

Environmental Factors Affecting Oxidation of Manganese in Pinal Creek, Arizona

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ABSTRACT

The objectives of the laboratory work reported here were to quantify the net rates of removal of manganese [Mn(II)] by streambed sediments collected from a metals contaminated, perennial stream system (Pinal Creek near Globe AZ) and to determine the key variable(s) responsible for the limited removal of Mn(II) observed at this field site. Pinal Creek is characterized by significant spatial gradients in pH, alkalinity, and Mn(II) along its length and by spatial gradients in pH, dissolved oxygen, and Mn(II) across hyporheic zones of varying thickness. These gradients are established by mixing of surface water and entering shallow ground water in the sediments. The mixing of waters in the hyporheic zones define the local chemical environments in which Mn(II) is removed by incorporation into pre-existing and newly formed mineral surfaces through abiotic and biotic processes. As a consequence of the site characteristics, particularly the spatial gradients in the hyporheic zone, the primary chemical parameters included in the test matrix were pH, initial Mn(II) concentration, and dissolved oxygen. Streambed sediments collected from the site were used in laboratory batch investigations of the rate of Mn(II) removal. Results of these studies indicate that removal of Mn(II) within the hyporheic zone primarily occurs via biotic oxidation processes, is approximately first-order with respect to the Mn(II) concentration and inversely proportional to $[H^+]$, and independent of dissolved oxygen concentration except at very low levels.

INTRODUCTION

Quantifying the interdependence of biogeochemical factors that affect natural remediative processes of dissolved metals in mine-drainage-contaminated stream systems provides a basis for interpretation of field observations and, potentially, identification of inherent factors that limit the ability of a system to remediate itself. In small streams gradients in pH, dissolved oxygen (O_2), metals concentrations, and other chemical parameters in stream-bed sediments are established by mixing of surface and entering contaminated ground water in the hyporheic zone. The distinct character and the importance of hyporheic zone to microbial communities within the sediments and the fluxes of dissolved O_2 (DO) and nutrients (e.g., particulate and dissolved organic carbon and nitrate) within a stream system are well documented and accepted as a key aspect of stream ecosystems [Grimm and Fisher, 1984;

Findlay and others, 1993; Triska and others, 1993; Jones and others, 1995a, 1995b; Valett and others, 1996]. The significance of hyporheic exchange in the biogeochemistry of metal contaminants in coupled surface water/ground water systems has also received attention but a quantitative understanding of its role is still being developed [Cerling and others, 1990; Bourg and Bertin, 1993; Kimball and others, 1994; Benner and others, 1995; Broshears and others, 1996; Harvey and Fuller, 1998].

The work reported herein focuses on biogeochemical processes occurring in a small, perennial stream, Pinal Creek near Globe, Arizona. Overall removal rates of Mn(II) from Pinal Creek have been determined by Harvey and Fuller (1998), however, the dependence on key parameters has not been quantified. The specific aims of this work were to quantify the net rates of removal of Mn(II) under different conditions using sediments collected from the perennial reach of

Pinal Creek and to identify the key variable(s) responsible for the limited removal of Mn(II) observed at the field site. Because pH and Mn(II) values change along the perennial reach and spatial gradients across the hyporheic zone are observed for pH, Mn(II), and O₂, it was hypothesized that one or more of these chemical parameters controlled removal of Mn(II) from the system. To test this, a set of laboratory experiments was conducted to establish the dependence of the rate of removal of Mn(II) on these chemical parameters.

SITE DESCRIPTION

Pinal Creek is the outlet of the Pinal Creek basin (a typical alluvial basin of the Southwest) and the perennial stream reach (approximately 13 km (kilometer) length from head of flow to the confluence with the Salt River) is fed by groundwater from the alluvial aquifer that has been contaminated by copper-mining activities in the area [e.g., Eychaner, 1989]. Surface water chemistry in the upper 4-km length of the perennial reach is dominated by discharge of partially neutralized, metals-contaminated groundwater (pH 5.5 – 6). Manganese is the primary metal contaminant in the perennial reach and its concentration in surface waters near the head of flow has remained approximately constant at about 1.2 mM (millimolar) from 1990 to 1996 [Gellenbeck and Hunter, 1994; Konieczki and Angerth, 1997, Marble, 1998]. Other dissolved metals present in the upper length of the perennial reach include Ni (10 μM, micromolar), Zn (15 μM), Co (10 μM), and Cu (1 μM) (Marble and Corley, unpublished data). Since October, 1998, these concentrations have changed due to remediation activities (unpublished data). This paper reflects the situation prior to that date.

