td>Three Dimensional Graphical Representations</td>
<td>29</td>
</tr>
<tr>
<td>Conclusions and Discussion</td>
<td>35</td>
</tr>
<tr>
<td>Bibliography</td>
<td>36</td>
</tr>
</tbody>
</table>
# List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Dissolved O₂ and redox measurements for microcosms</td>
<td>12</td>
</tr>
<tr>
<td>2.</td>
<td>Lemmon’s soil reactor experiment</td>
<td>14</td>
</tr>
<tr>
<td>3.</td>
<td>Redox potentials for soil, open and closed head-space wells</td>
<td>16</td>
</tr>
<tr>
<td>4.</td>
<td>Fe(II), PO₄, NO₃ concentrations and redox potentials for the center transect</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>at the Lake Creek watershed; Julian day 154 (1997).</td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>Schematic diagram representing the sub-surface stratigraphy of a transect at</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>the Lake Creek Site</td>
<td></td>
</tr>
<tr>
<td>6.</td>
<td>Redox potentials for the Agricultural Site</td>
<td>19</td>
</tr>
<tr>
<td>7.</td>
<td>Redox potentials for the Transitional Site</td>
<td>20</td>
</tr>
<tr>
<td>8.</td>
<td>Redox potentials for the Riparian Site</td>
<td>21</td>
</tr>
<tr>
<td>9.</td>
<td>Cumulative Fe(II) concentrations for the three sites</td>
<td>22</td>
</tr>
<tr>
<td>10.</td>
<td>Cumulative Mn(II) concentrations for the three sites</td>
<td>23</td>
</tr>
<tr>
<td>11.</td>
<td>Cumulative PO₄ concentrations for the three sites</td>
<td>24</td>
</tr>
<tr>
<td>12.</td>
<td>Concentration profiles for Fe(II) at the three sites for day 487</td>
<td>26</td>
</tr>
<tr>
<td>13.</td>
<td>Concentration profiles for Mn(II) at the three sites for day 487</td>
<td>27</td>
</tr>
<tr>
<td>14.</td>
<td>Concentration profiles for PO₄ at the three sites for day 487</td>
<td>28</td>
</tr>
<tr>
<td>15.</td>
<td>Concentration profiles for Fe(II) for the three sites over one year</td>
<td>30</td>
</tr>
<tr>
<td>16.</td>
<td>Concentration profiles for Fe(II) for the three sites over two years</td>
<td>31</td>
</tr>
<tr>
<td>17.</td>
<td>Concentration profiles for Mn(II) for the three sites over one year</td>
<td>32</td>
</tr>
<tr>
<td>18.</td>
<td>Concentration profiles for PO₄ for the three sites over one year</td>
<td>34</td>
</tr>
<tr>
<td>Appendix</td>
<td>Title</td>
<td>Page</td>
</tr>
<tr>
<td>------------</td>
<td>--------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>Appendix 1</td>
<td>Soil $\text{PO}_4$ Concentration Profiles</td>
<td>37</td>
</tr>
<tr>
<td>Appendix 2</td>
<td>Soil $\text{Fe(II)}$ Concentration Profiles</td>
<td>41</td>
</tr>
<tr>
<td>Appendix 3</td>
<td>Soil $\text{Mn(II)}$ Concentration Profiles</td>
<td>45</td>
</tr>
<tr>
<td>Appendix 4</td>
<td>International Degree Experience</td>
<td>49</td>
</tr>
</tbody>
</table>
Introduction

Wetlands and riparian zones play an important role in the processing of N, S, trace metals, and degradation of pesticides. In wet soil ecosystems, water fills soil pores, thus dramatically slowing the transport of O₂. When oxygen is unavailable because of soil saturation, the microorganisms must use other terminal electron acceptor processes to ensure their survival. The maximum amount of biogeochemical energy is obtained through aerobic respiration (O₂) followed by denitrification (NO₃), oxide reduction (Mn(IV) and Fe(III)), sulfate reduction (SO₄), and finally methanogenesis (HCO₃) (Patrick, 1992). As Fe(II) and Mn(IV) oxide minerals dissolve, inorganic P and trace metals may be released. Thus the reduction process can exert an important influence on the water quality aspects of riparian zones and wetlands.

