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Controlling soluble iron and manganese in a water-supply reservoir using hypolimnetic oxygenation

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ABSTRACT

Soluble metals such as iron (Fe) and manganese (Mn) often reach problematic levels in water-supply reservoirs during summer stratification following the onset of hypolimnetic hypoxia. The behavior of soluble and particulate Fe and Mn was studied following the installation of a hypolimnetic oxygenation system in Carvins Cove Reservoir, a water-supply impoundment managed by the Western Virginia Water Authority. During oxygenation, manganese concentrations were very low in the bulk hypolimnion ($<0.05 \text{ mg l}^{-1}$), but high concentrations ($>2.0 \text{ mg l}^{-1}$) were still observed in the benthic region close to the sediment, despite near-sediment dissolved oxygen concentrations in excess of 5.0 mg l^{-1} . Oxygenation appears to affect the location of the oxic/anoxic boundary sufficiently to restrict substantial transport of soluble Mn to the bulk water of the hypolimnion. However, the position of the oxic/anoxic boundary was not uniformly affected along the reservoir bottom, allowing horizontal transport of soluble Mn from higher elevations in contact with hypoxic sediments. During one summer, when the oxygen system was turned off for a month, the soluble Mn in the bulk hypolimnion increased substantially. Oxygen concentrations were quickly restored after the system was turned back on, but elevated levels of soluble Mn persisted until the sedimentation rate of detritus through the hypolimnion increased. When operated without interruption, the oxygenation system was able to reduce the bulk average hypolimnion soluble Mn concentration by up to 97%, indicating that source water control of soluble Mn and Fe can be accomplished with hypolimnetic oxygenation in water-supply reservoirs.

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1. Introduction

Manganese (Mn) is a nuisance contaminant for the water treatment industry (Stauffer, 1986), which tends to remain in the reduced form, particularly under anoxic or even hypoxic conditions (dissolved oxygen (DO) $<16\%$ of saturation; Baden et al., 1995). It is especially prevalent at the oxic/anoxic boundary or redoxcline (Kristiansen et al., 2002; Granina et al., 2004; Koretsky et al., 2006). Manganese has complicated redox

kinetics and is very difficult to chemically oxidize in pH environments typical of natural waters (pH 6–8) (Baden et al., 1995; Kristiansen et al., 2002; Roitz et al., 2002), often persisting in soluble forms despite unfavorable thermodynamics (Balzer, 1982; Dortch and Hamlin-Tillman, 1995). Mn-oxidizing microbial communities are often necessary for oxidation (Crittenden et al., 2005; Gabelich et al., 2006). Iron, in contrast, is easily oxidized chemically in the presence of oxygen at the oxic/anoxic boundary (Schaller et al., 1997), which makes it easier to control.

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Soluble Fe/Mn is typically managed during the treatment process by applying oxidants such as potassium permanganate, chlorine dioxide, chlorine, or ozone. Even though Mn can be oxidized via chemical addition and pH manipulation, it has been observed to resolubilize in sedimentation basins due to the formation of anoxic regions within the settled sludge (Budd et al., 2007). Managing Mn in the treatment process can be difficult and there is growing interest in improving raw water quality before it enters the treatment plant, essentially making the reservoir itself the first stage in the water treatment process.

Several methods of lake and reservoir management have been employed to address anoxia and its negative effects, including aeration (using compressed air as oxygen supply), oxygenation (using pure oxygen as oxygen supply) (Beutel and Horne, 1999; Singleton and Little, 2006), and artificial destratification. Published research on source water control of Mn, however, is limited primarily to artificial destratification (Burns, 1998; Zaw and Chiswell, 1999; Ismail et al., 2002; Chipofoya and Matapa, 2003; Grochowska and Gawronska, 2004) and laboratory experiments (Beutel et al., 2007). In addition, there are conflicting results on the behavior of Mn with respect to oxic conditions near the sediment–water interface. Beutel et al. (2007) performed laboratory experiments and reported that maintenance of a well-oxygenated sediment–water interface would decrease or inhibit the accumulation of Mn in the overlying waters. In contrast, the in situ experiments of Pakhomova et al. (2007) showed that Mn fluxes from sediments were independent of oxygen conditions over the sediment, suggesting that Mn fluxes were driven by Mn deposits at or just below the sediment–water interface, which control the Mn gradient between the sediment porewater and overlying waters. These conflicting results, coupled with the fact that published research on reservoir management is predominantly focused on artificial mixing, justify the need for further research on controlling Mn in source water. This research directly addresses this issue by studying a full-scale hypolimnetic oxygenation system installed to control Mn in a drinking water-supply reservoir. In light of the emerging global drinking water crisis (NRC, 2004) and increasing problems with Mn removal in treatment plants (Kohl and Medlar, 2006), finding alternative methods to improve water supplies is crucial.

The Western Virginia Water Authority maintains several water-supply reservoirs in southwest Virginia. Carvins Cove Reservoir has traditionally experienced increased soluble Mn concentrations in the hypolimnion during summer stratification, resulting in influent Mn levels at the treatment plant being too high for successful treatment. Although Fe has been much less of a problem than Mn, Carvins Cove experienced increased Fe levels during summer stratification as well. The Western Virginia Water Authority installed an oxygenation system (also referred to as a diffuser) in Carvins Cove in 2005 to address summer anoxia and to control Mn and Fe in the bulk hypolimnion. In this study, we provide detailed results of Mn and Fe behavior in both soluble and particulate forms at various locations in the reservoir during artificial oxygenation of the hypolimnion. We consider the distribution of DO within the reservoir, mixing induced by the oxygenation system, and the effect that the location of the oxic/anoxic boundary has on

dissolved metals and their subsequent mobility during both the stratified summer and naturally mixed winter periods.