Manganese entering the perennial reach is oxidized to produce a mixture of Mn(III,IV)-oxyhydroxide precipitates (Mn oxides) of various textures from fine flocculent materials to layered concretions within the stream sediments resembling asphalt at some locations [Lind, 1991; Hulseapple, 1995; Flinchbaugh, 1996; Harvey and Fuller, 1998; Marble, 1998]. The biogeochemical processes responsible occur predominantly in the hyporheic zone at Pinal Creek and result in an overall reactive loss of about 20% of dissolved Mn(II) along the upper 4-km length of the perennial reach [Harvey

and Fuller, 1998]. The hyporheic zone varies in depth along the perennial reach from less than 2 cm (centimeter) below the sediment-surface water interface to greater than 20 cm [Harvey and Fuller, 1998], and is typical of the depths expected for perennial systems [White, 1993]. DO concentrations in the hyporheic zone at Pinal Creek typically decrease with depth from about 60 μM at the interface with surface water to the merging groundwater value of about 3 μM. Spatial and depth gradients across this zone are also observed for pH (6 to 7.8 for surface water to 5.5 to 6 for emerging ground water) and for the different metal contaminants (e.g., shallow groundwater Mn(II) concentrations range from 1.2 mM to 0.1 mM, depending on the location along the reach, Corley and Marble, unpublished data). In addition, over the 4-km length of the perennial reach the pH of surface water increases from 6 to 7.8. and Mn(II) in surface water decreases from 1.2 mM to about 0.9 mM.

MATERIALS AND METHODS

A series of batch experiments were conducted to determine the net rates of Mn(II) removal from aqueous solution in the presence of streambed sediments. Sediments collected from different sites along the perennial reach of Pinal Creek were used: 1) sediments from site 4 to investigate Mn(II) and pH dependence; 2) sediments from sites 2 and 3 to determine the dependence on DO; and, 3) sediments from site 1 and at Inspiration Dam (about 2.2 km downstream of site 4) were used in an initial set of experiments (see Figure 1). At each site, the top 2.5 cm layer of sediments was pushed aside and the sample was taken from the sediments immediately below in order to minimize or eliminate the introduction of algae into the batch bottles. The sediments were wet-sieved to collect the < 250 μm (micrometer) or the < 2 mm (millimeter) size fraction depending on the experiment. Approximately 15 g (gram) of sediments were added to each batch bottle containing 100 mL (milliliter) of artificial stream water. The batch bottles were placed on shaker tables and agitated during the different experiments.

An artificial stream water (ASW) based on the measured major ion composition of Pinal Creek was used in these experiments after tests confirmed

that identical results were obtained whether filtered (0.45 μm , mixed cellulose acetate

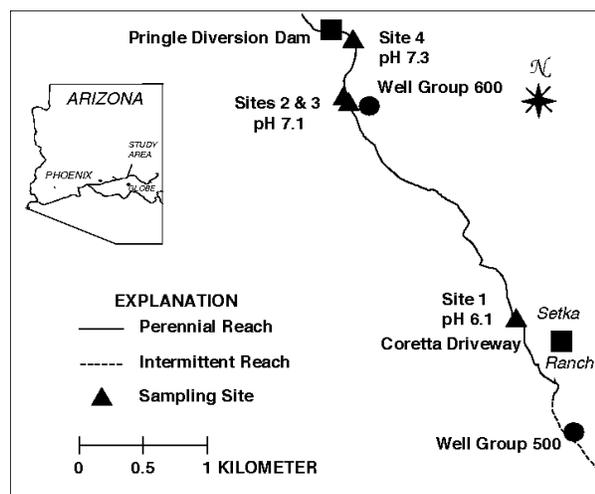


Figure 1. Field site and sampling locations in the upper perennial reach.

and nitrate) surface water or ASW was used. The use of ASW allowed experiments with the same sediments to be conducted at different pH values and at different Mn(II) concentrations.