Biogeochemically mediated redox reactions play an important role in controlling the solubility of PO₄ containing minerals (Ponnamperuma, 1972). One of the dominant pools of P is in the form of an Fe(III)-PO₄. Inorganic phosphate is released as the microorganisms reduce the Fe(III) to Fe(II). Inorganic phosphate may then become soluble in the soil and more easily absorbed by plants. Under oxidizing conditions (e.g. well-drained soil), PO₄ forms mineral solids with Fe(III) and therefore becomes immobile. Based on the discussion above, it is likely that PO₄ may be much more soluble in wet soils than currently believed. There is no quantitative data available on the annual reductive dissolution of Fe, Mn, and associated PO₄ at the landscape level (Stumm, 1992). This thesis addresses the question of the temporal dynamics of Fe, Mn, and PO₄
of the some poorly-drained soils of the Willamette Valley. These processes have
important implications in the leaching of PO$_4$ into streams, degradation of
chlorinated pesticides, and behavior of trace metals.

In this thesis I explored two hypotheses:

1. When sampling shallow reduced soil ground water for soluble Fe(II),
   Mn(II), and PO$_4$, the water sample must be protected from oxidation.
   Failure to exclude O$_2$ will result in the oxidation of Fe, resulting in the
   precipitation of Fe, P and other metals.

   Current methods of sampling soils and shallow soil ground waters for
   Fe(II), Mn(II), and PO$_4$ do not exclude oxygen from entering the system that is to
   be sampled. When sampling soils that are under reduced conditions, care must
   be taken to prevent oxygen from entering either the sampled soil or the water
   samples. If oxygen was allowed to enter, the samples may show lower amounts
   of minerals and nutrients than are truly present in the soil.

2. Concentrations of KCl/HCl extractable Fe(II), Mn(II), and PO$_4$ in poorly
   drained soils of the Willamette Valley are low during the summer, but
   steadily increase as the soil become saturated and peak in the early
   spring when the temperatures are warm, and the soil is still saturated.

   The Willamette Valley is characterized as a xeric moisture regime. The
   soils experience cycles of dry summers and wet winters and springs. This
   annual wetting and drying cycle results in interesting soil biogeochemical
   conditions. Study of the cyclic nature of biogeochemical reduction in these soils
may lead to an understanding of their role in water and soil quality. This knowledge may lead us to make changes in the way we manage these soils.

Methods and Materials

Soils Microcosm Experiment

Three controlled soil microcosms were created in 19 L buckets. Each bucket was filled half-full with surface soil (0-20 cm) collected from a mesic Typic Alpaqualf (Dayton series) at the Lake Creek West site. The effect of the amount and chemical nature of organic amendments was tested; microcosm A served as a control and received no extra source of carbon, 1 kg C m\(^{-2}\) corn straw was added to microcosm B and microcosm C was given 1 kg C m\(^{-2}\) calcium acetate (CaC\(_2\)H\(_3\)O\(_2\)). A standard 5 cm diameter piezometer, equipped with an internal platinum electrode, was inserted to a depth of 20 cm in each soil microcosm. Two additional platinum electrodes were placed directly in the soil at depths of 5 and 15 cm. Water was added to the microcosms until there was 5 cm of standing water above the soil surface. The water level was maintained at that level for the duration of the experiment. Water was continuously pumped (~100 mL h\(^{-1}\)) from inside the piezometer to the standing water surface to ensure that the water in the piezometer was at least somewhat equivalent to the soil solution.