2. Materials and methods

2.1. Study site

Carvins Cove (Fig. 1) is a man-made, monomictic, and eutrophic water-supply reservoir for the City of Roanoke and surrounding counties in southwestern Virginia, USA. Carvins Cove is located on a private, heavily forested watershed and is supplied by two natural tributaries that flow from agriculturally dominated lands and by two creeks from an adjoining watershed that are routed through diversion tunnels. Carvins Cove experiences increased soluble metals concentrations and subsequent poor water quality during summer stratification as a result of hypolimnetic anoxia. Two linear bubble-plume diffusers (considered as a single oxygenation system) were installed and supplied with pure oxygen in 2005 to improve water quality during summer stratification. Carvins Cove has a maximum depth of 23 m, a surface area of 2.5 km², and a volume of 24 hm³. Other characteristics of the reservoir and the oxygenation system have been summarized elsewhere (Gantzer et al., in press).

2.2. Data collection and analysis

Monthly water samples were collected between 1999 and 2005 by Carvins Cove staff at each withdrawal elevation at the water intake tower. There are six water withdrawal elevations positioned 3.1 m apart, with the highest located at 353.6 m elevation, which is 3.1 m below the surface at full pool. During this preliminary phase (1999–2005), samples were analyzed for total Fe and Mn by the colorimetric spectrophotometer method (Clesceri et al., 1998).

After the oxygenation system was installed, the sampling strategy was modified to more closely monitor Fe and Mn. This included water column samples collected with a 1.2-L Kemmerer bottle as a function of depth and sediment porewater samples collected with in situ porewater analyzers (“peepers”; Hesslein, 1976) from a single location in 2006 (CC) and from two locations in 2007 (CC and C3) (see Fig. 1). CC is located at the deepest point in the reservoir, which is approximately 150 m from the intake tower and has a bottom elevation of 335.3 m (21.3 m deep). C3 is located approximately 2000 m upstream of CC and has a bottom elevation of 341.4 m (15.2 m deep). In addition to the six withdrawal elevation sample depths, a bottom sample depth was added following the installation of the oxygenation system at an elevation located just above the sediment (353.3 m). The additional sample depth was collected as close to the sediment as possible, which was approximately within 0.3 m of the bottom, and is referred to as the benthic region. Samples for total metal analyses were transferred from the Kemmerer bottle directly to pre-acidified plastic bottles. Samples for soluble metals were filtered through 0.45 μm Millipore filter paper before being transferred to pre-acidified plastic bottles. All samples collected during 2006 and 2007 were analyzed for Fe and Mn concentrations using the inductively coupled

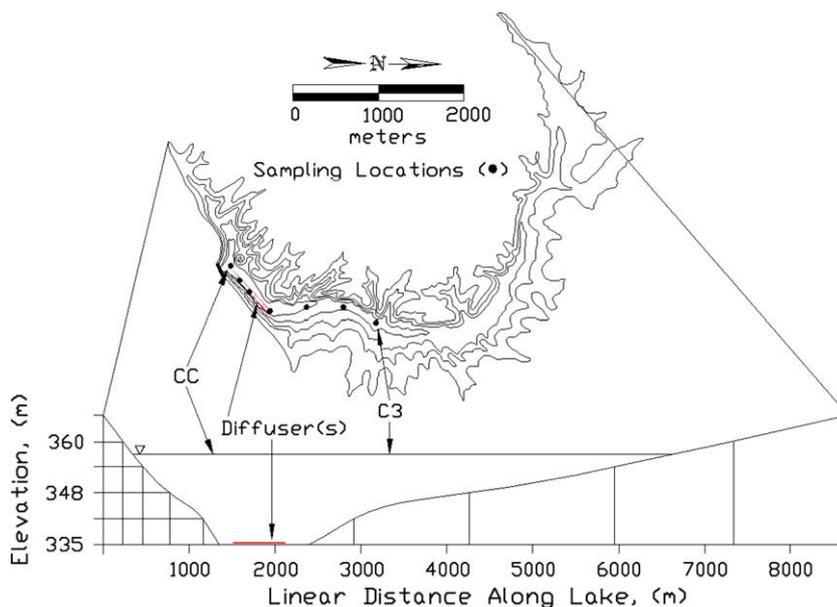


Fig. 1 – Bathymetry, bottom profile, diffuser locations, and sampling stations in Carvins Cove Reservoir. ‘CC’ and ‘C3’ are the sampling stations where porewater analyses were also conducted.

plasma (ICP) method (Clesceri et al., 1998). Sediment traps were also deployed in Carvins Cove in 2007 and were positioned 2 m above the sediment at three locations in the immediate vicinity of the diffuser and at locations 600 and 1150 m away from the diffuser (Fig. 1), which were monitored bi-weekly for Fe, Mn, Total Organic Carbon (TOC) and total solids between September and October.

2.3. Water column profiles

A Seabird Electronics SBE 19plus (4 Hz sampling rate) high-resolution profiler (CTD) was used to collect conductivity, temperature and DO profiles throughout the year. The DO probe has a response time of 1.4 s at 20 °C, allowing data to be collected at about 0.1 m increments. The CTD has a stainless steel cage around it, thus allowing positioning within a few centimeters of the bottom. To verify these measurements, bottom DO profiles obtained with the CTD were compared to microsensor DO profiles obtained from extracted sediment cores and in situ measurements (Bryant et al., in preparation) and were found to be essentially the same.