The test matrix for these experiments included: 1) fixed pH (7.1 or 7.3), atmospheric O_2 concentration, and different initial Mn(II) concentrations (0.2 to 1.5 mM); 2) fixed initial Mn(II) concentration (0.82 mM), atmospheric O_2 concentration, and different pH values (6 to 7.8); and, 3) fixed initial Mn(II) concentration (0.82 mM) and pH (7.1), and different DO concentrations (0.015 mM to 0.45 mM).

DO concentrations were varied by mixing gas streams of nitrogen (N_2), air, and O_2 in a simple manifold system and introducing the resulting gas mixture into the headspace of the batch bottles. Mass flow controllers were used to maintain accurate control of the individual gas flows and therefore the mixture composition. The O_2 concentration in the headspace and DO were measured periodically with a minielectrode to make sure that conditions did not change during the course of specific experiments. The lids to the bottles for DO independent studies were left loosely attached during experiments conducted at atmospheric O_2 levels to prevent production of anaerobic conditions.

Different buffers (HEPES, MES and PIPES) were used to minimize or eliminate any changes in

pH. Although a recent paper (Yu and others, 1997) indicates that HEPES may complex metals, particularly copper, no evidence of such an interference was observed in our studies as the use of different buffers for the same pH value gave the same results. The initial pH values for each batch bottle were achieved by adding HCl or NaOH until the target value had been reached.

Since it was anticipated that the biogeochemical processes responsible for Mn(II) removal in Pinal Creek would involve a strong biotic component, the batch experiments were conducted under “poisoned” and “unpoisoned” conditions. Of the choice of biological poisons that have been used in studies of Mn(II) oxidation by bacteria [Kepkay, 1985; Adams and Ghiorse, 1987; Moffet, 1994], sodium azide (NaN_3) was selected for use in these studies. The key factor in choosing NaN_3 was the fact that it has been shown not to interfere with manganese chemistry. Batch bottles with NaN_3 added were designated abiotic and those without NaN_3 were designated biotic. Although it is recognized that both biotic and abiotic mechanisms participate in experiments without NaN_3 , the unpoisoned batch studies are designated biotic only. Controls were conducted without sediments present.

Aliquots (0.25 mL or less) of the solution were removed at specific times after the start of the experiments and analyzed for Mn(II) via flame atomic absorption spectroscopy (FAAS) after appropriate dilutions to reach the linear region of the instrument’s response. Partial dissolution of the sediments with acidified hydroxylamine hydrochloride [Chao, 1972] was used to determine total Mn in the sediment coatings via FAAS of the supernatant.

The net rates of removal of Mn(II) were determined from slopes of the linear sections of semi-logarithmic plots of the measured Mn(II) concentrations versus time. The slope represents a pseudo first-order rate constant and the rate was calculated by multiplying by the Mn(II) concentration. The resulting value of the net rate of Mn(II) removal is the sum of all processes releasing Mn(II) into solution minus the sum of all processes removing Mn(II) from solution. As a result, the observed net rate of Mn(II) removal may be positive, negative, or zero.

RESULTS AND DISCUSSION

An initial set of experiments used sediments and filtered surface water collected from sites 1 and 4 and at Inspiration Dam to determine the relative rates of Mn(II) removal by sediments from the perennial reach. These locations were characterized by different surface water pH values (6.1, 7.3, and 7.8, respectively), different surface water Mn(II) concentrations (1.25 mM, 0.90 mM, and 0.82 mM, respectively), and different densities of aquatic vegetation and algae.

No measurable removal of Mn(II) occurred using sediments and filtered surface water collected from the pH 6.1 site during the 34 days that these experiments were run. The initial and final concentrations of Mn(II) were identical for abiotic and biotic conditions and for the controls run without sediments. As no net release of Mn(II) was observed, the results of these experiments indicate that dissolution of the Mn oxides did not occur on the timescale of these experiments.