The experiment was initiated on July 5, 1995 and lasted for eight weeks. Redox potentials (mV vs. SHE), and dissolved oxygen concentrations (mg O\(_2\) L\(^{-1}\))
were taken five times weekly. Dissolved oxygen was determined using a polarographic dissolved oxygen probe. Redox potentials were determined by connecting the platinum electrodes to a voltmeter and a reference electrode placed in the standing water of the microcosm. Redox measurements were converted to values equivalent to the standard hydrogen electrode (SHE) by addition of the reference electrode potential to the measured laboratory value. During the initial phase of experiment, no attempt was made to exclude O₂ from the piezometers and the water within. This type of well is referred to as an open head-space well. On day thirty of the experiment, N₂ gas was bubbled into the piezometers to limit the transport of O₂ into the piezometers. This phase of the well performance is referred to as a purged head-space well. After two weeks the flow of N₂ gas was stopped to determine the rate of O₂ diffusion into the soil microcosm.

Field Experiment

Three sites representing differing soil biogeochemical regimes were chosen along a gradient of soil drainage (water table levels). The agricultural site was located in the somewhat poorly drained soil of the field (Holcolm series, a fine montmorillonitic mesic Mollic Albaqualf); a transitional site was located at the interface between the agricultural and the riparian soils. The riparian site was located in the poorly drained soil (Dayton series, a fine, montmorillonitic mesic Typic Albaqualf) 20 m from the creek. Approximately 60 m separate the three sites.
Soils samples were taken bimonthly at depths of 0 to 15 cm, 15 to 30 cm, 30 to 45 cm, and 45 to 60 cm using a soil probe. Immediately after collection, while still in the field, soil samples were cut in half, perpendicular to the profile. One-half of the sample was placed into a sampling cup to be dried. The other half was again divided in half perpendicular to the profile. One portion (~8-12 g) was placed into a preweighed 50 mL centrifuge tube containing 20 mL of an extracting solution of 1M KCl / 0.1 M HCl. While the remaining quarter was placed into another 50mL centrifuge tube and mixed with 1 M ammonium fluoride at pH 3 (Bray II Solution) (Bhiyan, 1995).

After returning from the field, the tubes were again weighed and placed on a shaker for 16 hrs in the dark. The soil slurry extracts were centrifuged at 2000 x g (5000 rpm) for 20 minutes. Ten ml aliquots were decanted off and stored in a refrigerator prior to analysis. The remainder of the supernate was decanted off the soil and discarded. The soil was rinsed three times with tap water to entrained salts and acid prior to the drying process. The soil was then placed into a sampling cup, air dried, and dry soil mass determined.

The concentrations of Fe(II), total Fe, ortho-PO₄, NH₄, and NO₃ in the extracts were measured by flow injection analysis. Extractable Mn was determined by atomic absorption spectroscopy.

Redox potentials were measured on a weekly schedule. Sites were chosen on a transect parallel to the soil sampling area, but about 5 m away to prevent the redox electrode sites from being disturbed by the soil sampling. Each site had six platinum electrodes. The agricultural site had three electrodes.
at depth 25 cm and three at depth 45 cm, while the riparian and transitional sites each had three electrodes at depth 15 cm, and three at depth 45 cm. Redox measurements were taken using a voltmeter and a reference electrode placed in a hole in the soil that when dry was filled with tap or creek water that contained ions to complete the electrical circuit through the soil. Redox measurements were converted to values equivalent to the standard hydrogen electrode (SHE).

Results

*Evaluation of Closed-Headspace Well Performance for the Soil Microcosm Experiment*

Differences in the respective redox potentials between the microcosms (A-C) were not significant. Apparently adequate soil carbon was already present so that the added carbon sources for microcosms B and C made little or no perceivable impact in redox potential when compared to the control (microcosm A). Averaged values (microcosm A-C) for the redox potentials and dissolved $O_2$ content are plotted in Figure 1.
The average daily values for the soil redox potentials revealed a clear trend in the biogeochemical process of reduction. At the beginning of the experiment, the soil redox potential started at just above +50 mV (SHE), and dropped to a minimum value of approximately -225 mV after approximately three weeks. The redox value reached an equilibrium value of approximately -175 mV after five weeks.

The concentration of dissolved O₂ in the well pore water followed the same trend as redox potential. The concentration of oxygen started at around 1 mg O₂ L⁻¹ and steadily decreased to a value near zero. Both the soil redox
potentials and O₂ profiles appeared to follow a logarithmic path with time, indicative of a biological rate process.

