Final Report

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Improving Passive Mine Drainage Treatment for Manganese Removal – Phase II

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IMPROVING PASSIVE MINE DRAINAGE TREATMENT FOR MANGANESE REMOVAL – PHASE II

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1. Introduction

We have been studying biological Mn(II) oxidation in AMD limestone treatment systems since the summer of 2005, at the request of United States Office of Surface Mining (OSM) and Pennsylvania Department of Environmental Protection (PA DEP) personnel. We received our first grant from the OSM NTTT Applied Science Program in the summer of 2007 (Cooperative Agreement S07AP12478). For that grant we characterized the microbial communities and mineral precipitates found in two Mn(II)-removal systems in western Pennsylvania. From that research we found that fungi accounted for as much as 80% of Mn(II) oxidation activity in these Mn-removal beds.

Based on this surprising finding, the objectives of our "Phase II" project were to: 1) expand the number of Mn(II)-removal systems studied to confirm the relative importance and abundance of fungi versus bacteria in these systems, 2) test a variety of soluble organic amendments representative of wetland-derived dissolved organic carbon for their ability to stimulate Mn(II) oxidation, and; 3) test a variety of solid-phase organic amendments for their ability to stimulate Mn(II) oxidation.

2. Background

The removal of Mn(II) from AMD is a significant problem for both operating and abandoned mines in Appalachia and across the United States. It has been shown that Mn(II) removal can double or triple treatment costs due to the chemical consumption needed to achieve high pH conditions (Means and Hilton, 2004). Passive removal of Mn(II) is desirable as it eliminates the need for chemical reagent and the annual treatment costs can be a small fraction of those required for active treatment. The success of passive Mn(II)-removal systems has been variable due to a lack of design criteria and a poor understanding of the mechanisms that govern Mn(II) oxidation at near-neutral pH.

Based on results from our first OSM Applied Science project we found that in the two Mn(II)-removal systems we studied, fungi constituted 88% of the Mn(II)-oxidizing cultures while bacteria constituted just 12% (Burgos et al., 2010). In laboratory experiments using sediments collected from the Mn-removal beds (as the microbial inoculum) and sterilized site influent water, fungi accounted for over 80% of Mn(II) oxidation activity in these Mn-removal beds. Fungi isolated from these two Mn(II)-removal systems displayed an extremely high resistance to Mn(II) toxicity (e.g. up to 10,000 μM) as compared to well-studied Mn(II)-oxidizing bacteria (e.g. up 100 μM) (Santelli et al., 2010). We also characterized the minerals that accumulated in the Mn-removal beds. We found that the predominant Mn oxides at all sites were poorly crystalline birnessite and buserite with smaller amounts of todorokite (Tan et al., 2010). The surface morphology of the MnO_x precipitates from all sites was coarse and "sponge-like" composed of nanometer-sized lathes and thin sheets. Trace metals such as Ni, Zn and Co were removed effectively, in most cases preferentially, into the MnO_x precipitates.

3. Results

Eight field sites (seven in western Pennsylvania and one in eastern Tennessee) were selected for this study to obtain a broad comparative view of how these different Mn(II)-removal beds performed and to gain a better understanding of the Mn(II)-oxidation processes that influence the success of Mn remediation from CMD (Luan et al., 2012). The systems varied with respect to their influent geochemistry, flow rate and hydraulic residence time (Table 1). While these systems all started with "clean" limestone, over time an abundance of MnO_x precipitates coated the limestone cobbles and/or filled the porous voids in the beds. In collecting MnO_x-rich sediments for our experiments, we noted that in four of the eight beds (Ace, Glady Fork, De Sale 2, De Sale 1) the sediments accumulated as very thick and soft soils in the porous voids between cobbles that were completely armored by MnO_x coatings (Figure 1). In contrast, in the other four beds (De Sale 3, Fairview, Derry Ridge, PBS) the sediments accumulated as thin, hard MnO_x coatings (i.e., "crusts") that had to be mechanically scraped from the stones for collection.