At the higher pH values, significant Mn(II) concentration changes were observed over time and identical results were obtained using either filtered surface water or ASW. Representative results are shown in Figures 2 and 3 for the sediments and filtered surface water collected at Inspiration Dam (pH 7.8 and initial Mn(II) ~ 0.93 mM) and for the sediments collected at site 4 using ASW (pH 7.3 and initial Mn(II) ~ 0.80 mM), respectively. It is apparent from these plots that the addition of NaN_3 suppresses the rate at which Mn(II) is removed from solution as well as the fraction removed. The concentration versus time data at pH 7.8 yield an apparent first-order rate constant for Mn(II) removal under abiotic conditions of $(8.2 \pm 0.4) \times 10^{-7} \text{ s}^{-1}$ (per second) and a value of $(1.7 \pm 0.3) \times 10^{-5} \text{ s}^{-1}$ under biotic conditions, i.e., the biotic net rate of removal is approximately a factor of 20 times that of the abiotic rate. The results in Figure 3 yield an apparent first-order rate for Mn(II) removal of $(0.44 \pm 0.18) \times 10^{-5} \text{ s}^{-1}$ for abiotic conditions versus $(1.7 \pm 0.05) \times 10^{-5} \text{ s}^{-1}$ in the absence of NaN_3 , a factor of 4 difference.

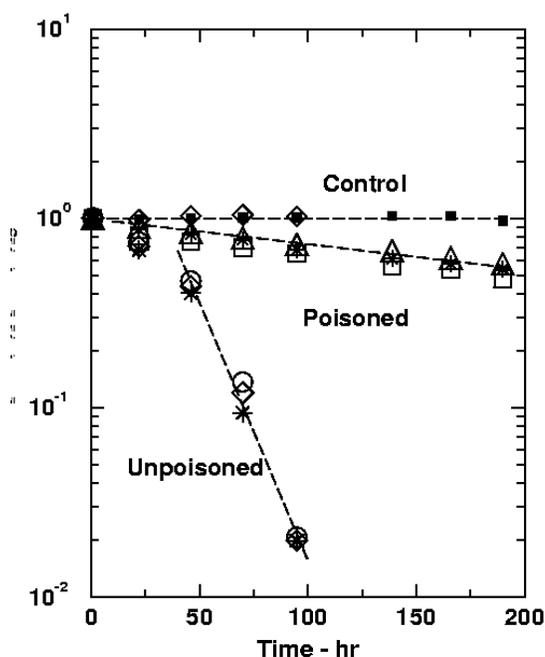


Figure 2. Removal of Mn(II) using sediments and filtered surface water from Inspiration Dam (pH 7.8). Dashed lines are for visual aid.

The normalized concentration versus time plots in Figures 2 and 3 also illustrate a feature of the batch experiments that was dependent on the length of time between collection of sediments and the start of the experiment. A “lag time” was observed at early times in a subset of the experiments in which the decrease in Mn(II) concentration with time was essentially the same for both abiotic and biotic conditions. In Figures 2 and 3 the divergence between the abiotic and biotic Mn(II) profiles began after 24 and 10 hours, respectively. This lag time increased with the interval between collection of sediments and the start of an experiment but disappeared completely if the sediments were used within 2-3 days of collection. It should also be noted that the differences in Figures 2 and 3 between the Mn(II) concentration profiles for abiotic and biotic conditions were still obtained with sediments that had been stored at $< 10 \text{ }^\circ\text{C}$ for up to 6 months.

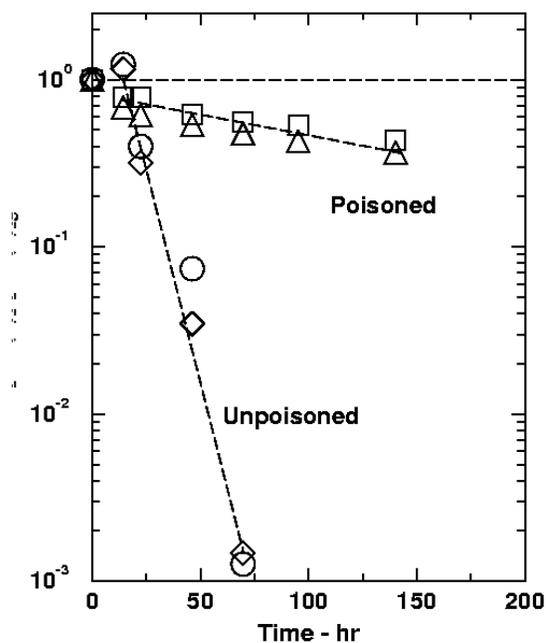


Figure 3. Removal of Mn(II) using sediments from site 4 and ASW (pH 7.3). Dashed lines are for visual aid.