The initial aqueous piezometer redox potential of +350 mV (SHE) dropped to a minimum value of just less than zero on around day 20 before stabilizing at approximately +100 mV. This was almost 300mV more positive than the soil values. This large difference in redox potential suggest there is something different about the chemical and physical environment of soil pores as sampled in open head-spaced wells when compared to actual soil pores. The most likely explanation is that the open head-spaced wells act as a large pore or a conduit for the transport of O₂ into the water in the piezometer. The presence of O₂ would be expected to oxidize the piezometer water leading to the higher redox potentials and lower values of soluble Fe, Mn, and PO₄.

N₂ gas was bubbled through the piezometers on day 32 of the experiment and the redox potentials in the piezometers decreased to that of the soil electrodes on day 40. On Day 43 of the experiment the N₂ gas was turned off, and the redox potential in the piezometers returned to just under +100 mV, in just one day. This suggests that O₂ transport is a rapid process. The redox potential in the piezometers after that day fluctuated due to the formation of an iron oxide crust on the free water surface inside the piezometers. The crust broke periodically allowing oxidation of the piezometers. This formation and destruction of the iron oxide crusts caused the erratic, but predictable, behavior of the redox potentials after that point.
During the last week of the experiment, it was hypothesized that a small sampling well, completely sealed from the atmosphere and initially purged with N₂, would be able to reproduce the same effect as was being observed in the purging of the piezometers with N₂. A small bottle with perforations to allow water flow, a redox electrode, and a sampling tube was buried in each microcosm. Electrode measurements confirmed this hypothesis (Figure 1). Redox potentials started above +100 mV (SHE) and decreased to almost the redox potential of the soil.

![Graph](image)

**Figure 2. Lemmon’s soil reactor experiment**

Water samples from the microcosm experiments oxidized much more rapidly than we expected. I therefore abandoned the use of these data and drew inferences from Lemmon’s (1995) experiment performed in a soil reactor (Figure 2). Redox potentials were controlled and the concentration of water soluble iron and phosphates were determined at selected time intervals. She found that the
concentration of Fe(II) and ortho-PO₄ were negatively correlated to the redox potential. Applying this to my microcosm experiment, I would expect that the concentrations of Fe(II) and ortho-PO₄ in the soil pores would be higher than the open piezometers as the result of the lower redox potentials. After the piezometers were purged with N₂, the concentrations of Fe(II) and ortho-P in the piezometers should have become more similar to the concentrations of Fe(II) and ortho-P in the saturated soil pores where O₂ diffusion is limited.

These two observations are supported by the formation of Fe(III) mineral oxide crust in the piezometers after the N₂ bubbling was turned off. The results of this experiment were further confirmed in the field studies (Baham et al. 199X). They installed purged head-space wells at the Lake Creek West site, there were three transects with six sampling piezometers along each transect. Each site had an Ar-gas purged head-space well with redox electrode, and an open piezometer with redox electrode. Soil redox electrode values were also measured at each site. The redox potentials of the open piezometers rarely went below +250 mV (SHE), while the Ar-gas purged head-space wells at times were less than 0 mV (Figure 3). Again, as in the microcosm experiment, the difference between open and purged head-space wells was as much as 250 mV. The redox potentials of the soil electrodes was closer to the purged head-space wells redox values than to those measured in the open head-space wells.
Solution sampled from the purged head-space wells across the middle transects show results similar to Lemmon's experiment. When the redox potential is high (oxidized conditions), the concentrations of Fe(II) and ortho-P are low (Figure 4). When redox potentials were lower, higher concentrations of Fe(II) and ortho-P were observed. Nitrates, which are also terminal electron donors before Fe(III) followed the opposite trend as would be expected, other than piezometer number 7 which had a lower level of nitrate that would be expected.