Reactors containing wet-sieved (<2-mm) MnO_x-rich sediments and their associated natural microbial communities were operated in a fed-batch mode with respect to dissolved Mn(II), i.e., experiments were repeatedly spiked with dissolved Mn(II) for the purpose of distinguishing adsorptive

Table 1. Physical characteristics of the eight Mn removal beds, and geochemical characteristics of the influent waters.

	Ace[a]	Glady Fork[b]	De Sale 3[c]	De Sale 2[c]	Fairview[d]	Derry Ridge[e]	De Sale 1[c]	PBS[f]
Flow rate (L/s)	1.73±0.61	54.2±21.5	0.74±0.15	6.10±2.48	0.63	0.85±0.30	2.23 ±0.75	0.63
Size: *l*×*w*×*d* (m)	38×14×0.6	143×18×0.9	12×9×1.5	55×18×1.5	30×15×1	40×20×1	37×18×1.5	70×7×1
Hydraulic residence time (h)[g]	26	6	32	35	100	130	64	108
pH	6.54±0.34	6.79±0.60	6.03±1.09	6.08±0.57	4.84±0.27	6.60±0.20	6.14±0.40	4.88±0.19
Mn (mg/L)	34.7±14.0	9.4±1.4	55.5±37.0	31.2±0.10	150 ±13.8	19.4±3.1	19.9±7.1	18.4±1.1
Fe (mg/L)	0.16	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.27
Al (mg/L)	0.04	0.04	0.25	1.29	8.25	0.06	0.16	2.48
Ca (mg/L)	190	269	343	183	311	285	167	187
Mg (mg/L)	101	117	183	102	387	166	100	177
Na (mg/L)	1.94	10.6	26.2	11.5	42.7	2.17	9.34	17.6
K (mg/L)	0.75	13.8	7.84	17.5	28.4	5.78	15.1	5.91
Si (mg/L)	8.49	4.17	3.46	8.51	5.15	6.16	9.63	3.59
Organic Carbon (mg/L)	41.9	0.86	0.96	0.79	2.09	10.1	0.76	12.1
Total Nitrogen (mg/L)	1.53	0.92	0.64	1.34	0.33	3.38	0.16	0.72
Phosphorus (mg/L)	0.18	0.08	0.06	0.12	0.11	0.10	0.09	0.09
GDM (g Mn(II)/d m^2)	6.9	14	14	7.4	9.7	1.8	-1.0	1.9
GPS coordinates	40°29'12" N, 78°30'51" W	35°33'40" N, 85°26'10" W	41°08'32" N, 79°50'16" W	41°08'40" N, 79°49'55" W	41°2'105" N, 78°39'16" W	40°18'45" N 79°18'25" W	41°08'33" N, 79°49'48" W	40°03'01" N, 78°48'39" W

Values reported as mean or mean±standard deviation for n measurements. a. Values were averaged from 2009-2010, n=5 (03/09, 06/09, 12/09, 04/10, 08/10).

b. Values were averaged from 2009, n=26 (01/09 - 12/09).

c. Values were averaged from 2009-2010 using data from http://www.datashed.org/. De Sale 1, n=6 (03/09, 06/09, 09/09, 12/09, 04/10); De Sale 2, n=4 (06/09, 09/09, 12/09, 04/10); De Sale 3, n=4 (03/09, 06/09, 12/09, 04/10).

d. Values were averaged from 2005-2010, n=9 (12/05, 04/06, 06/06, 01/07, 06/07, 10/07, 06/09, 11/09, 04/10).

e. Values were averaged from 2009-2010, n=3 (10/09, 07/10, 08/10).

f. Values were averaged from 2006-2010, n=5 (02/06, 07/06, 06/07, 10/07, 08/10).

g. Hydraulic residence times were calculated using the average flow rate and assuming a bed porosity of 0.5 vol/vol (Watzlaf et al., 2004).