Stratification in Carvins Cove begins in April and the thermal structure typically stabilizes in May. The reservoir usually remains stratified until it is naturally mixed in early November. Water column profiles were collected three times per week during summer stratification and bi-weekly during the completely mixed winter period along a longitudinal transect at seven locations, as shown in Fig. 1. These locations span the entire hypolimnion, including locations both upstream and downstream of the diffuser. Water column profiles were used to identify the thermocline position (as defined by Wetzel, 1975), to determine metalimnion and hypolimnion DO (Gantzer et al., in press), and to estimate the relative location of the oxic/anoxic boundary.

2.4. Oxygenation system (diffuser) operation

The oxygenation system (diffuser) was installed and first operated in August 2005. It has subsequently been in continuous operation, with the exception of a month-long test period (between June 15 and July 14, 2006) when the oxygen supply was turned off. The diffuser was operated at flow rates ranging from ~8 to 100 normal cubic meters per hour (NCMH) with the applied gas flow rate based on DO requirements needed to maintain DO in the bulk water at or above 7 mg l⁻¹.

3. Results and discussion

3.1. Historical observations

Contour plots of soluble Fe and Mn (using a Kriging interpolation scheme) based on monthly water column samples are shown in Figs. 2 and 3, respectively. The DO concentration isopleth of 5.0 mg l⁻¹ is superimposed as a blue line labeled ‘DO 5’. Focusing on the historical data obtained during the years preceding diffuser installation in 2005, Figs. 2 and 3 show that concentrations of soluble Fe/Mn fluctuated annually, that low DO coincided with increased soluble Fe/Mn in the bulk water during summer stratification, and that increased DO during naturally mixed winter conditions paralleled lower soluble Fe/Mn concentrations.

It is clear from Fig. 2 that reduced Fe reached problem levels following the annual depletion of DO. When DO in the bottom water was replenished due to mixing after fall turnover, soluble Fe quickly decreased. In contrast, Mn oxidation is less directly controlled and not so easily explained, as expected based on the complex Mn redox kinetics previously discussed. Thus, the behavior of Mn in response to elevated

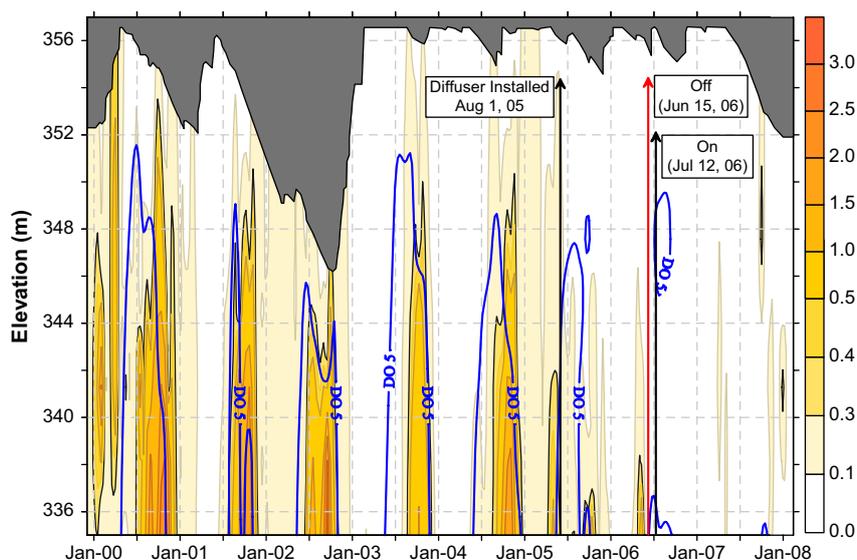


Fig. 2 – Soluble Fe (mg l^{-1}) in Carvins Cove Reservoir from 2000 to 2008.

DO concentrations in the bottom water and the bulk hypolimnion requires closer examination.

3.2. Comparison between stratified and naturally mixed periods

More recent Mn data (collected after diffuser installation) with increased temporal sampling resolution are detailed in Fig. 4 (with no distortion as a result of interpolation), which shows soluble Mn concentrations in the benthic region and at three elevations in the water column (338.3, 341.4 and 344.4 m) representing the bulk of the hypolimnetic water during both 2006 and 2007. In the naturally mixed winter period, the water column is isothermal, which promotes a more uniform distribution of DO as well as turbulence at the sediment–water interface, thus driving the oxic/anoxic boundary deeper into the sediment (Balzer, 1982; Granina et al., 2004; Katsev et al.,

2007). It is hypothesized that large-scale dilution, oxidation and precipitation (Yagi, 1996; Michard et al., 2001), coupled with the movement of the oxic/anoxic boundary into the sediment on a reservoir-wide scale and the corresponding shift in the Mn-oxidizing microbial community, are factors that control the decrease in Mn concentrations during winter, as shown in Fig. 4 between December 2006 and April 2007.

During summer stratification, the hypolimnion is isolated from the epilimnion and becomes relatively quiescent, as described by Schoemann et al. (1998). The isolated hypolimnetic water experiences DO depletion, which can lead to hypoxia (Gantzer et al., *in press*). The quiescence and low levels of DO at the sediment–water interface cause the oxic/anoxic boundary to move out of the sediment and into the water column, allowing reductively solubilized species, such as Fe and Mn, to be released into the overlying water (Kristiansen et al., 2002; Roitz et al., 2002).