Figure 3. Redox potentials for soil, open and closed head-space wells
Field Experiment

Redox potentials

Soil morphology and edaphic characteristics play an important role in understanding the results of the field experiment at the Lake Creek field site (Figure 5). The Dayton soil series underlied much of the riparian zone. This soil had a B₁ horizon of very low hydraulic conductivity which restricted the vertical movement of water through the soil. Ponding of water during the rainy season is common. As a result, the Dayton soil was considered to be a poorly drained soil. The agricultural soil was identified as the Holcomb soil and did not have the same restrictive layer. Although the soil at the agricultural site was a somewhat poorly drained soil, the water table is usually much lower and drops much more rapidly than the water table in the riparian zone. The soil in the transitional zone.
Figure 5. Schematic diagram representing the sub-surface stratigraphy of a transect at the Lake Creek Site

was also a Holcomb soil, however the difference between the agricultural and transitional zones was that the transitional zone was uncultivated and allowed to grow naturally. Natural vegetation can provide a conduit for the flow of O₂ to the rhizosphere (Engelaar, 1995). This process can lead to the oxygenation and thus higher redox potentials in the soil horizon where active plant growth occurs (Kludze, 1994).

I have observed that vegetation grows slowly at the riparian site in the early spring, which in most years is saturated until June. Vegetation appears to grow the fastest at the Transitional site, while vegetative growth at the agricultural site was somewhere between the transitional and riparian sites. These characteristics of the different sites act in concert to yield differences in the redox potentials of the sites over time.
Redox potentials declined for both the shallow and deep electrodes from +450 mV (SHE) on Julian day 325 (mid-November, 1995) to about an average of +50 mV by Julian day 425 (end of February 1996) (Figure 6). From Julian day 425, the value for the electrodes climbed steadily back to the soil's usual dry potential of around +500 (SHE). The shallow electrodes maintained lower redox potential values for a longer time period and their mean values climbed more slowly. The shallow electrode did not reach the usual dry redox potential by the time the experiment ended on Julian day 525 (May 17). A reasonable explanation for higher redox potentials in the deeper horizons is that the soil was managed so that the majority of the soil organic matter was near the surface of the soil. Therefore, the lower horizons supported little biogeochemical activity and were not as great a sink for O₂ and hence the redox potentials were higher.
Figure 7. Redox potentials for the Transitional Site

The deeper soil electrode readings at the transitional site (Figure 7) were lower (more reduced) than the agricultural site. The redox potential remained near zero mV (SHE) until Julian day 490 (May 1). This was probably the result of a procedingly higher water table level in moving towards the intermittent stream. The rapid growth of vegetation, in early April, pumped oxygen into the shallower soil horizons resulting in a increase in redox potential for the shallow electrode.

The lowest redox potential values were observed at the riparian site (Figure 8). This is evidently the result of a relatively high water table coupled to a warming of the soil in spring while the soils are still saturated. The redox potential of both the shallow and the deep electrodes decreased until Julian day 500 (May 1) with a final low of around -100 mV (SHE). Redox potentials below
+200mV were low enough to result in significant reductive dissolution of the soil Fe- and Mn- oxide minerals.

![Riparian Site](image)

**Figure 8.** Redox potentials for the Riparian Site

**Cumulative Soluble Nutrients**

The cumulative amounts of each KCl/HCl extractable Fe(II), Mn(II), PO₄, NO₃, and NH₄ in units of g m⁻² integrated to the sampling depth of 60 cm was a useful measure for interpreting overall effects on biogeochemical reduction. Examination of these values against a backdrop of the redox potentials on a temporal scale revealed the recognizable trends between the sites.