Figure 1. Freshly collected sediments from the Mn(II)-removal beds. A) Ace, B) Glady Fork, C) DeSale 2, D) De Sale 1, E) De Sale 3, F) Fairview, G) Derry Ridge, and H) PBS. Soil-like sediments in A – D. Sediments with MnOx crusts in E – H. Ruler scale = cm.

from oxidative Mn removal processes. The rate of Mn(II) removal from our laboratory sediment reactors varied considerably with the different sediments (Table 2). Typically Mn(II) was removed very quickly in the first several fed-batch cycles due to fast adsorption and then slowed in the later cycles. Because of the variation in rates we chose to calculate a lumped zero-order Mn(II) removal rate over the final four fed-batch cycles (denoted by time period right of dashed line and arrow in Figure 2).

Table 2. Summary of operationally defined contributions to the Mn(II) removal rate measured in laboratory experiments, and Mn(II) removal rates calculated based on field performance.

	Ace	**Glady Fork**	**De Sale 3**	**De Sale 2**	**Fairview**	**Derry Ridge**	**De Sale 1**	**PBS**
Sediment texture	soil-like	soil-like	MnO_x crust	soil-like	MnO_x crust	MnO_x crust	soil-like	MnO_x crust
Total Mn(II) removal rate (µg/h*g sed)[a]	318.0	267.7	174.2	123.2	25.4	20.1	18.3	14.1
Relative rate of Mn(II) removal rates	Fast	Fast	Fast	Fast	Slow	Slow	Slow	Slow
Adsorption + Anoxic MnO_x Oxidation Mn(II) removal rate (µg/h*g sed)[b]	3.9	46.9	64.3	29.2	9.4	15.0	11.9	8.0
O_2-driven Oxidation Mn(II) removal rate (µg/h*g sed)[c]	314.1	219.8	109.9	94.0	16.0	5.1	6.4	6.1
Bacterial + Oxic MnO_x Oxidation Mn(II) removal rate (µg/h*g sed)[d]	291.1	210.5	103.9	91.2	12.3	3.2	4.2	4.0
Fungal Oxidation Mn(II) removal rate (µg/h*g sed)[e]	23.0	9.3	6.0	2.8	3.7	1.9	2.2	2.1
Field Mn(II) removal rate (mg/h*m^3 limestone)[f]	469	639	386	202	403	73	-28	80

a. Total rate calculated from “live” reactors according to Eq. 1 from Luan et al. (2012)

b. Adsorption + Anoxic MnOx Oxidation Mn(II) removal rate calculated from “sterile/N_2” reactors according to Eq. 1.

c. O_2-driven Oxidation Mn(II) removal rate calculated as the difference between the “live” and “sterile/N_2” reactors according to Eq. 2.

d. Bacterial + Oxic MnO_x Oxidation Mn(II) removal rate calculated as the difference between the “live+fungicide” and “sterile/N_2” reactors according to Eq. 3.

e. Fungal Oxidation Mn(II) removal rate calculated as the difference between the “live” and “live+fungicide” reactors according to Eq. 4.

f. Field Mn(II) removal rate calculated according to Eq. 5.