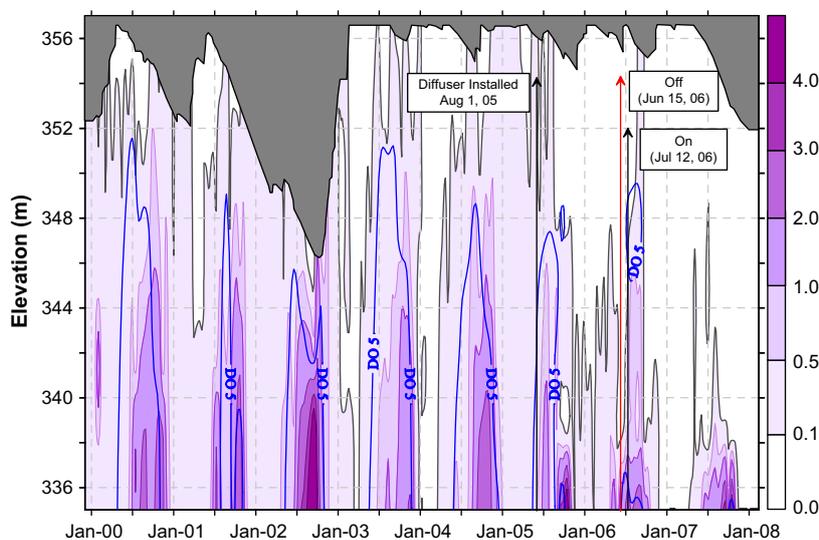


Fig. 3 – Soluble Mn (mg l^{-1}) in Carvins Cove Reservoir from 2000 to 2008.

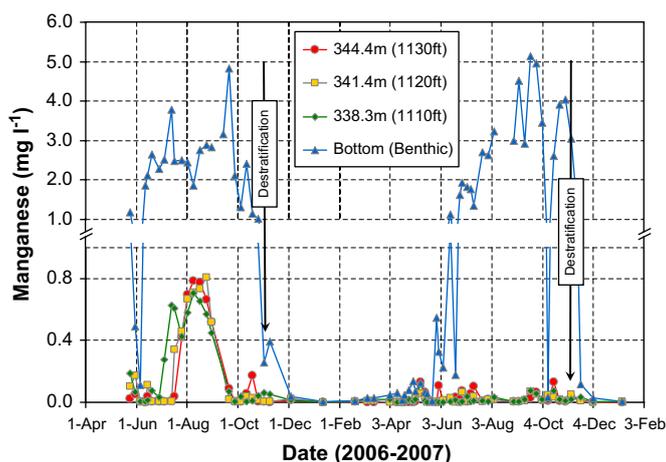


Fig. 4 – Soluble Mn in Carvins Cove Reservoir showing elevated Mn concentrations in the benthic region compared to the bulk hypolimnion.

To estimate the relative position of the oxic/anoxic boundary, bottom DO measurements (obtained with the CTD cage resting on the sediment surface) along the reservoir were analyzed. The bottom DO measurements followed a similar trend to the bulk hypolimnion DO, but were consistently lower. Fig. 5 shows the volume-averaged hypolimnion DO (Gantzer et al., in press) and the lowest recorded bottom DO of the seven sample locations. The lowest bottom DO was observed at CC, where the bottom depth is below the diffuser, and at C3, located approximately 1500 m up-reservoir from the diffuser. The bottom DO measurements indicate that conditions were favorable for the oxic/anoxic boundary to be positioned in the water column during summer hypoxia.

During summers when the oxygenation system was in operation (2006 and 2007), mixing in the hypolimnion is primarily governed by diffuser operation (Gantzer et al., in press). Increased turbulence in the hypolimnion has been shown to cause a decrease in the thickness of the diffusive boundary layer, a viscous layer of water immediately above the sediment-water interface (Lorke et al., 2003; Hondzo et al., 2005). Although variations in diffusive boundary layer thickness were measured at locations both near and far from the diffuser (Bryant et al., in preparation), thus indicating turbulence in the hypolimnion, the degree of induced mixing is lower and less uniform than that observed during naturally mixed conditions in winter. This is apparent in Fig. 5 which shows that, regardless of applied gas flow rate or bulk hypolimnion DO concentration, the oxygenation system did not produce equivalent DO conditions uniformly at the bottom.

3.3. Diffuser operation in 2006

During 2006, the oxygenation system was shut down between June 15 and July 14 in order to allow hypoxic sediment conditions to develop as part of an experiment designed to ascertain the full effect of the oxygenation system on the oxic/anoxic boundary without the influence of winter mixing. Following the 1-month shut down, the applied gas flow rate

was steadily increased (see Fig. 5). The volume-averaged hypolimnion DO was observed to increase from 5.0 to 10.0 mg l⁻¹ between July 14 and October 16, exceeding 8 mg l⁻¹ by September 25.

After the diffuser was turned off, the DO below 338.3 m elevation (3 m above the bottom) rapidly dropped below 5.0 mg l⁻¹, as shown in Fig. 6. During the month-long shutdown period, total Mn increased in the lower hypolimnion (3 m above the bottom) while total Mn decreased in the upper hypolimnion (6 and 9 m above the bottom), as shown in Fig. 6. More importantly, bottom DO was observed to decrease to less than 1.0 mg l⁻¹ (see Fig. 5). A mass balance on total Mn in the upper hypolimnion reveals that total Mn in this region decreased by approximately 700 kg during this month-long period, with a corresponding increase of 880 kg in the lower hypolimnion and benthic water. Correspondingly, soluble Mn concentrations in the lower hypolimnion were also observed to increase rapidly in conjunction with the substantially depleted DO observed at this depth, which is believed to be caused by transport of soluble Mn from the benthic (near-sediment) region.

