RETENTION OF MANGANESE BY A CONSTRUCTED WETLAND TREATING DRAINAGE FROM A COAL ASH DISPOSAL SITE[1]

by

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Abstract: A 3,200 m^2 wetland was constructed in 1988 to treat drainage from an ash disposal site at a coal-fired electricity generating plant in western Pennsylvania. Concentrations of Fe and Mn in the drainage range from 30-80 mg/L and 10-20 mg/L, respectively. Acidity levels of 60-180 mg/L and a pH between 5-5.6 are typical. The wetland has always produced a high quality effluent with respect to Fe concentrations (usually less than 1 mg/L) and pH (about 7). Initial performance of the wetland with respect to Mn was encouraging, with reductions in Mn concentrations of over 50% being common during the first six years of operation. The system was modified in 1994 by adding limestone riprap below some dams and covering diversion dikes with limestone. These alterations were followed by a significant improvement in Mn removal by the system, with effluent concentrations seldom exceeding 1 mg/L. Seasonal observations indicate that Mn removal in the wetland slows during the winter. In laboratory studies, wetland limestone increased Mn removal rates by as much as 6-7 times. These rates exhibited a temperature optimum of 27°C. The rate at near 0°C was about one half that at 27°C and the rate fell to near zero at 43°C. This suggests that biological activity associated with the limestone is an important factor in the success of this wetland.

Additional Key Words: ash disposal, manganese oxidation

Introduction

In 1988, the Pennsylvania Electric Company constructed a wetland to treat drainage from a completed ash disposal site at Keystone Generating Station, Armstrong County, PA. The wetland, with an area of 3,200 m^2, was designed as a surface-flow, mushroom compost system planted with cattails. We have monitored water quality in this wetland since its completion, at first casually, more recently on a monthly basis.

The Keystone wetland has always produced a high quality effluent with respect to acidity, alkalinity, pH, and iron concentration. The wetland's removal of manganese during the first six years of operation was encouraging, with reductions in Mn concentrations of 50% or more often observed. In 1994, the operators of the wetland began modifying the system in order to improve Mn retention.

In the first modification phase, the earthen diversion dikes in the main body of the wetland were dropped to a lower level and crossed with plastic pipes containing perforations on their upper surfaces. The pipes were covered with limestone and limestone riprap was also added below three dams at the head of the wetland. The riprap has been replaced three times per year since its addition. These changes, completed by 1995, were followed by significant and consistent improvements in the wetland's retention of manganese. The purpose of this paper is to describe these improvements and to present laboratory observations which support the proposition that microbial activity plays an important role in reducing Mn levels within the Keystone wetland.

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Methods

Water samples from six sites in the wetland (Figure 1) were collected, preserved, and stored according to standard methods (APHA, 1992). Water temperatures were determined in the field using a portable temperature probe. In the laboratory, on the day of collection, pH was measured, alkalinity was determined using Orion Total Alkalinity Test Kits and acidity titrations were performed according to methods described by Hedin et al. (1994a). Metal concentrations were determined colorimetrically using the phenanthroline (Fe) and periodate (Mn) methods (APHA, 1992; Strickland and Parsons, 1968).

Limestone, covered with black deposits, was collected from the dam at sampling site 3 in February 1997, and transported to the laboratory in water-filled buckets. Approximately 50 L of wetland water was collected at the same time and place. Upon arrival in the laboratory, wetland limestone was added to two Plexiglas columns (6 in. dia.) and 1.6 L of wetland water was added to each of those columns and to two additional columns containing no limestone. Two columns, one with limestone and one without, were placed in an incubator set at 0 °C. The two remaining columns were placed in an incubator set at 27 °C. Both incubations where in the dark, and 50 ml water samples for Mn determinations were collected periodically over 144 hours. Similar incubations followed temperature adjustments and water replacements until Mn reductions in columns with and without limestone had been compared at eight different temperatures. Manganese concentrations declined in the stored wetland water supply toward the end of the incubation series. Additions of $MnSO_4 \cdot H_2O$ were then made to bring initial Mn concentrations to about 10 mg/L. Mn removal rates in different incubations were estimated by subtracting the final Mn concentrations from the initial concentrations and dividing by the hours incubated.