The highest concentrations of extractable Fe(II) produced by reductive weathering was approximately 600 g m⁻² Fe(II) for the riparian site on Julian day ~440 (~April 10, 1997) (Figure 9). The agricultural site, which was the most well-drained and had the highest redox potentials, produced less than 100 g m⁻² Fe(II).
Figure 9. Cumulative Fe(II) concentrations for the three sites

The time course trends for Mn were similar to those for Fe(II). This was reasonable, since both Fe and Mn would be expected to originate from an oxide
mineral source. When the redox potential of the soil initially declined, the concentration of extractable Mn(II) increased. At some point however, Mn(II)

![Graph showing Mn concentrations for three sites](image)

**Figure 10. Cumulative Mn(II) concentrations for the three sites**

concentrations decreased as the soil continued to become more deeply reduced (Figure 10). This suggests the formation of a mineral (e.g. MnS\(_s\) or MnHPO\(_4\)\(_s\)) which is not completely soluble in the extracting solution. Another trend that is
important to clarify is the observed greater values of extractable Mn(II) at the transitional site than at the riparian site. Krebs et al. (1997), also found that

![Graphs showing cumulative PO4 concentrations for Agricultural, Transitional, and Riparian sites.](image)

*Figure 11. Cumulative PO4 concentrations for the three sites*

extractable Mn was low at the riparian site. However, the riparian site had the highest amount of Mn extracted when expressed as a percentage of the total soil Mn when compared to the transitional and agricultural sites. Therefore, much of
the manganese at site three had weathered and transported out of the soil via 
"reductive dissolution."

The cumulative exchangeable phosphate concentration increased as the 
soil became reduced and decreased as the redox potentials returned to more 
oxidized conditions (Figure 11). However, the largest amount of ortho-P was 
found in the soil of agricultural site. This observation points to a large input of 
phosphorus through fertilization. The cumulative concentrations of extractable P 
at the riparian site were lower than at the transitional site; most likely due to the 
riparian site being more weathered than either the agricultural or the transitional 
sites.

Soil Profiles

Once the cumulative trends were understood, it then became important to 
understand the concentration gradient of Fe(II), Mn(II), and ortho-PO₄ in a soil 
profile. When looking at a concentration profile for a given day, it was instructive 
to know the redox potential for that day. Julian day 487 (April 20, 1997) was a 
particularly interesting profile from which to discuss to the differences in redox 
potentials for the three different sites.

Most of the extractable Fe(II) was concentrated in the upper horizons 
(Figure 12). This is the result of greater biological mineralization of carbon 
coupled to Fe reduction under limited O₂ conditions (i.e., saturated soil with a 
high water table). Since the redox potentials at the agricultural site were quite 
high, it was not surprising to find high concentrations of extractable Fe(II), nearly 
three orders of magnitude smaller than the riparian site. The transitional site,
Figure 12. Concentration profiles for Fe(II) at the three sites for day 487

however, had a lower redox potential in the lower horizon than in the upper horizon. As mentioned earlier, this was due most likely to the pumping of oxygen into the soil by plant roots. The highest concentration for Fe(II) at the transitional site occurred in the 15 to 30 cm layer. Since the shallow electrode was placed at 15 cm, it becomes apparent that the plant roots were mostly only to a depth of about 15 cm and therefore only pumped oxygen down to about that depth. The lack of extractable Fe(II) below 30 cm, even though the redox potential in that region was quite low, was due to the fact that there was little reducible Fe in that region. At the riparian site, the extremely low redox potential was fairly constant throughout the entire profile. As a result, Fe(II) concentrations in the riparian site are the highest of all the sites.
Mn was more susceptible to reductive weathering than Fe. The surface riparian soil profile showed a lower concentration of extractable Mn(II) than subsurface soils as a result of the intense reductive weathering (Figure 13). The amount of exchangeable Mn was a moderate percentage of the total pool of Mn under even fairly oxidized conditions, whereas, Fe(II) was almost nonexistent at similar redox potentials. This means that even when the soil is completely dry, a fairly large fraction of the Mn remains in the extractable pool. For this reason, the largest amount of extractable Mn(II) was found at the surface of the soil at the transitional site, which had a much higher redox potential.
Although trends in concentration of inorganic \( \text{PO}_4 \), which are released when Fe-\( \text{PO}_4 \) minerals are reduced, tend to follow similar trends as extractable Fe(II), other factors have considerable influence (Figure 14). Considerations for fertilization and plant uptake of ortho-\( \text{PO}_4 \) must be made in order to fully understand the soil profiles. Both these considerations are extremely important to understand the profile at the agricultural site. Unlike either Fe(II) or Mn(II), ortho-\( \text{PO}_4 \) was more highly concentrated at the Agricultural site. Extractable \( \text{PO}_4 \) is also higher in the subsurface horizons of both the agricultural site and the transitional site due to plant uptake in the upper horizons and possible differences in parent materials.