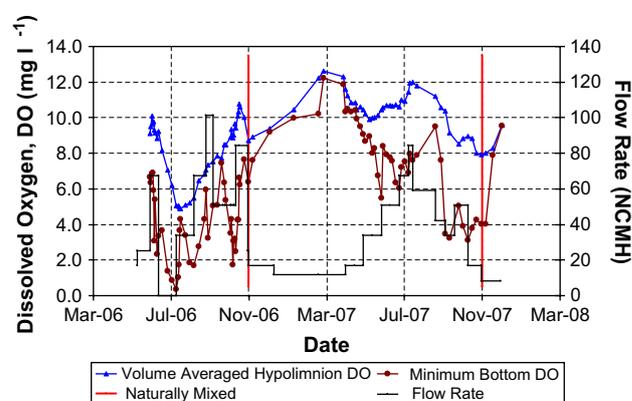


Fig. 5 – Volume-averaged hypolimnion DO, minimum bottom DO, and applied oxygen gas flow rate. Vertical lines in November identify when the reservoir was naturally destratified or mixed.

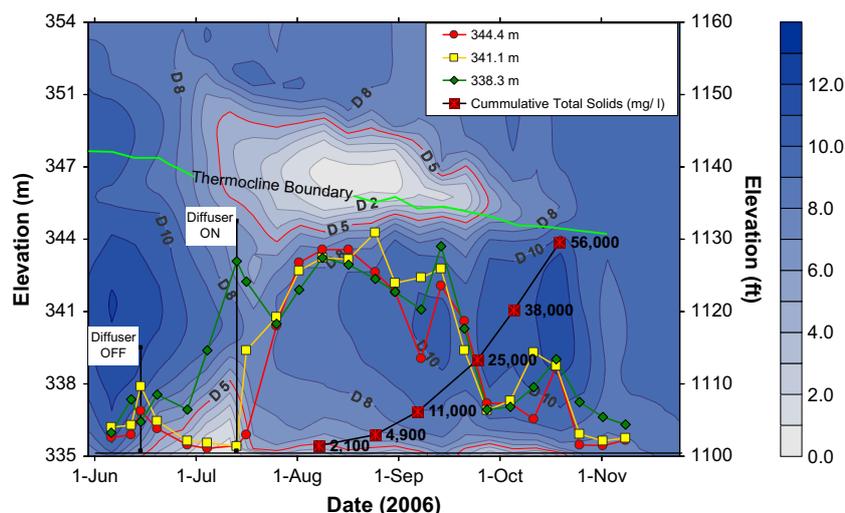


Fig. 6 – Total Mn concentration as well as total solids accumulated in sediment traps, superimposed on DO (mg l^{-1}) contours. For numerical values of the Mn concentrations, see Fig. 4.

Within 10 days of restarting the oxygenation system, Mn levels in all regions (upper and lower) of the hypolimnion were almost completely homogeneous, as shown in Fig. 6 where the Mn concentrations at the three bulk hypolimnion elevations converge. This relative homogeneity in the bulk hypolimnion Mn concentration was observed at all times when the diffuser was in operation and is evident in both Fig. 4 (soluble Mn) and Fig. 6 (total Mn). Surprisingly, despite increasing and maintaining the volume-averaged hypolimnion DO above 5 mg l^{-1} after the oxygenation system was turned back on, soluble Mn concentrations continued to increase. It could be argued that the benthic region continued to be a source to the bulk hypolimnion; however, a mass balance suggests that insufficient Mn mass was available in the benthic region to serve as a continuous source to the upper waters. Therefore, the observed increase is most likely due to transport of Mn from elevations in the upper hypolimnion that are in contact with hypoxic sediments further away from the deeper basin. This idea will be addressed more thoroughly in a subsequent section of this paper.

Soluble Mn concentrations remained high in the hypolimnion and did not begin to decrease until the volume-averaged hypolimnion DO was nearly 7 mg l^{-1} , which occurred more than a month after oxygenation system operation was restored. While this may be attributed to the slow oxidation kinetics of Mn, at the pH of ~ 8 typically observed in the hypolimnion, it is unlikely that chemical oxidation is the sole cause of Mn oxidation. Furthermore, in addition to the slow temporal response of Mn to oxygenation, it is interesting to note that the observed decrease in soluble Mn coincided with the time when organic detritus from the metalimnion entered the hypolimnion following summer algal growth. Increased organic loading in the hypolimnion is supported by (1) elimination of the metalimnetic minimum (Gantzer et al., *in press*), as shown in Fig. 7 and (2) increased sediment loading in sediment traps, where increased sedimentation rates of Fe, Mn, TOC, and total solids were observed during this period (total solids accumulation shown in Fig. 6). This suggests that

Mn oxidation in the hypolimnion may have been accelerated by an increase in the amount of organic matter in the presence of a well-oxygenated environment, as observed by other researchers (Wann et al., 1997; Schoemann et al., 1998; Zaw and Chiswell, 1999).