Results

Wetland Water Quality

The final limestone additions to the wetland were completed between the 30 Dec 94 and the 2 Feb 95 sampling dates. Mn concentrations within the wetland remained at levels observed in previous years until April 1995, when obvious reductions in Mn concentrations occurred (Figure 2). The improvement in Mn retention was most notable at sampling sites 5 and 6. Mn concentrations at site 5 varied somewhat, especially during 1995, but were usually below 2 mg/L. Effluent concentrations of Mn (site 6) were well below 2 mg/L from April 1995 through November 1997. The most conspicuous increases in Mn concentrations at sites 5 and 6 occurred during winter months and coincided with low water temperatures (Figure 3).

Effluent concentrations of Fe from the wetland have always been well below regulatory limits (Figure 4). The majority of Fe removal occurs early in the wetland so that concentrations are below 10 mg/L in water at site 3. Only small amounts of Fe are found in water at sites 5 and 6.

The pH of the water at site 1 fluctuates within a 4 to 6 range but is often above 5 (Figure 5). The pH levels in the effluent were usually around 7 prior to the limestone additions. Slight increases in pH at sites 5 and 6 were observed after June 1995. The increase in alkalinity (Figure 6) and decrease in acidity (Figure 7) of water flowing through the wetland has always been excellent, and limestone additions seem to have been followed by further increases in effluent alkalinity.

The basic mechanisms by which the wetland removes Fe are straightforward. Fe (II) oxidizes and precipitates readily when water is aerobic and has a high pH. Visual observations and water chemistry data suggest that this is what occurs in the upper portions (above site 3) of the wetland. Oxidation of Fe(II) to Fe(III) results in a decrease of pH. Many surface-flow systems, such as that at Keystone, remove Fe but sometimes produce effluents with an unacceptably low pH. Such reductions in pH do not occur at Keystone. The influent water at sampling site 1 is net acid, but the pH is usually high and the system has sufficient alkalinity generating capacity to more than compensate for any decreases in pH resulting from Fe oxidation.

Removal of Mn in wetlands is much more difficult to accomplish than the removal of Fe. Retention of manganese requires the oxidation of soluble Mn(II) to Mn(III) and Mn(IV), which can precipitate as Mn oxides. Spontaneous oxidation of Mn(II) occurs slowly below pH 10 (Gounot, 1994). Mn oxidation is inhibited by high levels of Fe(II) because Fe(II) oxidizes more rapidly than does Mn(II). It has been suggested that Mn retention in wetlands is reduced by Fe concentrations above 3 mg/L (Stark et al., 1994). The retention of Mn at Keystone is probably enhanced by the removal of Fe early in the system. Mn concentrations drop precipitously in the system only after most of the Fe is removed.

In the absence of Fe(II), significant removal of Mn in the 6-9 pH range may involve chemical and physical processes such as the autocatalytic reduction of Mn(II) by Mn oxides and adsorption of Mn(II) on Mn oxides, Fe oxides, or organic matter. Even so, in constructed wetlands Fe oxides have little effect on Mn retention (Hedin et al., 1994b).

Biological processes can also accelerate the oxidation and precipitation of Mn. A variety of microorganisms including algae, fungi, and bacteria oxidize Mn via a variety of mechanisms (Gounot, 1994; Spratt et al., 1994). Microorganisms have been shown to be important agents in wetland Mn retention (Gordon and Burr, 1989). However, it is technically difficult to experimentally inhibit microbial activities without also affecting Mn chemistry. In wetland studies, it is not possible to ascertain the relative importance of physical, chemical, and biological processes with certainty (Sikora et al., 1996).

While it is not possible to identify a mechanistic link between the limestone additions at Keystone and the increase in Mn retention, the two are probably related. Additions of limestone rock filters have been shown to enhance Mn retention in other wetlands. This could result from strictly chemical reactions to increases in alkalinity or from metabolic activities of microbes colonizing the stone surfaces (Gordon and Burr, 1989). The passage of some 2 months between the final limestone applications and the obvious increase in Mn retention suggested to us that time was required for microbial colonization to occur. Recent observations that some eight weeks are required for black slime to form on limestone placed in a wetland support this idea (Brant and Ziemkiewicz, 1997)

If microbial activity is of major importance in Mn removal, it is possible that seasonal temperature fluctuations could affect system performance. Increases in Mn concentrations were observed during winter at sites 5 and 6. This led us to investigate the roles of limestone and temperature on Mn removal in laboratory systems

Laboratory Experiments

Both temperature and the presence of limestone had strong effects on the removal of Mn from water in the experimental columns (Table 1). Appreciable declines in Mn concentrations occurred in the limestone columns at temperatures up to and including 33 °C. Concentrations of Mn in columns without limestone declined slightly in some incubations but actually increased in two experiments (0 °C and 25 °C). No Mn removal occurred at 43 °C and 53 °C. It seems likely that the removal of Mn in the absence of limestone was so low that random variations within the systems and in the sampling make comparisons between temperatures difficult in those columns.

