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Analytical Methods for Iron and Manganese Determinations in Reservoir Tailwaters: Laboratory Investigations

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Purpose

This technical note describes a laboratory investigation conducted to evaluate colorimetric methods for determining the oxidation states (species) of iron and manganese and methods of filtration for differentiating species. The techniques evaluated were selected based on their applicability to field studies of reservoir tailwater processes.

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Background

Water quality processes in reservoirs affect the quality of release waters and water quality processes in the tailwater region. Major impacts are often associated with the release of hypolimnetic water, which is often low in dissolved oxygen concentrations and high in concentrations of nutrients and reduced forms of metals. Many of these processes have been described in recent studies of selected reservoir tailwaters (Nix and others 1991). Based on these studies, the Tailwater Quality Model (TWQM) was developed (Dortch, Tillman, and Bunch 1992). This one-dimensional steady-state model, which describes the fate of selected water quality constituents in reservoir tailwaters, offers the opportunity for improved water quality management and decision-making. However, additional process description information is needed for evaluating reservoir tailwaters and improving model applications.

Major concerns about tailwater quality are associated with temporal and spatial patterns in temperature, dissolved oxygen dynamics, and the fate of nutrients and metals. The chemical reactions of iron species in reservoir tailwaters are of particular concern since they affect water clarity and oxygen dynamics. For example, oxidation of reduced iron results in the formation of particulates (decreasing water clarity) and the consumption of dissolved oxygen. The change in oxidation states of manganese is also

of interest since oxidation rates are relatively slow, and mechanisms other than oxidation may account for considerable processing in release waters.

The fate of iron and manganese species in reservoir releases is affected by several chemical, physical, and biological processes, including complex formation, sorption/desorption, oxidation/reduction, hydrolysis, and precipitation. Iron and manganese speciation is controlled primarily by the pH and redox potential (Eh) of the system (Baas Becking, Kaplan, and Moore 1960; Gotoh and Patrick 1974). However, interpretations of stability diagrams are often limited by the assumptions related to thermodynamic equilibria.

Equilibrium under the given conditions is assumed, and no reaction rates or kinetics are considered. This has important implications in open systems where continuous inputs of materials and energy promote disequilibrium (Stumm and Morgan 1981). These inputs may inhibit or catalyze reactions, yielding results that are contrary to those predicted by thermodynamic reactions. For instance, organic matter complexation of iron and manganese can be an important process in aquatic systems, affecting cycling, adsorption, and oxidation state (Florence 1982). Organic complexes can result in high steady-state levels of iron (Fe^{2+}) where oxidation rates are slower relative to the rates of reduction (Theis and Singer 1974). Microbial oxidation of manganese significantly increases oxidation rates over those predicted by thermodynamic equilibria (Chapnick, Moore, and Nealson 1982; Ghiorse 1984; Nealson, Tebo, and Rosson 1988). Consequently, consideration of mechanisms other than those described by thermodynamics is important in evaluating the results of field studies.

Quite often, as in the above studies, the speciation of iron and manganese (that is, the oxidation state; Fe^{2+} and Mn^{2+}, reduced, or Fe^{3+} and typically Mn^{4+}, oxidized) is determined by the physical separation using filtration through various pore size filters. The assumption is that reduced iron/manganese is soluble and oxidized iron/manganese is not. Therefore, determinations on a filtered sample yield concentrations of reduced species, and determinations on an unfiltered sample yield a measurement of oxidized (or reduced and oxidized) species, depending on analytical methods. (Total concentrations are reported if a digestion/reduction has been conducted on the unfiltered sample prior to analysis.)

The choice of pore size generally varies from 0.1 to 0.45 µm, with some uncertainty in speciation for colloidal size fractions in between. While the use of filtration to differentiate oxidation states of iron and manganese is easily conducted in field studies, results from the above studies suggest that speciation of iron by filtration may not always be applicable and that removal of manganese may be attributed to mechanisms other than oxidation and precipitation.