*Figure 14. Concentration profiles for \( \text{PO}_4 \) at the three sites for day 487*
Three Dimensional Graphical Representations

Three dimensional graphical representation of extractable Fe(II), Mn(II), and PO₄ concentrations for temporal scales which encompass the entire reduced season can provide some interesting perspectives on reductive dissolution. These graphs represent interpolated smoothed fits to the triplet data. The actual surface generated by the 3-D numerical fitting routine (Sigma Plot) is not intended to represent an exact concentration. However, since only the trends are important, these assumptions are acceptable. The highest concentrations and the longest duration of Fe(II) occurred in the riparian soil profile (Figure 15). Conversely, the agricultural site had the lowest concentration of Fe(II) of all three sites and had shortest duration of it's presence. This was exactly what would be expected based on the proposed hypotheses.
Figure 15. Concentration profiles for Fe(II) for the three sites over one year.
When viewed over a two year period (Baham et al., 1997) the same trends for iron at the different sites were again reproduced making the annual cyclic biogeochemical nature of the soils clearly visible (Figure 16).

Figure 16. Concentration profiles for Fe(II) for the three sites over two years

Extractable Mn(II) followed a similar trend as Fe(II), but the proportion of manganese that was extractable when dry was much higher than for Fe, even
when the soil was dry. Therefore, the effects of redox potential were not as obviously apparent (Figure 17). As mentioned earlier, the apparent lower concentrations of extractable Mn(II) at the riparian site than the transitional site must be attributed to the more intense reductive weathering.

Figure 17. Concentration profiles for Mn(II) for the three sites over one year

Phosphorus also followed the same overall trends as Fe(II) and Mn(II), at the agricultural and transitional sites (Figure 18). These same trends continued in the riparian site until the redox potentials went well below zero. At low redox
potentials, the concentration of extractable PO₄ decreased markedly. This suggests the possible formation of vivianite, an Fe(II)-PO₄ mineral (Lindsay p.179). As redox potentials decreased, Fe(III) comprised in a mineral with PO₄ reduced to Fe(II), and the mineral was dissolved. Further reduction caused the solubility of vivianite to decrease.
Figure 18. Concentration profiles for $PO_4$ for the three sites over one year.
Conclusions and Discussion

In general, the experiments supported the proposed hypotheses. It is often common, especially in the Willamette Valley, to sample soils for nutrients that are susceptible to redox reactions in soils that are under reduced conditions. At these times, it is important to sample in a way that prevents oxygen from interfering as well as to protect the samples themselves from oxidation in order to have samples which are truly representative of the soils from which they have been taken. Unprotected sampling can cause the nutrients to become insoluble, leading the researcher to believe there was less soluble nutrients than what actually existed in the soils.

Certain nutrients in poorly drained soils undergo cyclic periods of changing solubility following quite closely the cycling change in redox potentials of these soils. Linking these effects with vegetative growth call for serious considerations for amounts and timing of fertilization, especially for phosphorus and possibly for nitrates and other nutrients as well as in soils that are linked to climatic redox reactions. Phosphorus has been considered to be mostly insoluble in well drained soils, reconsideration of this paradigm for poorly drained soils clearly need more study to understand the possible linkage to groundwater and stream pollution.
Bibliography


Baham J., R. King, R. Krebs, S. M. Griffith. 199_. Changes in Fe and Mn – Oxide Mineralogy in Poorly drained Agricultural and Riparian Sites. Soil Science. (in prep.)