The sediments collected from Inspiration Dam (surface water pH 7.8) had a total Mn concentration of (2230 ± 250) mg kg⁻¹ dry sediment (milligram per kilogram dry sediment). The sediments from site 4 (surface water pH 7.3) had a total Mn concentration of (2920 ± 615) mg kg⁻¹ dry sediment. These values refer specifically to the sediments used for batch studies in presented in Figures 2 and 3.

Mn(II) Dependence

The dependence of the net rate of removal of Mn(II) on Mn(II) concentration is shown in Figure 4. All of these batch experiments were conducted with ASW and at a fixed pH of 7.3 using natural sediments from site 4. The results obtained under both biotic and abiotic conditions suggest that between 0.2 and 1.25 mM Mn(II) the net rate of removal is directly proportional to Mn(II) and that a simple first-order dependence on Mn(II) is a reasonable assumption. However, it is apparent from Figure 4 that the net rates of Mn(II) removal

for these natural sediments do not extrapolate to a zero intercept at zero Mn(II) concentration.

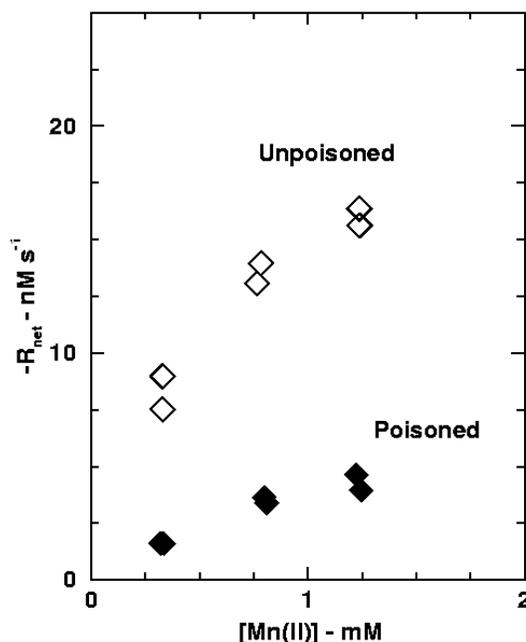


Figure 4. The net rate of Mn(II) removal increases with Mn(II) concentration.

In other studies of Mn(II) removal (oxidation) in microbially active media without sediments present (pure and enriched cultures and unfiltered water samples) it has been demonstrated that the rate of Mn(II) removal is consistent with a Michaelis-Menten-type of rate expression [e.g., Tebo and Emerson, 1985; Tebo and others, 1997],

$$-\frac{d[Mn(II)]}{dt} = V_m \frac{[Mn(II)]}{[Mn(II)] + K_m},$$

where V_m is the maximum rate (e.g., nM s⁻¹, nanomolar per second) and K_m is the Michaelis constant (e.g., mM). If this equation held for the current studies then an apparent linear dependence of net removal on Mn(II) would be expected over some range of initial concentrations with a distinct curvature over a wider concentration range and an asymptotic plateau value for the net rate at high Mn(II) concentrations. Although the derived rates of Mn(II) removal can be fitted to the Michaelis-Menten functional form (r^2 values ≥ 0.96), a more

rigorous test is obtained by considering the integrated form for Michaelis-Menten kinetics and plotting the data in transformed coordinates [Levenspiel, 1996];

$$\frac{\ln \frac{C_0}{C}}{(C_0 - C)} = -\frac{1}{K_m} + \frac{V_m}{K_m} \frac{t}{(C_0 - C)}.$$

Results of this test show that our data are inconsistent with a simple Michaelis-Menten-type mechanism, or extensions to a mechanism with simple competitive and noncompetitive inhibition or substrate inhibition. This suggests that the reaction mechanism responsible for a net removal of Mn(II) in our experiments is more complicated, or may reflect indirect oxidation mechanisms associated with microorganisms [Wehrli and others, 1995; Tebo and others, 1997].