The objective of this research was to evaluate analytical methods that would allow differentiation of oxidized and reduced iron and manganese to better describe processes in the tailwater and improve application of the TWQM and interpretation of field study results. Determination of iron and manganese species was conducted as a function of physical size fraction and oxidation state.

Methods

Tests were conducted on simulated reservoir water of known concentrations of iron and manganese. The simulated reservoir water was treated with nitrogen to remove dissolved oxygen and thus simulate anoxic hypolimnetic conditions and the associated speciation of iron and manganese. Specific methods for determining reduced forms of iron and manganese and total concentrations were used; concentrations of oxidized forms were calculated by subtraction of reduced from the total concentration.

Samples of simulated reservoir water were collected immediately before aeration began (0 hr) and at 6, 26, and 50 hr after aeration. One aliquot was collected without filtration, while the remaining sample was filtered through 0.4-, 0.2-, and 0.1-μm Nucleopore filters with in-line syringe holders. Ferrous (Fe^{2+}) iron was determined in both filtered and unfiltered samples with a,a',-dipyridyl and ferrozine. One milliliter of each sample (unfiltered and 0.4-, 0.2-, and 0.1-μm filters) was added to 1.0 ml of $4\underline{M}$ $NaC_2H_3O_2$ and 1.0 ml a,a',-dipyridyl. This was diluted to 10 ml total volume with distilled, deionized water, and absorbance was measured at 520 nm (a,a',-dipyridyl) or 526 nm (ferrozine) on both a Perkin Elmer Lambda 3 and a Milton Roy Mini 20 spectrophotometer.

Total iron in each sample was determined by the same procedure with the addition of 1.0 ml 10-percent $NH_2OH \cdot HCL$ (hydroxylamine hydrochloride) prior to adding a,a',-dipyridyl or ferrozine. This reduced the Fe^{3+} to Fe^{2+} prior to complexation with the colorimetric reagent. Manganese was analyzed using formaldoxine colorimetric reagent, which is not specific to any form. However, Morgan and Stumm (1965) concluded that filtration through a 0.22-μm filter followed by colorimetric complexation with formaldoxine quantified the Mn^{2+} form of Mn.

Results and Discussion

The iron in the simulated reservoir water was in the reduced, ferrous (Fe^{2+}) form prior to the oxygenation treatment (Figures 1 and 2, 0 hr). There were no differences in iron concentration among sampling size fractions at 0 hr. After 6 hr of oxygenation, there was a small decrease (3 to 6 percent) in total iron concentration; however, essentially all of the iron in solution was still in the Fe^{2+} form. No differences in iron concentration among the sampling size fractions were observed after 6 hr of aeration.

There was a 23 percent (Figure 2, ferrozine) to 30 percent (Figure 1, a,a',-dipyridyl) reduction in total solution iron after 26 hr of aeration. The higher value of a,a',-dipyridyl was the result of the lower total unfiltered iron. Some ferric (Fe^{3+}) iron was detected at 26 hr, but it was less than 7 percent when measured with the a,a',-dipyridyl (Figure 1) and less than 5 percent when measured with the ferrozine (Figure 2). No differences were noted in iron concentration among the sampling size fractions.