Appendix 1: Soil PO₄ Concentration Profiles

Site 1 Julian day 365

Site 2

Site 3

Site 1 Julian day 375

Site 2

Site 3

Site 1 Julian day 395

Site 2

Site 3
Site 1  Julian day 453

Site 2

Site 3

Site 1  Julian day 473

Site 2

Site 3

Site 1  Julian day 487

Site 2

Site 3
Appendix 2: Soil Fe(II) Concentration Profiles

Site 1, Julian day 365

Site 2

Site 3

Site 1, Julian day 375

Site 2

Site 3

Site 1, Julian day 395

Site 2

Site 3
Site 1  Julian day 505

Site 2

Site 3

Depth Cm

mg Fe(II)/ Kg soil

-60 -50 -40 -30 -20 -10 0 100 200 300 400 500 600
Appendix 3:  Soil Mn(II) Concentration Profiles

Site 1  Julian day 365

Site 2

Site 3

Site 1  Julian day 375

Site 2

Site 3

Site 1  Julian day 395

Site 2

Site 3
Appendix 4: International Degree Experience

This appendix is a summary of my experiences and observations on Japanese research while in Japan. It is submitted for the partial fulfillment of the requirements for the International Degree.

During my year stay in Japan from September 1995 to August 1996, I learned much about the inner workings of the Japanese educational system, and the research of science in Japan.

The largest difference that I observed between the United States and Japan was the role universities played in scientific research. A large proportion of the research in the United States, is performed by professors and their graduate students. In Japan, however, applied research with economic benefits is usually reserved to private research institutes, while professors usually pursue only pure sciences which often have no immediate foreseeable economic application.

There are several reasons for this difference between the two countries. One reason is the source of income that professors use to supplement their university salaries. In the United States, professors fund the summer incomes through grants to research areas that the government or other industries have and interest. In Japan, one of the major ways a professor would supplement his or her income is from the commission on the sales of the textbooks to the students who enroll in his or her class. Although it is as common for faculty in Japan to act as consultants for the private sector as in the United States, Japanese professors maintain an air of "educational purity."
Another reason for the difference in private sector vs. public university research appears to be the result of the methodology upon which education is built. Students in the United States are expected to learn by working on an original research project, thus increasing the knowledge base. However, in Japan, the graduate student learns through an apprenticeship with the professor, and is not necessarily expected to work on original research. In this, they are not expected to make a large contribution to the world of science. In fact, it is assumed that as students, they lack the knowledge to yet work on their own and perform in the manner of their American counterparts. In order to be regarded by science they must work under a professor for several years to slowly gain the understanding of how science works.

Industries often place higher importance on the reputation a student's professor or university then the student's academic record. Since it is assumed that a good professor or university will have students that are able to learn the tasks required of them during their career with a company.

During the last term of my stay in Japan, I was allowed an inside view of a professor's laboratory where I spent several hours a week learning technical Japanese from Dr. Sugiura. Much of my time was also spent learning about his research and his scientific interests. I found Dr. Sugiura's laboratory to be run in a manner unlike any that I have ever seen in the United States. First year graduate students were supervised by upper level students and spent much of their time doing the menial work of the laboratory. Sometimes they were interrupted from their work to learn by watching upper level graduate students do
something that the lower level students had never seen or done. Likewise, if Dr. Sugiura were to use some of the equipment, he would call on all the student to gather around him while he worked on equipment that even upper classmen were not allowed to use.

Although this may seem an unlikely way of doing things, as it did to me at first, it is closely related to the Japanese ideology of education. In the American system, the student may be essentially equal to the professor with the exception of lacking the knowledge of the professor. It is for this knowledge and the professors’ willingness to teach the student that the student respects his or her professor. However in Japan, this difference in knowledge puts the professor and student on completely different levels. It is expected that the student must do everything that he or she can to learn as much as possible from the professor. Any responsibility is then placed upon the student to learn and not the professor to teach.

This is idea is not restricted to formal education. It is the standard method through which all knowledge or skill is passed from a master of an art to a student hoping to someday attain the level of master. It is an idea deeply ingrained in most Asian countries that have a history of strong Confucian beliefs.

It is for these reasons that industries most often hire private research institutes to perform any research in which they are interested. And research performed at universities is often restricted mainly to areas of pure science.