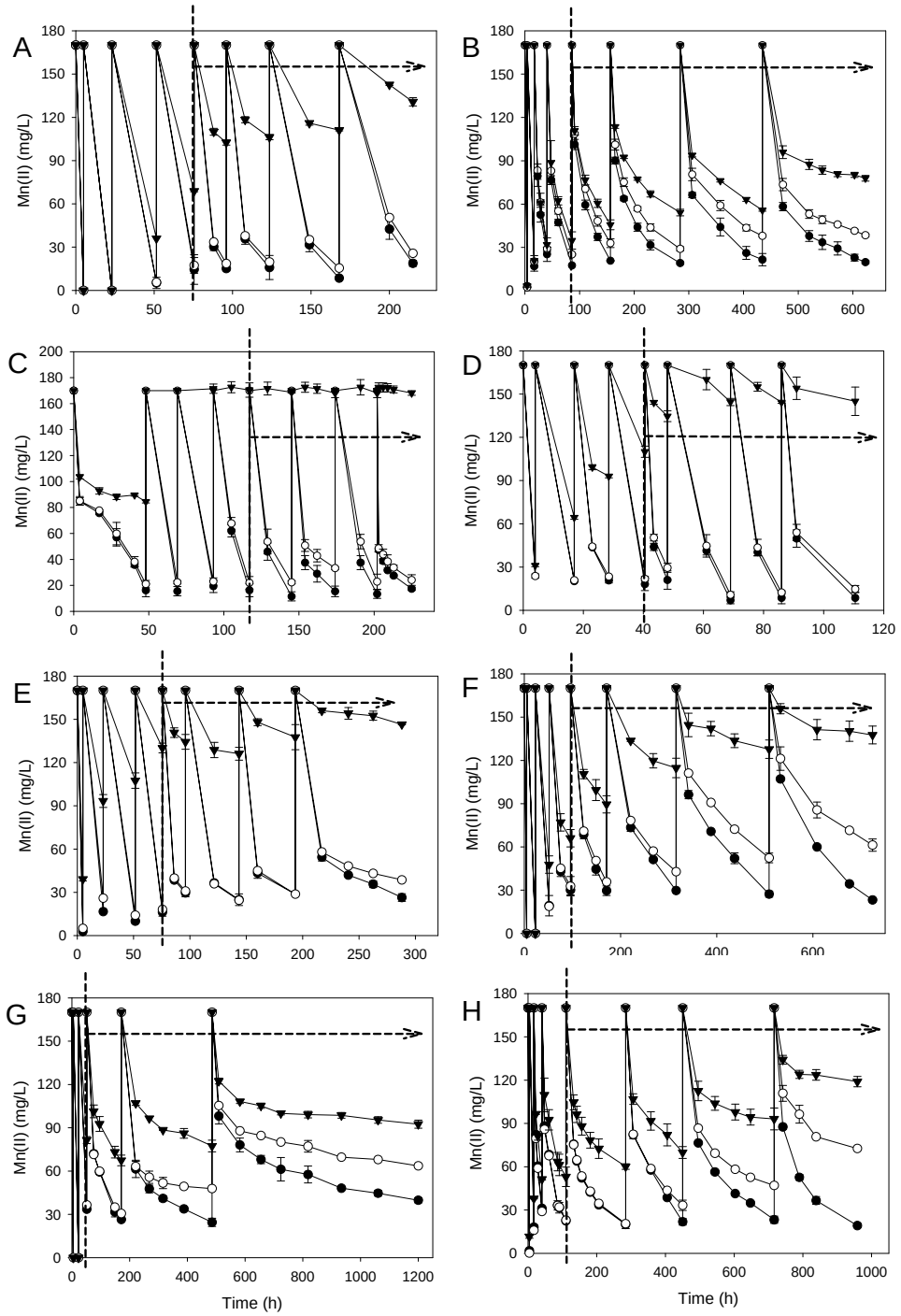

Figure 2. Mn(II) loss from solution in laboratory sediment incubation experiments. A) De Sale 3; B) Derry Ridge; C) Ace; D) Glady Fork; E) De Sale 2; F) Fairview; G) De Sale 1; H) PBS. Black circles were "live" reactors; white circles were "live+fungicides" reactors; black triangles were "sterile/N2" (γ irradiation) reactors. Live reactors were maintained under air while the sterile reactors were maintained under 100% N2. Mn(II) was repeatedly spiked (as MnCl2) to increase the Mn(II) concentration back to ca. 170 mg/L once it dropped below ca. 30 mg/L. Experiments were conducted with 0.50 g MnOx (dry) and 50 mL filter sterilized influent site water. Lumped zero-order Mn(II) removal rates were calculated over the final four fed-batch cycles, which are denoted by the time period right of the dashed line and arrow. Results for the six other sediments are shown.

The laboratory-based rates estimated from our fed-batch experiments agreed well with field-based estimates of Mn(II) removal rates from seven sites (Figure 3). The Fairview site was not included in this correlation because the bed was temporarily off-line when sediments were collected for the laboratory experiments. Using this approach, the field-based and lab-based rates of Mn(II) removal were well correlated ($R^2 = 0.87$; $p = 0.002$; Figure 3).