Calculations of removal rates (Figure 8) make it clear that limestone significantly increased Mn removal in the experimental systems. These data also illustrate the strong effect that temperature had on removal rates, even in columns containing limestone. Those rates increased with temperature up to about 27 °C, then declined abruptly to negligible levels when the temperature increased above 33 °C. This pattern of temperature response, being more typical of biological as opposed to chemical processes, suggests that microorganisms associated with the limestone are responsible for most of the Mn removal observed in these systems. It is becoming increasingly apparent that microbial oxidation is an important mechanism for precipitating soluble Mn, at least in aerobic zones (Joye et al., 1996; Watzlaf, 1997)

Summary and Conclusions

The ability of the Keystone wetland to retain Mn markedly increased following the addition of a moderate amount of limestone to the system. We believe that this resulted in increased Mn oxidation carried out by microorganisms colonizing the limestone surfaces. Although careful monitoring revealed a slight decrease in Mn retention within the wetland during winter, the effluent Mn concentrations remained well below 2 mg/L. If Mn oxidation in the wetland is indeed microbial in nature, the system is capable of performing adequately at low temperatures.

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Figure 1.

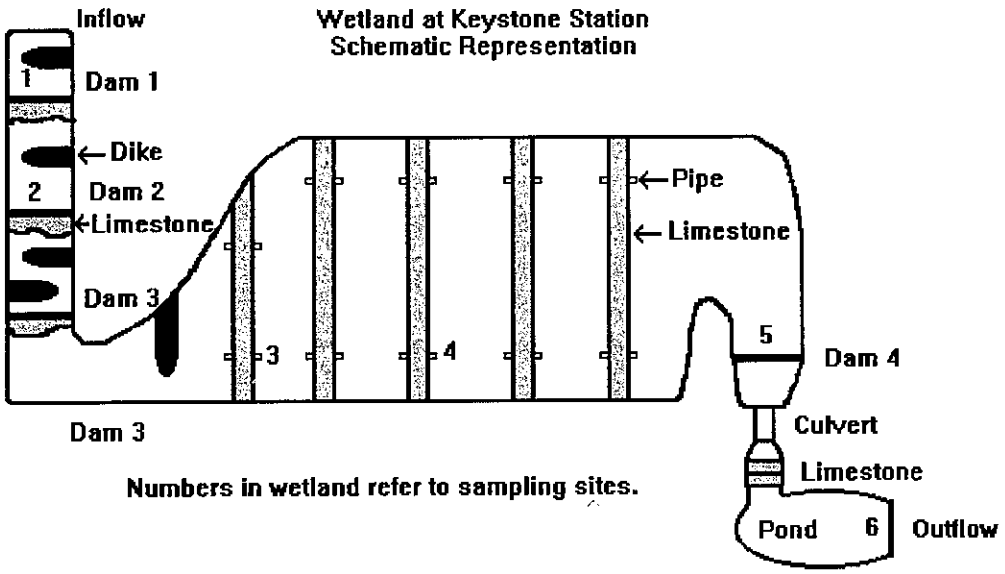

Figure 2.
Manganese Concentrations

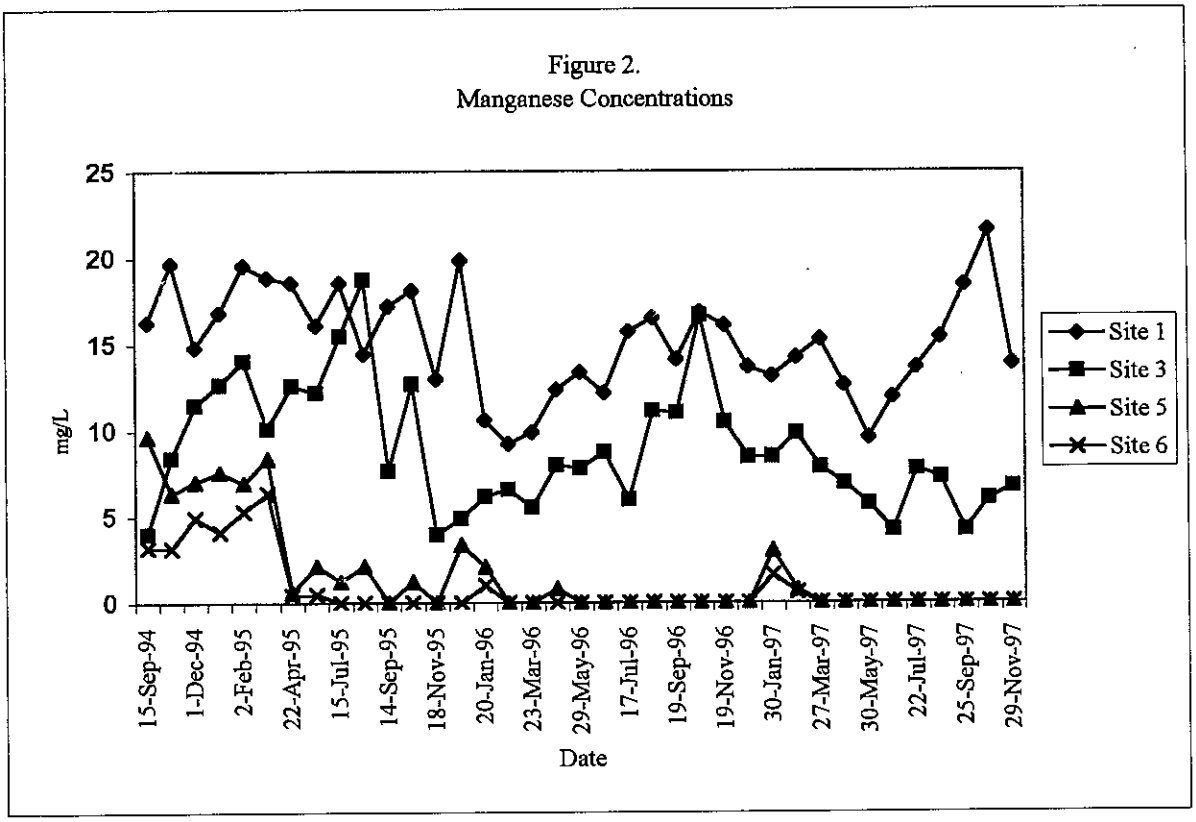