An alternative explanation of our results may be inferred from the results of abiotic experiments conducted with Mn-oxide coatings removed from sand filter materials used in water treatment facilities in Europe to remove Mn(II) from ground water [Graveland and Heertjes, 1975]. The coatings collected from these “biologically ripened sands” were a mixture of Mn(II,III,IV)-oxyhydroxides (MnO_x , $x \sim 1.33$) and were sterilized by drying at 70 C under a N_2 atmosphere. Based on the results of their sorption and oxidation experiments, these researchers concluded that a single site, or Rideal reaction mechanism, in which Mn^{2+} in solution reacts with O_2 sorbed at the surface, provided a consistent explanation of the linear dependence for abiotic uptake. Since the Mn-oxide coatings on the sediments collected from Pinal Creek were also formed predominantly through biological processes involving Mn-oxidizing bacteria they may be similar to the coatings used by Graveland and Heertjes [1975] and a similar reaction mechanism may be applicable in part. However, the exact mechanism may not be critical in terms of the overall objective of these experiments, since the concentration range over which a linear dependence of net removal on Mn(II) was observed corresponds approximately to the range of Mn(II) concentration values observed at Pinal Creek (0.2 to 1.25 mM). Our rate data and rate coefficients can definitely be used to interpret field data within this common range of Mn(II) concentrations.

pH Dependence of Mn(II) Removal

The pH dependence of the net rates of Mn(II) removal is presented in Figure 5 on a semi-logarithmic scale. For natural sediments collected from site 4, a linear correlation was observed for both biotic and abiotic conditions. However, a net release of Mn(II) was observed under abiotic conditions for pH less than or equal to 6.5. This suggests that under these experimental conditions Mn(II) reversibly bound to surface sites or to other binding sites (e.g., extracellular polysaccharides) is released at a faster rate than adsorption and oxidation. Linear regression of the $\log_{10}[-R_{\text{net}}]$ versus pH data yielded a slope of 0.80 ± 0.12 for unpoisoned sediments and 0.75 ± 0.14 for poisoned sediments, i.e., statistically indistinguishable slopes that are statistically different from unity at the 95% confidence level.

The pH dependence of the net rate of Mn(II) removal indicates that the rate is approximately inversely proportional to H^+ , or proportional to OH^- . An increase of Mn(II) removal and oxidation with an increase pH has been reported for abiotic conditions with different metal oxide substrates [Brewer, 1975; Davies and Morgan, 1989] and Mn-oxide coatings from sand filter materials [Graveland and Heertjes, 1975], and for biotic conditions with soils [Gerretsen, 1937; Sparrow and Uren, 1987].

The experiments conducted by Graveland and Heertjes [1975] may again be most relevant to the current sets of batch experiments with streambed sediments removed from Pinal Creek. Results from these earlier abiotic experiments indicated that the rate of Mn(II) removal was directly proportional to $[\text{OH}^-]$, as observed in the current studies, and decreased to zero at pH 7, a slightly higher value than in our batch studies (pH \sim 6.5). The differences in the pH “cut-off” may be due to different Mn oxides or coverage on the sediment surfaces, to other adsorption phases, or to micro-environments created by micro-organisms that are not poisoned by NaN_3 . Our results for abiotic conditions may be consistent with the arguments proposed by Graveland and Heertjes [1975] who inferred that overall mass transfer of Mn^{2+} from solution to active sites at the surface decreased as pH decreased because of competition with H^+ .