By October, soluble Mn concentrations in the bulk hypolimnion and in the benthic region decreased substantially at all locations in the reservoir. This decrease coincided with an increase in soluble Mn, reaching levels in excess of 36 mg l^{-1} (Fig. 8), immediately below the sediment–water interface, as observed from porewater measurements obtained at Location CC. It is clear that oxidation and precipitation of Mn occurred throughout the bulk hypolimnion and benthic region. However, once the Mn precipitate was deposited on the sediment together with the newly deposited organic matter, it was likely resolubilized due to organic remineralization and microbial reduction under the highly reducing sediment environment, resulting in the increased levels of Mn observed immediately below the sediment–water interface. Interestingly, the soluble Mn was not observed to flux back into the overlying waters. At Location CC, where Mn porewater samples were collected, it appears that the oxic/anoxic boundary remained within the sediment (diffuser operations apparently promoted DO penetration into the sediment), thus limiting the mobility of soluble Mn into the water column. The predicted location of the oxic/anoxic boundary is supported in Fig. 5, which shows the volume-averaged hypolimnion DO in excess of 10.0 mg l^{-1} and DO in the bottom water directly over the sediments $>7.0 \text{ mg l}^{-1}$.

3.4. Manganese observations in 2007

A comparison of 2006 and 2007 results in Fig. 7 shows that both soluble and particulate Mn levels in the bulk hypolimnion were substantially lower in 2007, despite similar Mn concentrations in the benthic region (Fig. 4) for both years. The main differences between 2006 and 2007 are (1) the oxygenation system was turned off for 1 month in 2006, but was in

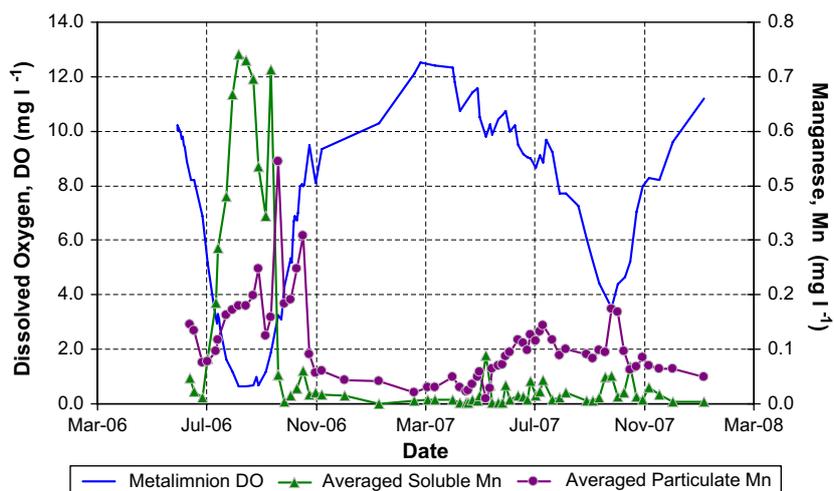


Fig. 7 – Average soluble and particulate Mn concentrations in the bulk hypolimnion as well as metalimnion DO, showing decreasing Mn concentrations coinciding with increasing metalimnetic DO.

continuous operation during 2007 and (2) in 2007 DO levels in the bottom water and in the bulk hypolimnion were substantially higher (maintained at DO levels above 5 and 10.0 mg l⁻¹ through September, respectively, as shown in Fig. 5). Furthermore, Fig. 3 shows Mn concentrations in the upper hypolimnion were somewhat higher than those observed in the lower hypolimnion in both 2006 and 2007. These increased Mn levels in the upper hypolimnion are likely due to Mn coming from locations where the upper hypolimnion water comes into contact with hypoxic sediments further away from the deeper, oxygenated basin, a phenomenon described as horizontal transport by Schaller et al. (1997).

3.4.1. *Manganese in the benthic region and bulk hypolimnion*
 During the 2007 stratified period, soluble Mn in the bulk hypolimnion remained low despite elevated Mn concentrations in the benthic region. More importantly, Mn in the

sediment porewater was observed to be approximately five times higher than in the benthic region, suggesting that Mn was accumulating in the near-surface sediment (Bryant et al., in preparation). It appears that Mn continued to flux from the sediments to the benthic region, despite the elevated DO observed in the bulk water and over the sediments. The accumulation of Mn in the benthic region in 2007 was similar to that observed in 2006 (see Fig. 4). The observed trend of Mn flux from the sediment occurring independent of DO concentration coincides with similar findings reported by Pakhomova et al. (2007). It could be argued that Mn continued to flux from sediment porewater to the benthic region and then ultimately to the bulk hypolimnion where it was then diluted by the larger bulk volume or oxidized in the very high DO conditions present in the bulk hypolimnion. In order for this to occur, an assumption would have to be made that Mn transport from the porewater to the benthic region and

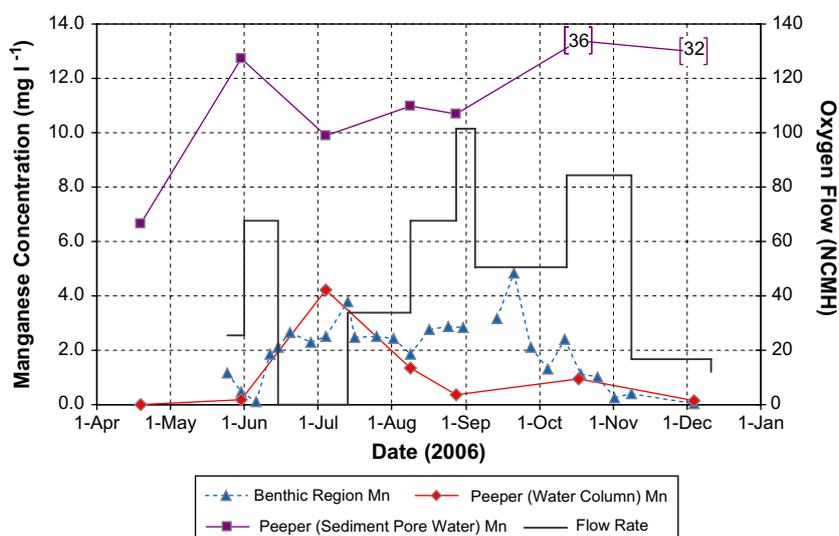


Fig. 8 – Porewater samples showing the relationship between sediment and benthic region Mn concentrations.