After 50 hr of aeration, 34 percent (Figure 2, ferrozine) to 43 percent (Figure 1, a,a',-dipyridyl) of the initial iron had been removed from solution. For the ferrozine-treated samples, ferrous iron still dominated the total iron content, with ferric
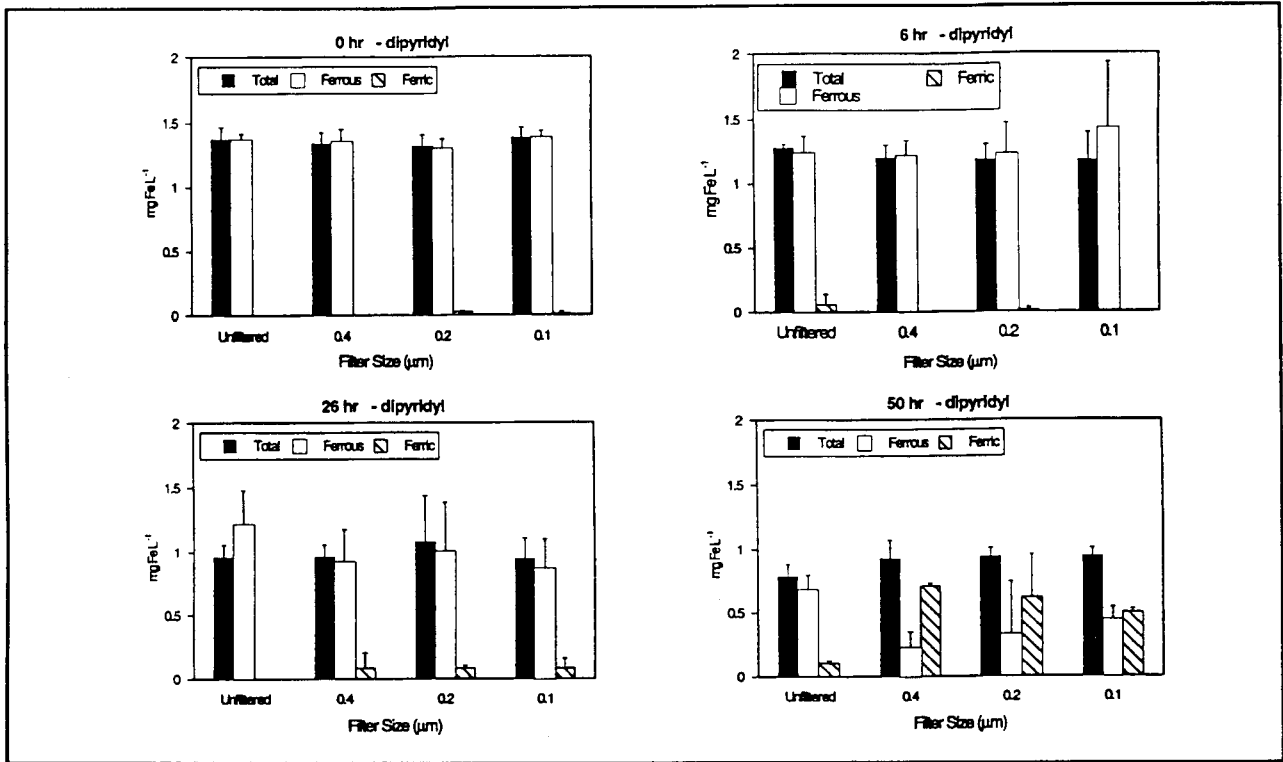
Figure 1. Iron speciation with a,a'-dipyridyl in anoxic simulated tailwater
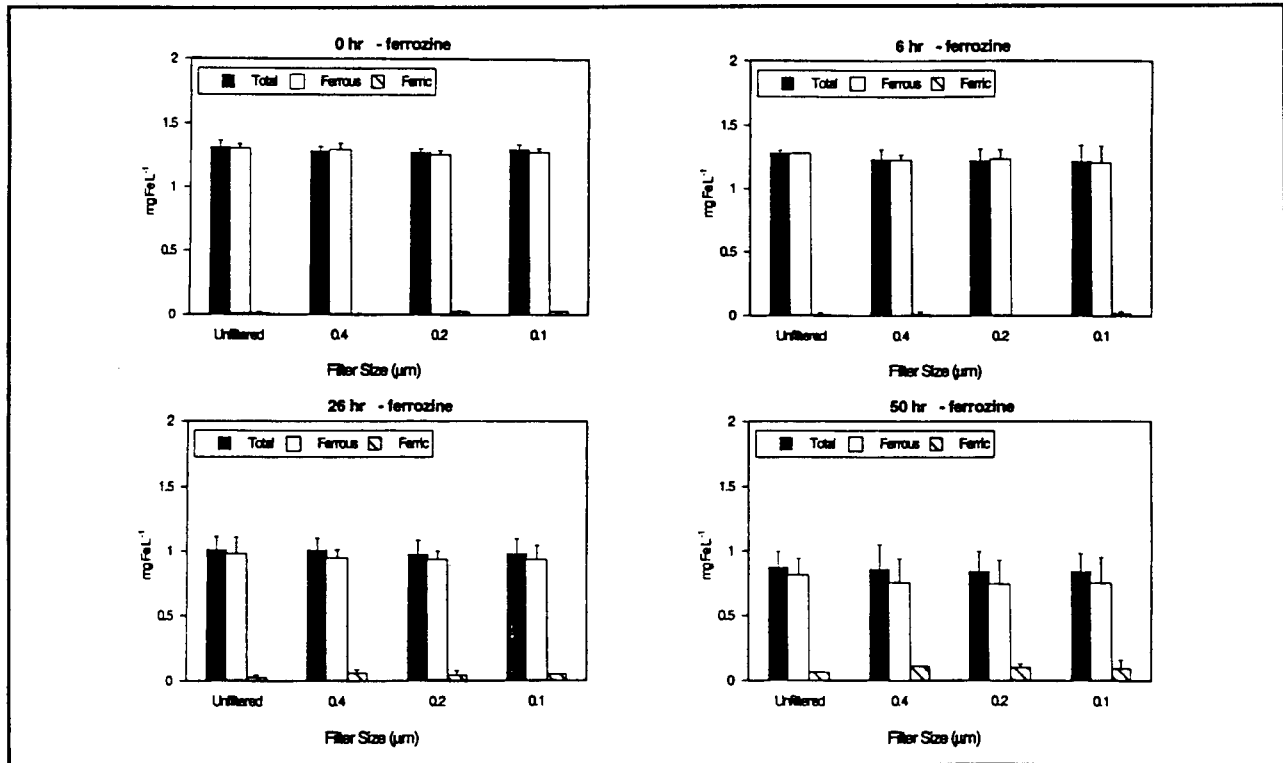following exposure to oxygen