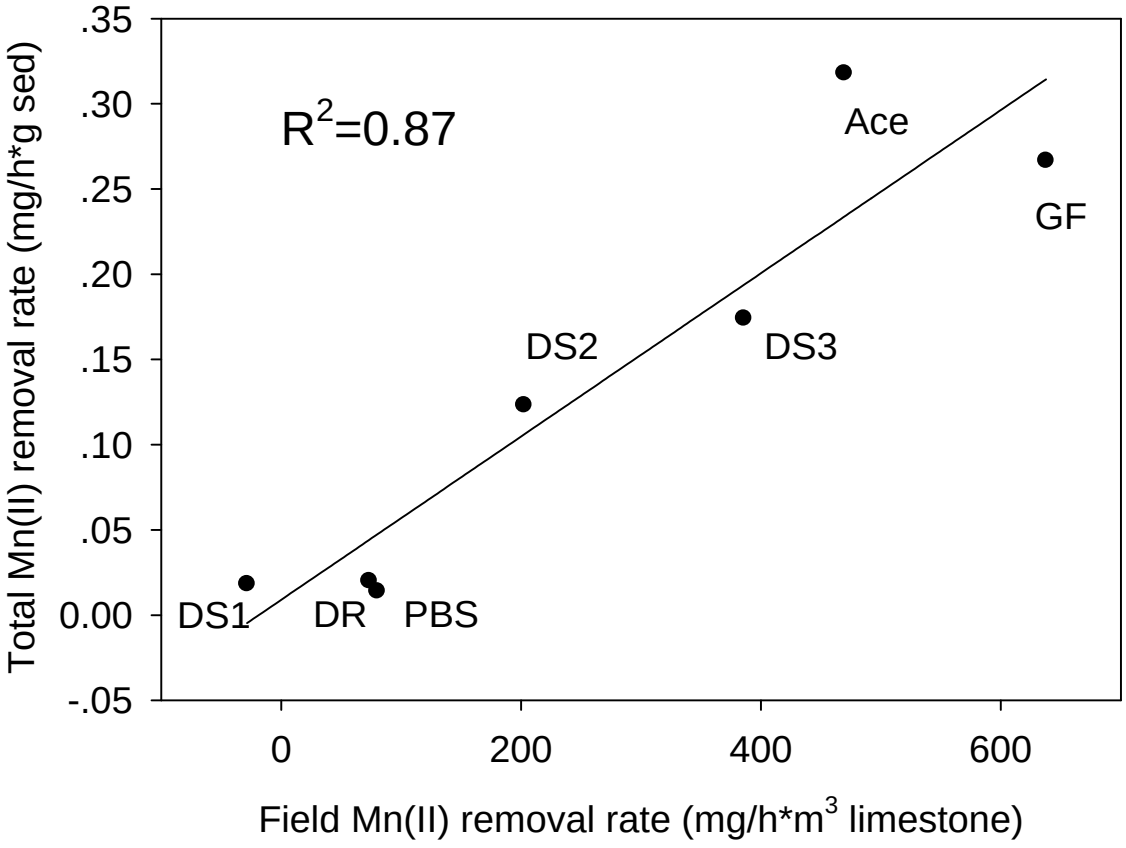

Figure 3. Correlation between total Mn(II) removal rates measured in laboratory experiments with Mn(II) removal rates measured in the field. Ace - Ace; DR - Derry Ridge; DS1 - De Sale 1; DS2 - De Sale 2; DS3 - De Sale 3; GF - Glady Fork; PBS - PBS.

Our first objective was to determine the relative importance of adsorption versus oxidation processes on the removal of Mn from CMD in the various treatment systems. We approached this objective by identifying the major Mn(II) removal mechanisms and operationally defining when these processes would be operative under different experimental conditions. We proposed that Mn(II) is removed by five dominant processes: (1) bacteria- mediated oxidation, (2) fungi-mediated oxidation, (3) O_2-driven MnO_x-mediated oxidation, (4) autocatalytic MnO_x-mediated oxidation under anoxic conditions, and (5) non-oxidative adsorption. Sediment-free controls under an air headspace showed no loss of Mn(II), so this process was not considered. We assumed that all of the potential processes were operative in the "live" reactors and that the relative contribution of individual or lumped processes could be calculated as differences between results obtained with the "sterile/N_2" and the "live+fungicide" reactors.