Figure 3.
Water Temperatures

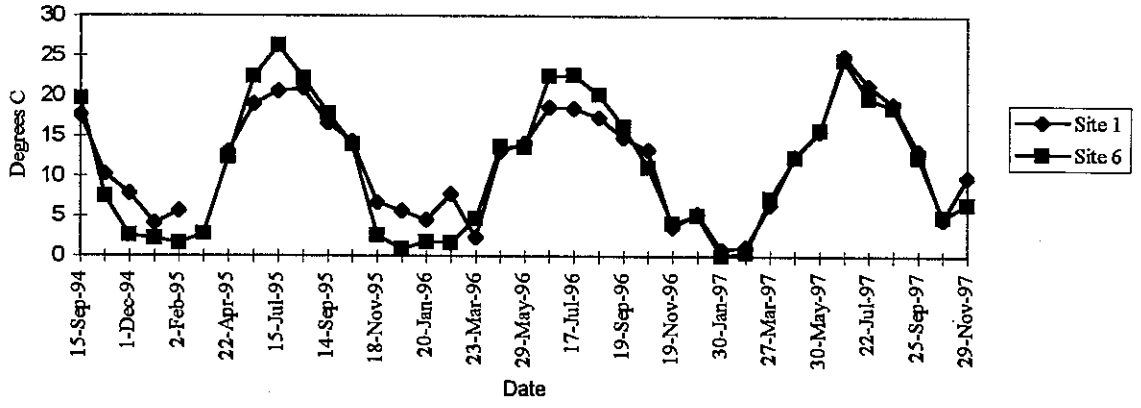

Figure 4.
Fe Concentrations

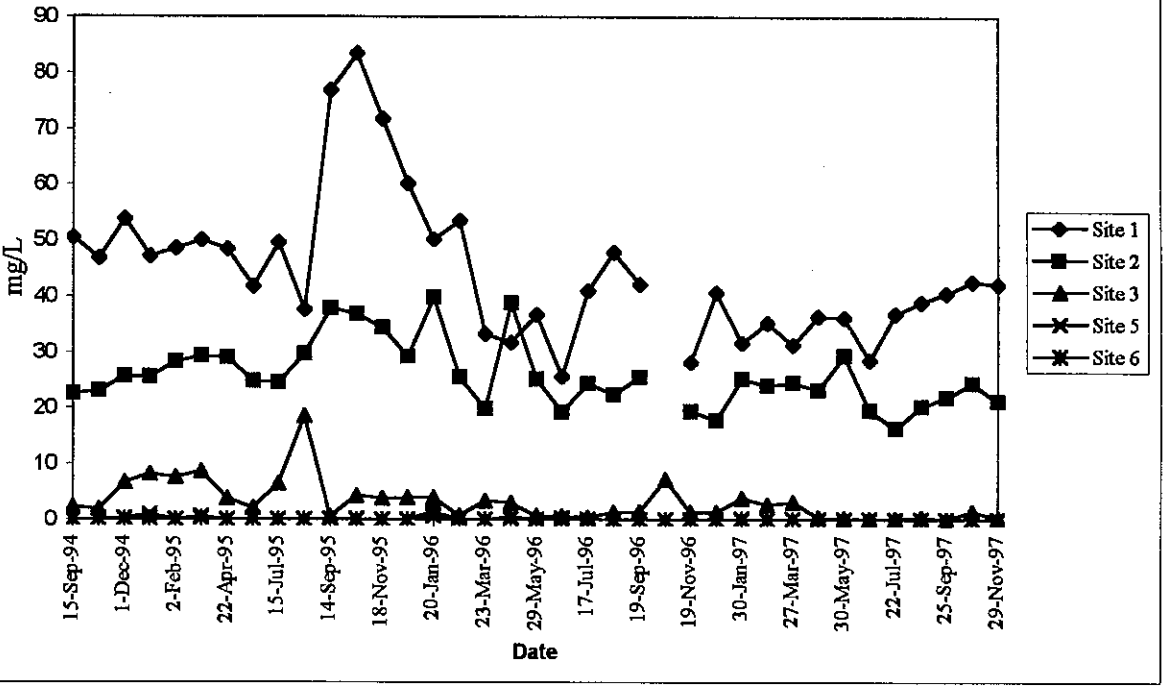

Figure 5.
pH

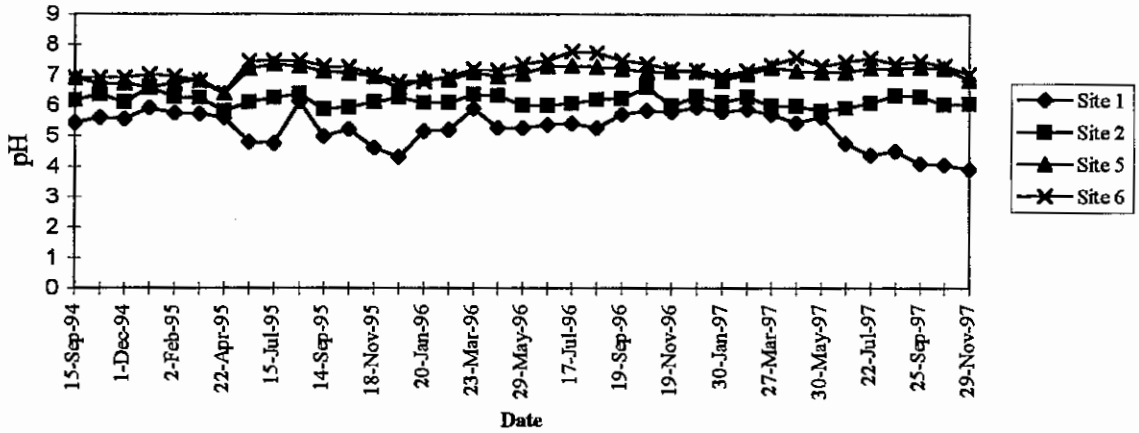

Figure 6.
Alkalinity

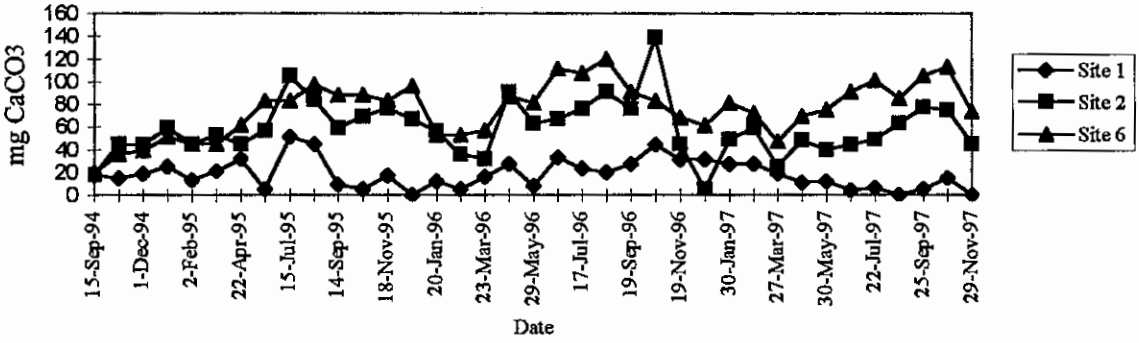

Figure 7.
Acidity

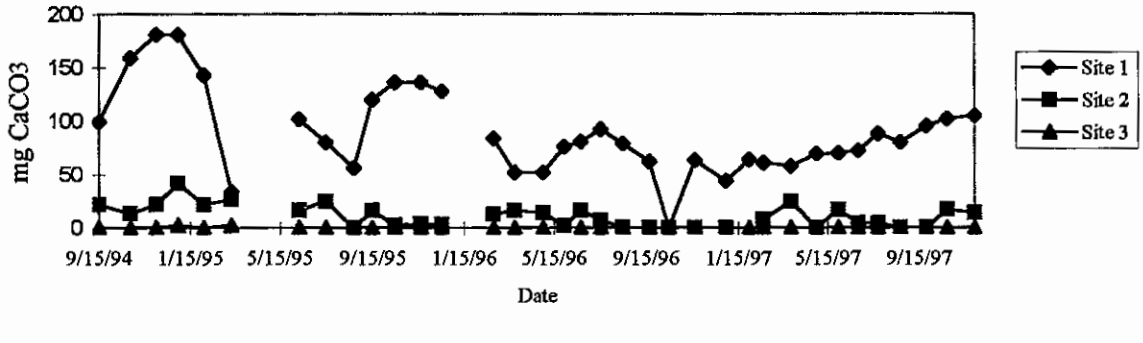

Table 1. Mn concentrations (mg/L) in laboratory systems when incubated at different temperatures.

0 °C Incubation		
time (hours)	with limestone	without limestone
0	10.81	8.78
24	8.07	9.52
96	5.58	9.43
144	5.18	10.23

5 °C Incubation		
time (hours)	with limestone	without limestone
0	9.53	8.31
6	10.35	9.19
18	8.52	9.34
24	8.74	8.89
68	4.84	9.04
82	3.22	9.22
141	0.72	7.03

15 °C Incubation		
time (hours)	with limestone	without limestone
0	10.96	10.06
8	10.14	10
24	6.95	9.97
62	4.76	9.86
100	3.01	8.38
120	2.9	8.3

25 °C Incubation		
time (hours)	with limestone	without limestone
0	9.77	9.01
6	8.19	8.43
18	6.3	8.31
24	5.11	8.37
68	0.45	9.41
82	0.45	8.83
141	0.2	9.19

27 °C Incubation		
time (hours)	with limestone	without limestone
0	10.38	10.44
24	3.95	8.87
96	0.53	9.55
144	0.01	8.87

33 °C Incubation		
time (hours)	with limestone	without limestone
0	9.73	9.48
8	8.22	8.93
24	7.15	8.38
62	3.01	7.94
100	2.05	7.8
120	1.53	7.56

43 °C Incubation		
time (hours)	with limestone	without limestone
0	12.17	12.17
12	12.11	12.14
23	12.09	12.14
48	11.89	12.14
120	11.65	11.95

53 °C Incubation		
time (hours)	with limestone	without limestone
0	12.83	12.77
12	12.83	12.79
23	12.88	12.79
48	12.74	12.77
120	12.77	12.74

Figure 8.
Mn Removal Rates in Laboratory Systems