Figure 2. Iron speciation with ferrozine in anoxic simulated tailwater
following exposure to oxygen

iron accounting for just 5 to 8 percent of the total. With the exception of the slightly higher ferric iron concentrations in the filtered samples, no differences in iron concentration among the sampling size fractions were noted (Figure 2).

Results for the a,a',-dipyridyl-treated samples after 50 hr aeration were markedly different than those for the ferrozine-treated samples. While total iron was similar, ferric iron contents increased from 7.5 percent in the unfiltered samples to as high as 51 percent in the 0.4-μm filtered sample. This result is an artifact of sample handling. Because of the large number of samples and a technical problem with the spectrophotometer, the filtered samples from this treatment were not analyzed until the following day. It was thought that acidifying the filtered samples and storing them overnight would not significantly alter the Fe^{2+}/Fe^{3+} status of the samples. This was obviously incorrect; ferrous (Fe^{2+}) analysis should always be conducted as soon as possible after sample collection.

Although both a,a',-dipyridyl and ferrozine are reliable colorimetric indicators of ferrous iron, the results of this experiment suggest that ferrozine is more appropriate at concentrations typically present in reservoir tailwaters. This is particularly true when the results are read as percent transmission on the portable Milton Roy Mini 20 spectrophotometer. Given the problems associated with storing samples for later analysis of ferrous iron, rapid onsite determination with a portable spectrophotometer is the recommended procedure.