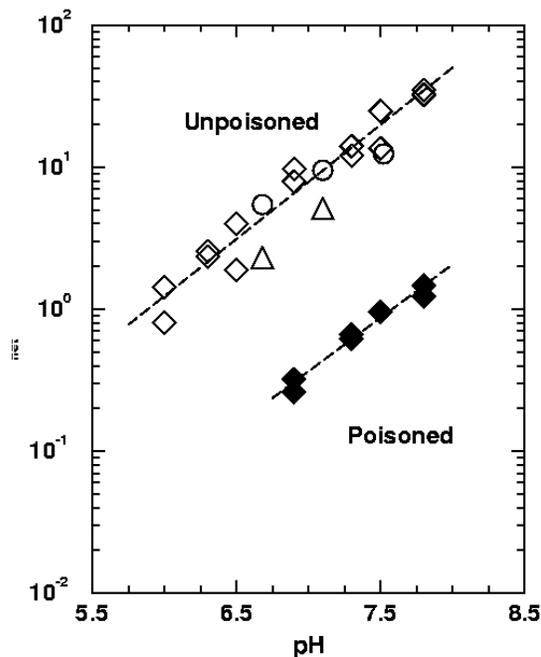


Figure 5. The net rate of Mn(II) removal increases with pH. Different symbols represent different experiments. Dashed lines represents results of linear regression.

The similarities that we observed between the pH dependence of the rate of Mn(II) removal under biotic and abiotic conditions suggest that an autocatalytic mechanism also participates in the

removal of Mn(II) under biotic conditions. The increased rate of Mn(II) removal under biotic conditions can be explained if bacteria, or other microorganisms, continually produce fresh Mn oxides via direct or indirect processes. This is an important point as it has been shown that the autocatalytic activity of Mn(III,IV)-oxyhydroxide coatings decreases as the coatings age and become more oxidized and crystalline [Graveland and Heertjes, 1975].

Dissolved-O₂ Dependence

The DO dependence of the observed net rate of removal is presented in Figure 6. Natural sediments from site 3 (pH 7.1) were used in these experiments but the samples were collected at two different times of the year. Above about 30% of

saturation, the data for the sediments collected in June 1998 exhibit no significant dependence on DO concentration. Below this value the net rate of Mn(II) removal was approximately first-order with respect to DO concentration, as shown by the log-log plot of the data. The data for the sediments collected in August 1998 suggest that these sediments were not dependent on dissolved- O₂ concentration until a value less than about 10-30% of saturation was reached. A marked change in rates of Mn(II) removal occurring at 5 to 15% air saturation has been previously reported in experiments with Mn-oxidizing bacteria present in marine waters [Tebo and Emerson, 1985; Tebo and others, 1991].

The lack of dependence of the rate of Mn(II) removal on DO above some “critical” O₂ level has also been observed in abiotic studies with Mn oxides that were biotically produced [Graveland and Heertjes, 1975]. These researchers reported no dependence of the rate of Mn(II) removal on DO above concentrations of about 1 mg L⁻¹ (milligram per liter) (~ 12% air saturation, or 0.03 mM) and an approximate linear dependence at lower DO values. Our data may reflect relative populations of macro- and micro-aerophilic Mn-oxidizers in Pinal Creek, a decrease in biotic activity at lower DO levels that results in lower production of a key chemical from microorganisms present on the sediments, and/or a decrease in surface adsorbed O₂.

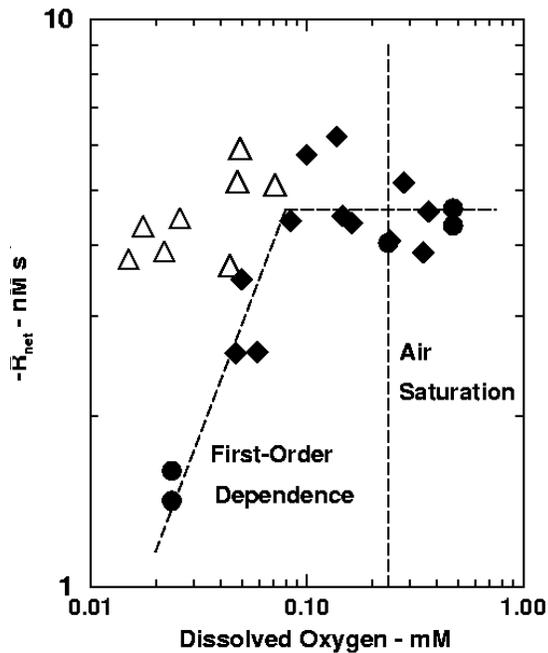


Figure 6. The net rate of Mn(II) removal is independent of DO above 30% air saturation (filled symbols from June, 1998; open symbols from August, 1998). Dashed lines are for visual aid.