subsequent loss to the overlying hypolimnion water were in steady-state; thus, Mn levels in the porewater would need to decrease while Mn levels in the hypolimnetic water increased. However, this was not observed to be the case. Mn levels in the porewater actually continued to increase throughout the summer from 9.6 mg l^{-1} in April to 42.0 mg l^{-1} in early October (Bryant et al., in preparation) while soluble Mn levels in the bulk hypolimnion remained relatively constant. A similar trend was observed in 2006, as shown in Fig. 8. It is hypothesized that the decreased Mn concentrations observed in the bulk hypolimnion during the 2007 summer stratified period were a result of the oxygenation system more efficiently increasing DO and turbulence near the sediment surface, thus keeping the oxic/anoxic boundary closer to the sediment-water interface over a greater surface area than in 2006 (Fig. 5). Therefore, it is possible that soluble Mn was oxidized as it passed through the benthic region and re-precipitated back to the sediment (forming a Mn redox cycle in the benthic region; Zhang et al., 1999). This suppression of soluble Mn to the benthic region during 2007 is supported by the observation that the proportion of soluble Mn relative to total Mn was lower during the 2007 stratified period than during 2006; thus, a greater percentage of the total Mn in the reservoir system was in the oxidized form.

As observed in 2006, an increase in soluble Mn in the benthic region did not occur until June. The delayed increase is believed to be caused by the location of the oxic/anoxic boundary remaining below the sediment-water interface prior to June (thus inhibiting diffusion of soluble Mn out of the sediment) and shifting upwards into the benthic region after June (as indicated by CTD profiles and microsensors measurements obtained by Bryant et al., in preparation), which is supported by the findings of Balzer (1982), Koretsky et al. (2006), and Katsev et al. (2007). Between April and June, DO concentrations were elevated ($>8 \text{ mg l}^{-1}$) throughout the reservoir, including in the benthic region (Fig. 5). Microsensor DO profiles indicated increased DO penetration during this period at all locations, with DO penetration ranging between 2 and 4 mm at C3, the sampling location farthest from the diffuser. As the summer progressed, decreased DO was observed near the reservoir bottom (Fig. 5), suggesting that the oxic/anoxic boundary shifted upward, closer to or slightly above the sediment-water interface. Despite elevated Mn concentrations in the benthic region, average Mn concentrations in the bulk hypolimnion were observed to be substantially lower (97%) in 2007 (0.02 mg l^{-1}) than historically observed between 2000 and 2005 (0.6 mg l^{-1}).

As observed in 2006, total Mn increased in the bulk hypolimnion during October 2007, although not to the same extent. Total Mn concentrations again decreased as the metalimnetic minimum was eliminated, suggesting accelerated removal due to adsorption and/or co-precipitation of Mn with organic detritus, as the organics settled through the hypolimnion to the sediment.

3.4.2. Horizontal transport

Manganese concentrations were observed to be higher in the upper hypolimnion than in the lower hypolimnion in both 2006 and 2007 (Fig. 3), which, as mentioned previously, may be attributed to horizontal transport from hypoxic regions up-

reservoir from the oxygenated, deeper reservoir basin. To further illustrate this phenomenon, the mass of Mn at each elevation in the hypolimnion (bottom (benthic) region, lower hypolimnion (3 m above sediment), and upper hypolimnion (6 and 9 m above sediment)) was calculated for 2006. Based on enhanced levels of Mn at the bottom during the period when the diffuser was turned off, these results indicate that Mn present at the benthic elevation can reasonably be assumed to be the source of Mn to the overlying water (Fig. 9). Once the diffuser was turned back on, the mass of Mn in the benthic region (335.3 m) was observed to be significantly lower than in the upper hypolimnion (341.4 and 344.4-m elevation). The increased mass of Mn 9 m above the bottom far exceeded that present 3 m above the bottom or in the benthic region. The Mn levels observed in the upper hypolimnion therefore appear to come from a soluble Mn source specific to this higher elevation, presumably where the hypolimnetic water comes into contact with hypoxic, reducing sediments. The Mn peak observed in the middle of the water column (Fig. 9) resembles results presented in other studies describing lateral transport from shallower, more hypoxic sediments (Schaller et al., 1997; Wann et al., 1997).