Singer and Stumm (1970) showed that the oxidation rate of ferrous iron in water at pH > 4.5 is defined by the equation

$$-d\,[\,Fe^{2+}\,]\,/\,dt = k\,[\,Fe^{2+}\,[\,P_{O2}\,[\,OH^-\,]\,]^2$$

where $k = 8.0 \pm 2.5 * 10^{13}\,L^2\,mol^{-2}\,atm^{-1}\,min^{-1}$ at 20.5 °C. The second-order dependence on [OH⁻] causes the oxidation rate to increase 100 times for every unit increase in pH. At a constant pH and P_{O2}, a pseudo first-order rate constant can be defined to estimate the minimum abiotic oxidation rate: $k^* = kP_{O2}[OH^-]^2$.

Comparing the actual ferrous concentrations with the predicted concentrations derived from both the average (8.0) and lower limit (5.5) theoretical k values, it is apparent that the observed rates are much slower than the theoretical values (Figure 3). This result is similar to that reported by Dortch, Tillman, and Bunch (1992) for actual reservoir releases. While Dortch, Tillman, and Bunch (1992) and Nix and others (1991) speculated that colloidal-sized ferric iron may have passed through the 0.45-μm filter causing erroneously high ferrous values, the use of ferrous-specific colorimetric indicators precludes that possibility in the simulated tailwater. In addition, no size partitioning was observed down to the 0.1-μm filter sizes. Knocke, Shorney, and Bellamy (1994) also found no differences in ferrous concentrations between unfiltered and 0.2 μm-filtered in laboratory samples prepared with dissolved organic carbon (DOC).

A more likely explanation is the combined effects of pH and complexing anions. The predicted values in Figure 3 were calculated using the measured pH at the time of sampling. Actual pH during the initial 6-hr period was probably lower than that
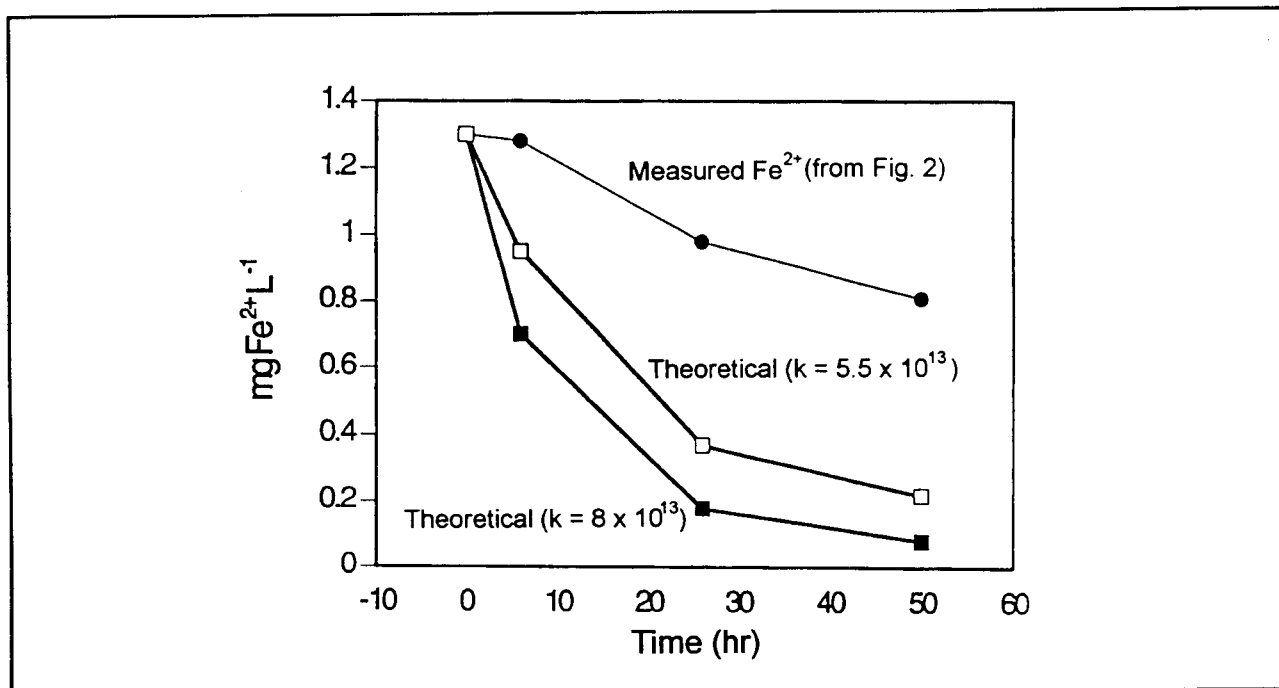
Figure 3. Comparison of observed and predicted Fe^{2+} concentrations in anoxic simulated tailwater following exposure to oxygen