Pre-existing Mn Oxides

The results of our batch experiments have identified the dependences of the net rate of removal of Mn(II) on initial Mn(II) concentration, pH, and DO. However, it is apparent from the data presented in Figures 2-6 that, depending on the date and the site at which the samples were collected the absolute values of the net rates of removal are different. The different rates may be due to differing amounts of active surface sites and/or different microbial populations. As we do not have a direct measure of active surface sites, the correlation of rate versus concentration of pre-existing Mn oxides was considered. This was done by scaling the rates obtained under different experimental conditions (initial Mn(II), pH), but at air-saturated O_2 levels, to a reference set of values for pH and Mn(II) using the functional dependences that have been determined in these studies. Different sediment samples with two size ranges ($< 250 \mu\text{m}$ and $< 2 \text{mm}$) were used. Figure

7 shows the results of such calculations (reference pH = 7.1 and reference Mn(II) = 1 mM) for sediments collected at different sites and on different dates plotted against Mn-loading of the solids. There is no

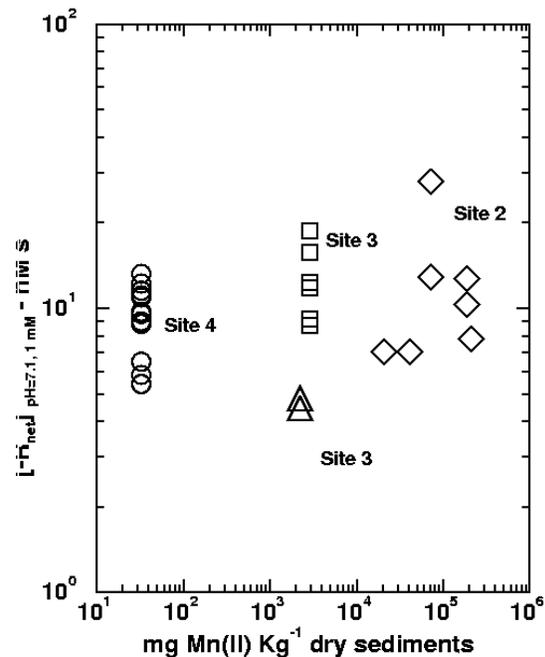


Figure 7. The net rate of Mn(II) removal on unpoisoned sediments is not affected by pre-existing Mn coatings. Different symbols refer to different experiments. Site refers to the site of sediment collection. The diamonds represent experiments done with $< 250 \mu\text{m}$ sediments; the other experiments used $< 2 \text{mm}$ sediments.

apparent (at least no strong) correlation between the total Mn-loading of the sediments and the rates after differences in pH and initial Mn(II) concentration have been taken into consideration, and there is no size fraction dependence. This finding does not preclude a key role for a specific form of Mn in the sediment coatings but it does indicate that total Mn-loading is not necessarily a good indicator of the potential Mn-oxidation rate. This inference is in contrast to the findings of Harvey and Fuller [1998] who reported an increase in the observed Mn-oxidation rate with an increase in pre-existing Mn-oxide concentration. The explanation for this difference is not obvious. The second possibility considered here, microbial

populations and/or activity, cannot be addressed with our current database, but it is a testable hypothesis that can be addressed in future work.

CONCLUSIONS

The findings of this study clearly indicate that biotic processes are key factors in determining the net removal of Mn(II) and the net rates of Mn(II) removal at Pinal Creek. The rate is approximately first-order with respect to Mn(II) concentration and inversely proportional to H^+ (directly proportional to OH^-), and independent of DO above about 0.05 – 0.07 mM. Comparisons between the results using poisoned and unpoisoned sediments strongly suggest that the microbial processes for Mn(II) removal in Pinal creek include both indirect and direct mechanisms. Finally, there is no significant evidence from our studies that pre-existing Mn-oxide concentrations influence the Mn-oxidation rate.

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