Based on these operational definitions for our kinetic analysis, we found that the eight field sites could be grouped into two categories of "fast" and "slow" with respect to the total Mn(II) removal rates (Figure 4). As noted above, three of the four "fast" sites contained soil-like sediments as compared to MnO_x crusts. For the fast group, *O_2-driven oxidation* accounted for 63 to 99% of the Mn(II) removal rate (Table 2), while *O_2-driven oxidation* accounted for 25 to 63% of the Mn(II) removal rate in the slow group. *Adsorption + Anoxic MnO_x Oxidation* tended to account for more of the Mn(II) removal rate in the slow group (37 to 75%) as compared to the fast group (1.2 to 37%).

Based on our experimental design and operational definitions the contribution of bacteria-mediated Mn(II) oxidation was much greater in the fast group (59.8 – 91.5% of the total rates) as compared to the slow group (15.9 – 48.4% of the total rates). The contribution of fungi-mediated Mn(II) oxidation was low in all eight soils, ranging from 2.3 – 7.2% of the total rates in the fast group and 9.5 – 14.9% of the total rates in the slow group. Interestingly, in our previous experiments with Fairview sediments, we found that fungal activity accounted for over 80% of Mn removal (Burgos et al., 2010). Our previous results were conducted with Fairview sediments collected while the bed was on-line and operational. Our current results with Fairview sediments (where fungi accounted for 15% of the Mn(II) removal rate) were conducted with sediments collected while the bed had been off-line for over a month (but still saturated). These differing results may suggest that the microbial community in any one Mn(II)-removal bed is a dynamic characteristic affected by hydrodynamic conditions and other factors (e.g., nutrient shifts, seasonal changes).

To better understand the biomass contribution and makeup of the microbial community existing in the sediments from the fed-batch incubation experiments, we measured the concentration of a variety of phospholipid fatty acids (PLFAs). PLFAs are a primary component of both eukaryotic and prokaryotic cell membranes that generally decompose rapidly upon cell death. Because of these characteristics, the quantification of PLFAs in an environment is an effective way to measure the living biomass. The total