measured at 6 hr due to the oxidation of ferrous iron. The presence of Cl^- and SO_4^{2-} in the simulated water is also not considered in the theoretical treatment. Sung and Morgan (1981) reported reduced rate constants in the presence of complexing anions. Since both Cl^- and SO_4^{2-} are present in the actual tailwater (Nix and others 1991), these anions may be causing some of the discrepancies between the ferrous oxidation model and the actual downstream concentrations (Dortch, Tillman, and Bunch 1992). Another possible explanation is the complexation of iron with DOC in the tailwaters. Theis and Singer (1974) outlined the likely mechanism of this interaction between DOC and iron (Figure 4). The DOC can cause high steady-state ferrous concentrations in two ways. One, it reduces the ferrous oxidation rate (Theis and Singer 1974; Knocke, Shorney, and Bellamy 1994) when complexed with ferrous iron. Another mechanism is the photochemical reduction of ferric-organic complexes which generates ferrous iron and oxidized organic matter. Photochemical reduction may also occur in low-DOC waters with inorganic ferric species (Figure 4) (Madsen, Morgan, and Good 1986; McKnight, Kimball, and Bencala 1988).

Manganese in the simulated reservoir water was primarily in the reduced manganous (Mn^{2+}) form (Figure 5). Although some oxidized manganese (Mn^{4+}) was measured at 0 hr, this amount was less than 5 percent of the total. The higher levels (14 to 33 percent) of oxidized manganese at 6 hr appear to be a sampling artifact since the composition at 26 and 50 hr was less than 7 percent oxidized manganese (Figure 5).