In 2007, to further examine the horizontal transport theory, soluble Mn concentrations were measured at two locations spaced approximately 1500 m apart (CC, in the immediate vicinity of the diffuser, and C3, 1500 m up-reservoir from the diffuser, as shown in Fig. 1), but at equivalent depths (341.4 m elevation) in the water column. This sample depth was 6.2 m above the sediments at CC and within 0.3 m of the sediments at C3, due to up-sloping reservoir bottom topography from CC to C3. Manganese concentrations at C3 were only slightly higher than at CC until mid-July, when they were then observed to increase markedly (Fig. 10). This Mn increase coincided with a decreased applied gas flow rate to the diffuser; thus, less DO was being supplied to the reservoir. Consequently, DO in the lower hypolimnion at C3 decreased from 10.2 to 3.9 mg l^{-1} between July 17 and October 12, although it did not reach complete anoxia. The impact of the diffuser, in terms of induced mixing and elevated DO concentrations, is logically observed to decrease with increasing distance up-reservoir from the diffuser location in the deep basin. The location of the hypolimnion in the C3

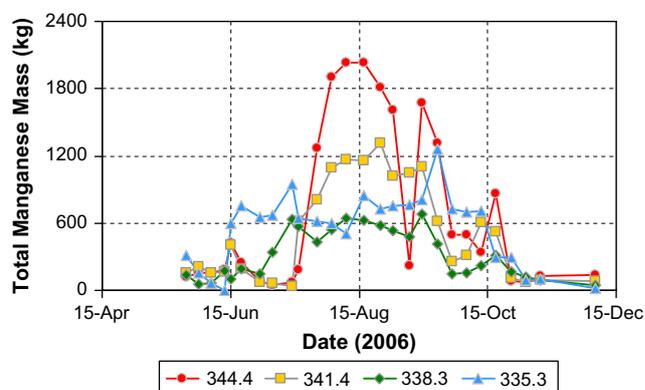


Fig. 9 – Total Mn mass as a function of elevation in the hypolimnion, showing higher Mn mass in the upper region compared to the lower region of the hypolimnion.

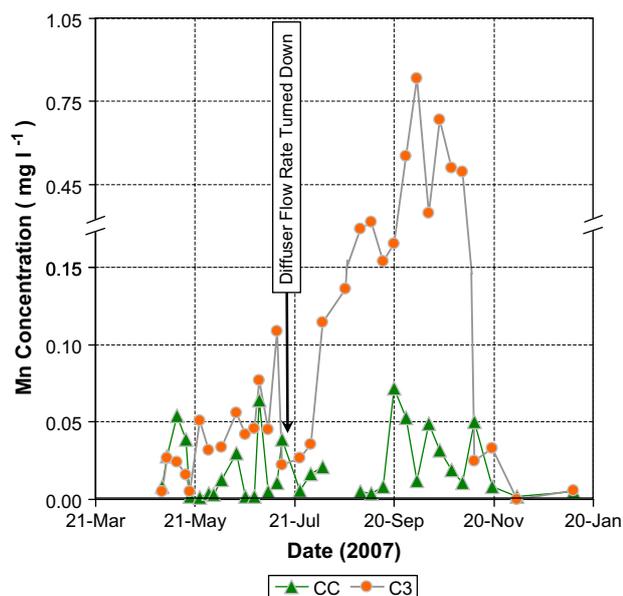


Fig. 10 – Soluble Mn collected at 341.4 m elevation 6 m above the bottom at CC (in the vicinity of the diffuser over the deep basin) and within 0.3 m of the bottom at C3 (approximately 1500 m up-reservoir of the diffuser). The Mn concentrations are consistently higher at C3 than at CC.

region in 2007 suggests that anoxic conditions would be present at the sediment–water interface even further up-reservoir, thus promoting the diffusion of soluble, reduced Mn from the sediment to the overlying waters at these remote locations not affected by oxygenation.

4. Conclusions

Oxygenation increased DO concentrations throughout the hypolimnion and down to the sediment–water interface, although DO levels were not uniformly maintained in the bulk hypolimnion or along the reservoir bottom. Oxygenation also induced less mixing than is typically observed during natural mixing in the winter. While decreased mixing results in reduced DO penetration into the sediment, diffuser-induced mixing does appear to maintain the oxic/anoxic boundary at a depth sufficient to restrict substantial flux of soluble Mn to the bulk hypolimnion. Major conclusions for this research on a full-scale application of hypolimnetic oxygenation to control Mn in source water are

1. Maintaining DO in the bulk hypolimnion ($8\text{--}10\text{ mg l}^{-1}$) coupled with elevated DO conditions at the bottom ($6\text{--}8\text{ mg l}^{-1}$) was ineffective in preventing soluble Mn flux from the sediments to the overlying bottom (benthic) water.
2. Hypolimnetic oxygenation did not establish DO or turbulent conditions at the sediment–water interface equal to those commonly observed during completely mixed winter conditions. This in turn prevents the oxic/anoxic boundary from being universally positioned below the sediment–water interface, leading to potentially anoxic conditions up-reservoir from the location of the diffusers.

3. The relative position of the oxic/anoxic boundary during periods of oxygenation appeared to be close enough to the sediment to prevent transport of soluble Mn from the bottom (benthic) waters to the bulk hypolimnion, thus promoting Mn oxidation in the benthic region and subsequent cycling back to the sediment.
4. Horizontal transport is a significant source of soluble Mn to the upper hypolimnion during summer as the oxic/anoxic boundary moves into the water column up-reservoir.
5. Hypolimnetic oxygenation successfully reduced bulk hypolimnion Mn levels by 97%, resulting in volume-averaged soluble Mn concentrations of approximately 0.02 mg l^{-1} in the hypolimnion.

We conclude that Mn control in source water is more complicated than previously understood, and is affected by a combination of factors including DO concentrations, hypolimnetic mixing, and sedimentation of organic matter, highlighting the need for continued research. Despite the complexities associated with Mn oxidation, levels of reduced, soluble Mn in the bulk hypolimnion were observed to decrease substantially due to elevated hypolimnetic DO and suppression of the oxic/anoxic boundary closer to the sediment. Hypolimnetic oxygenation was thus shown to be a viable method of improving drinking water quality by decreasing levels of soluble Fe and Mn in the source water.

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