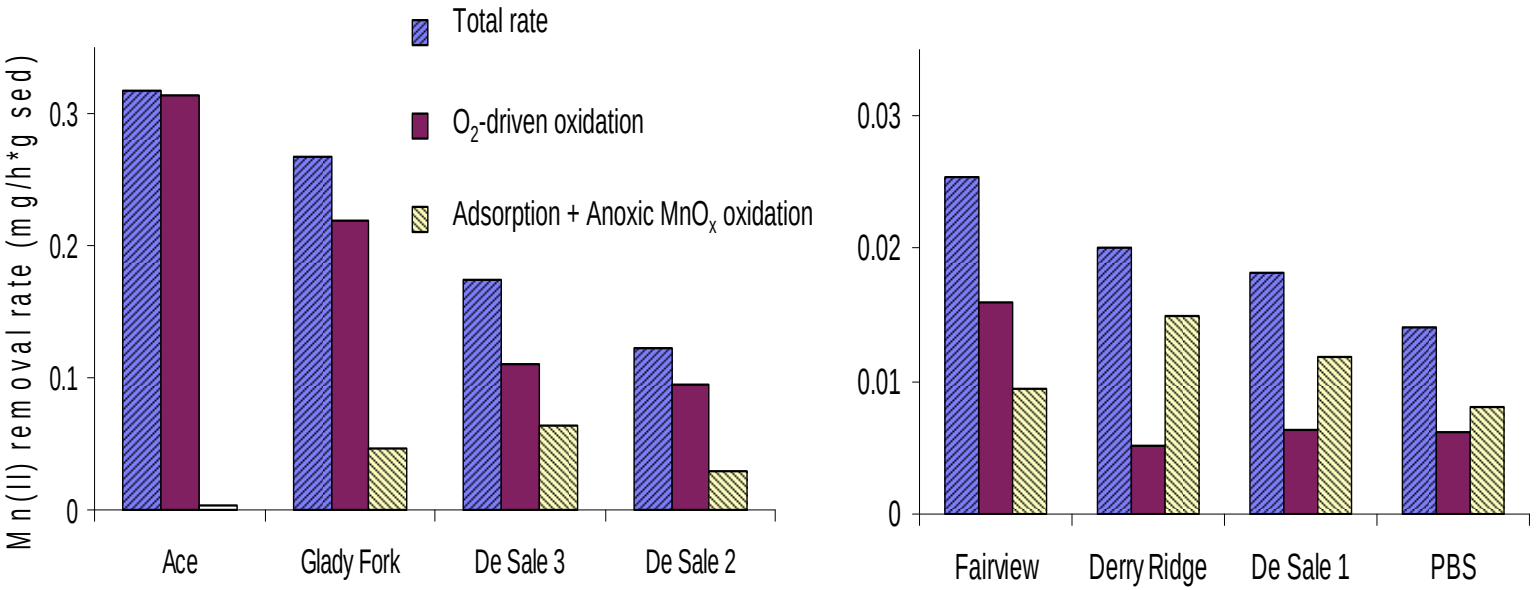

Figure 4. Relative contributions of O_2-driven oxidation (primarily biotic; calculated from "live" reactors) as compared to adsorption (abiotic; calculated from "sterile/N_2" reactors). Sediments were divided into "fast" and "slow" groups based on their total Mn(II) removal rate.

measured PLFA ranged from 2,960 pmol/g sediment in the Derry Ridge experiments to 108,000 pmol/g sediment in the Ace experiments – a difference of nearly two orders of magnitude in microbial biomass between the field sites. The sites supporting the greatest biomass included Ace, Glady Fork, De Sale 2, and De Sale 1 with >10,000 pmol/g sediment. All other sites (De Sale 3, Fairview, Derry Ridge, and PBS) supported a lower microbial biomass under these experimental conditions.

In addition to microbial biomass, PLFA analysis provides information about the general composition of the microbial community. Based on measured concentrations for a total of 36 different PLFAs the total eukaryotic biomass was significantly less than that for the total prokaryotic biomass (Luan et al., 2012). The only statistically robust correlation between microbial biomass (defined by PLFA) and Mn(II) removal rates was observed between the bacterial biomass and *O_2-driven oxidation*, which was positively correlated (R^2=0.62; p=0.020). The greater the concentration of bacterial biomass the faster the Mn(II) removal rates provides evidence that the bacterial community is responsible for a substantial proportion of the Mn(II) oxidation in these experiments.

Because fungal activity turned out to be less important than anticipated no experiments were conducted to evaluate our other proposed objectives regarding how soluble or solid-phase organic amendments might stimulate Mn(II) oxidation. It is still unclear why microbes oxidize Mn(II) (e.g., they cannot gain enough energy to grow via Mn(II) oxidation) such that the stimulatory effect of any bed amendment may be difficult to predict.

4. Conclusions

- Based on field performance of seven Mn(II)-removal beds, we found that Mn removal ranged from 1.8 – 14 grams Mn d^{-1} m^{-2} (GDM) with mean ± standard deviation values of 8.0 ± 5.0 GDM.
- A strong correlation (R^2=0.87) was established between rates measured in "fed-batch" laboratory experiments and rates measured in the field for seven beds.
- The fastest rates of Mn(II) removal were due to biological oxidation and lab rates of Mn(II) removal correlated (R^2=0.62) to bacterial biomass concentration.
- The "seeding" of new Mn(II)-removal beds with MnO_x-coated limestone and associated biomass (collected from older, operational beds and placed near the influent end of the new bed) may be a practical approach to building these beds in the future.

5. References

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