The absence of any notable manganese oxidation confirms the theoretical expectations based on pH and chemistry of the simulated tailwaters since, below pH 8, manganese oxidation is primarily biologically mediated (Morgan and Stumm 1965; Benefield and Judkins 1982; Chapnick, Moore, and Nealson 1982). Adsorption and precipitation
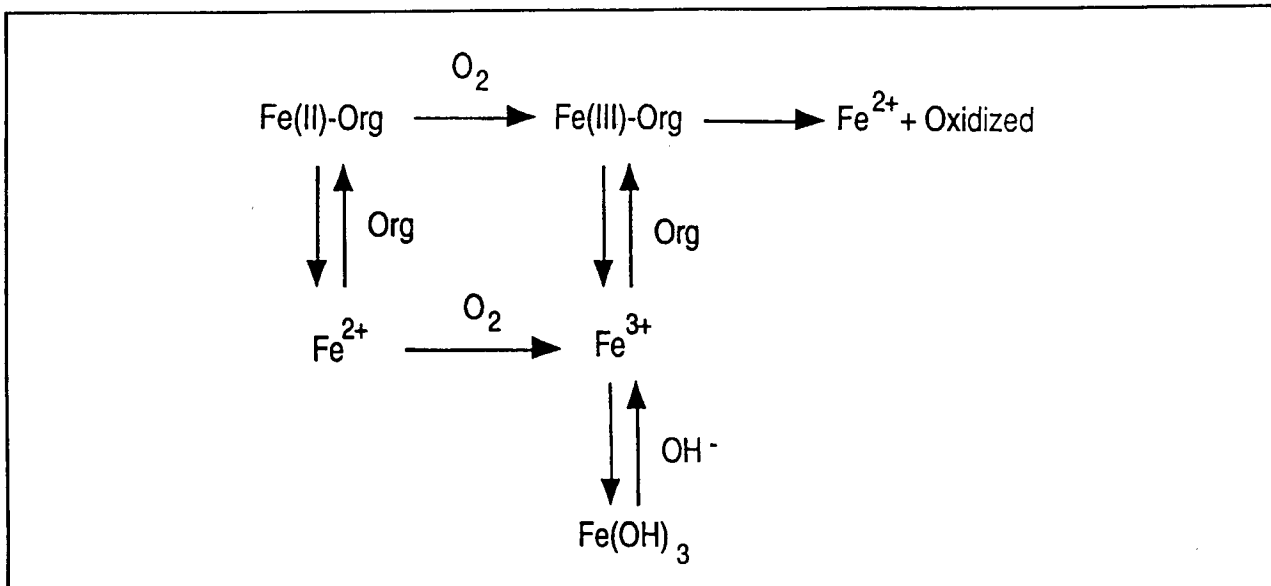
Figure 4. Complexation and redox reactions of dissolved organic matter and iron (after Theis and Singer 1974)
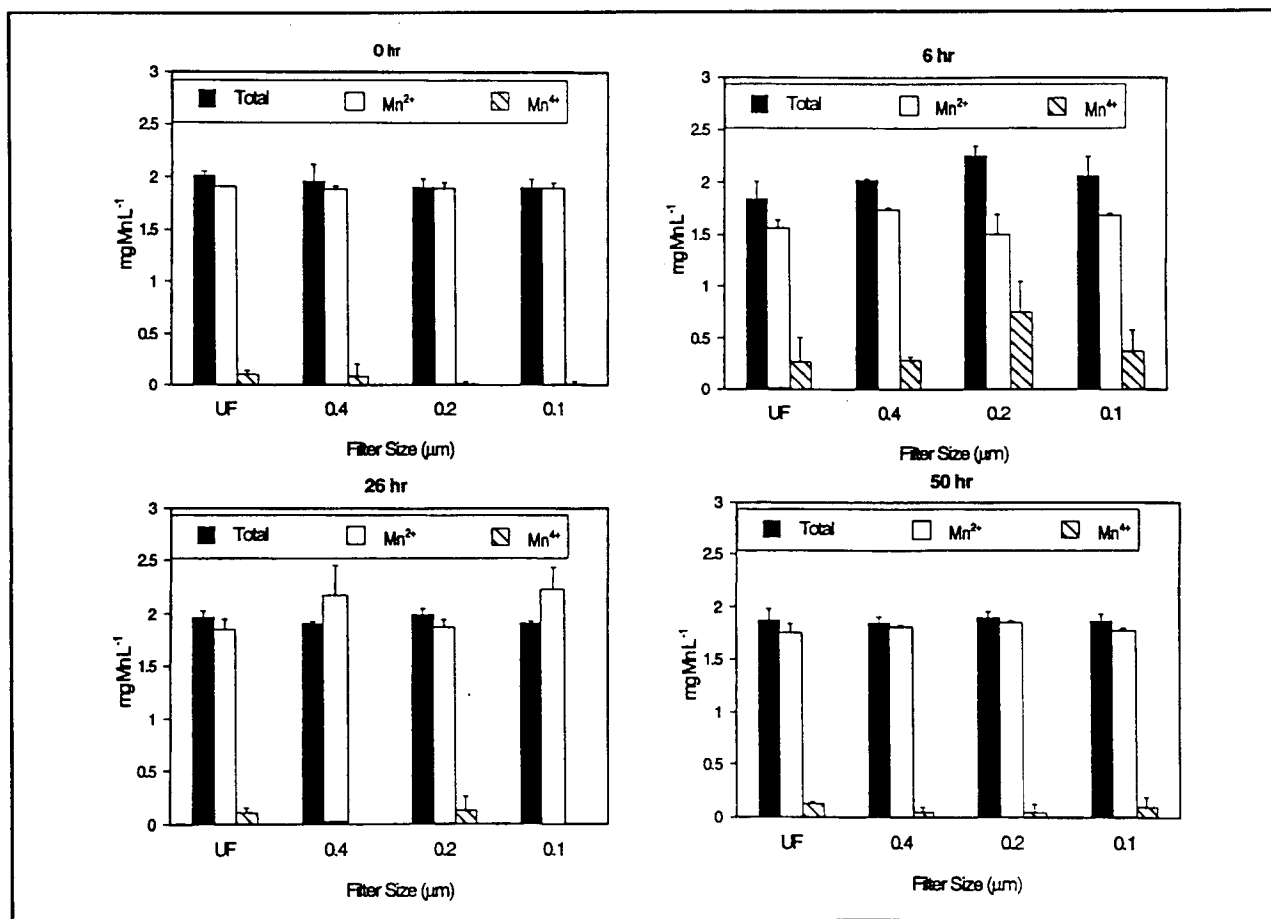

Figure 5. Manganese speciation in anoxic simulated tailwater following exposure to oxygen

reactions on alkaline sediment substrates or iron oxyhydroxides may also be important manganese removal mechanisms in actual tailwaters (Stumm and Giovanoli 1976, Wilson 1980, Sung and Morgan 1981) (see also Faulkner 1994[1]).

Summary and Conclusions

Use of simulated reservoir tailwater allowed this research to assess the effects of oxidation processes on the determination of iron and manganese species. Comparisons were conducted for analytical methods employing physical separation via filtration and colorimetric analyses for iron. The relevance of study results to interpretation of model studies was also considered.

Filtration of simulated reservoir tailwaters did not reveal any particle size differentiation or the presence of colloidal ferric iron in the 0.45 μm-filtered sample, suggesting that other methods for speciation of iron may be more applicable in assessing tailwater conditions. Ferrozine appears to be a better colorimetric indicator of ferrous iron at the study concentrations. In situ sampling with immediate analysis using complexation by ferrozine is recommended for determination of ferrous iron. Once total iron has been determined, ferric iron concentrations can be calculated by difference. The use of ferrous/ferric concentrations determined with this technique may improve model output. Manganese remained stable in the reduced form (Mn^{2+}), as predicted from the water chemistry of the system, and filtration for speciation appears to be of limited use.

As suggested by Dortch, Tillman, and Bunch (1992), interpretation of the applications of TWQM may be enhanced by these results and additional studies. Colloidal-size ferric complexes in actual tailwaters and reduction of ferric iron by organics and photochemical mechanisms are still possible mechanisms for discrepancies in laboratory and field data. Although manganese dynamics have been adequately described by the TWQM using mechanisms other than oxidation kinetics, biological removal and sorption/precipitation reactions should be investigated further.

Additional laboratory and field studies to evaluate complexation and photochemical mechanisms that may impact speciation are in progress. Results of this research will improve field investigations of iron and manganese dynamics in reservoir tailwaters and allow for better interpretation of model applications. Applications of these techniques for evaluation of water quality processes in reservoir tailwaters have been conducted at Nimrod Lake, Arkansas. Additional field studies are scheduled for July and August 1996.

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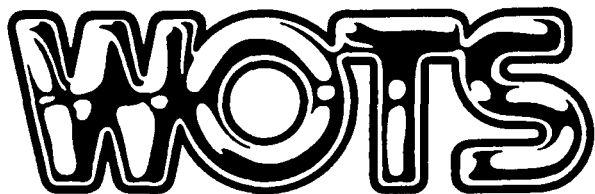
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