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Assessing Iron Dynamics in the Release from a Stratified Reservoir

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ABSTRACT

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Field and laboratory studies were conducted to describe the fate of total, dissolved, and ferrous (Fe^{2+}) iron in the release from a stratified reservoir with an anoxic hypolimnion. Concentrations of total iron in the tailwater indicated a first order removal process during a low flow release ($0.6 \text{ m}^3 \cdot \text{sec}^{-1}$), yet negligible loss was observed during a period of increased discharge ($2.8 \text{ m}^3 \cdot \text{sec}^{-1}$). Dissolved and ferrous iron concentrations in the tailwater were highly variable during both release regimes and did not follow responses based on theoretical predictions. Ferrous iron concentrations in unfiltered samples were consistently greater than concentrations observed in samples filtered separately through 0.4, 0.2, and 0.1 μm filters. Total iron removal in laboratory studies followed first order kinetics, but was twice that rate ($0.077 \text{ mg} \cdot \text{L}^{-1} \cdot \text{hr}^{-1}$) observed during low flow discharge in the tailwater ($0.036 \text{ mg} \cdot \text{L}^{-1} \cdot \text{hr}^{-1}$). Dissolved and ferrous iron losses in laboratory studies were rapid (~75% in the first 15 minutes and 95% within 1 hour), followed theoretical predictions, and were much faster than observations in the tailwater (~30% within the first hour). The presence of particulate forms of ferrous iron in the field and differences in removal rates observed in field and laboratory studies indicate a need for improved field assessment techniques and consideration of complexation reactions when assessing the dynamics of iron in reservoir releases and downstream impacts as a result of operation regimes.

Key Words: iron, ferrous, ferric, tailwaters, reservoirs, water quality.

The construction of a dam and reservoir results in changes to the river such as alterations in the magnitude, duration, and timing of discharge, physicochemical changes associated with water quality processes, and changes in the biotic community. Changes in water quality in the reservoir are often reflected in the releases and downstream reach, or tailwater region. Water quality impacts include varied temperature and dissolved oxygen concentrations, altered nutrient concentrations, and increased concentrations of redox-

sensitive metals such as iron and manganese. The formation of iron flocs, resulting from the oxidation of ferrous to ferric iron during aeration of anoxic release waters, is of particular interest since these flocs can impact physical, chemical, and biological processes. For example, these flocs can increase turbidity, clog the gills of aquatic organisms, and impact aquatic insect species diversity via precipitation on the body surface (Gerhardt and Westermann 1995 and Rasmussen and Lindegaard 1988).

Efforts to describe and quantify physicochemical changes in the tailwater region of reservoirs have been based on water quality processes described for aerobic processes in lakes and reservoirs using reaeration of anoxic hypolimnetic water (Chen et al. 1983), changes

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in chemical constituents (Gordon et al. 1984, Nix 1986, Nix et al. 1991), and impacts of reservoir operations (Mathur et al. 1988, Webb and Walling 1993, Barillier et al. 1993, and Ashby et al. 1995). Prediction of physicochemical changes during steady-state releases has been conducted for many variables with the Tailwater Quality Model (TWQM) developed by Dortch et al. (1992). However, chemical processes associated with iron oxidation have yet to be adequately described from field measurements for accurate prediction with the TWQM (Dortch et al. 1992). Dortch et al. (1992) suggested that prediction of oxidation of reduced iron in tailwaters was limited by inadequate speciation of iron via conventional field methods (e.g., filtration). Size fractionation, or use of chemical speciation based on pore size of a membrane filter, may not be adequate to describe and measure chemical species (Stumm and Morgan 1981, Laxen and Chandler 1982, Danielsson 1982). Membrane filtration data may also generate incomparable results between sites (Horowitz et al. 1992).

Stumm and Morgan (1981) suggest that no single method presently available provides specific identification of a metal species, and provide a general list of methods that may be used in combination to better describe the speciation of selected metals. Florence (1982) provides a review of speciation of trace elements in water, listing possible physicochemical forms of metals in natural waters and a discussion of a variety of analytical techniques. Recent advances in analytical techniques (e.g., colorimetric, polarographic, voltammetric, and atomic adsorption) have improved measurements of specific forms or oxidation states of selected elements. However, field application of most of these methods requires a level of expertise beyond the resources of many. While voltammetric microelectrodes have been successfully used in field applications (e.g., Brendel and Luther 1995), colorimetric methods are typically more easily implemented but are less precise.

A variety of complexing agents have been used for determining ferrous iron concentrations and a thorough review of analytical methods for measuring oxidation states of iron in natural waters is provided in Pehkonen (1995). However, colorimetric methods for measuring reduced iron may be subject to interferences such as fulvic acid in oxic waters (Suzuki et al. 1992). Interactions of biological, photochemical, homogeneous, and heterogeneous processes in iron oxidation kinetics described by Barry et al. (1994) demonstrate the complexity in assessing the chemistry and transport of elements in aquatic systems.

Equilibrium models often are used to determine the most likely complexes for a prescribed geochemical condition (e.g., concentrations, pH, Eh, temperature). Since analytical methods exist for determining the

oxidation state of selected elements, models that describe kinetics based on changes in oxidation states would benefit from application of these analytical methods.

The objectives of this study were to describe iron dynamics in reservoir releases as a function of operations, evaluate the adequacy of conventional field techniques used in assessing the fate of reduced iron, and describe factors that contributed to poor prediction of iron oxidation in reservoir releases.

Field Site Description

Field studies were conducted at Nimrod Lake, Arkansas to describe the fate of total, dissolved, and ferrous iron in the tailwater during two different discharges. Nimrod Lake was selected based on the availability of information about channel morphology, substrate type, travel time of steady-state releases, and dynamic iron processes in the release. Nimrod Lake is a reservoir on the Fourche La Pave River in west central Arkansas (Fig. 1), 101 km upstream from its confluence with the Arkansas River. The area of the rugged and wooded drainage basin is about 1760 km². Nimrod Lake is formed by Nimrod Dam, which is operated primarily for flood control and typically has a minimal release (approximately 0.6 m³ · sec⁻¹) during stratification to provide for low flow in the Fourche La Pave River.

Water quality has been described by Nix et al. (1991) and the lake can be characterized as a monomictic lake that exhibits seasonal thermal stratification from March/April until September/October, depending upon meteorological conditions. The hypolimnion of the lake typically develops anoxic conditions with subsequent increases in concentrations of nutrients, metals (e.g., manganese and iron), and hydrogen sulfide in the deeper (bottom) waters. Values for pH typically range from 6.5 to 9.0 standard units. In the tailwater, specific conductivity ranges from 55 to 120 $\mu\text{mhos} \cdot \text{cm}^{-2}$, alkalinity is relatively low (15-26 mg · L⁻¹ as CaCO₃), and sulfate concentrations are near 1-2 mg · L⁻¹. Total organic carbon concentrations range between 5 and 12 mg · L⁻¹ and are present primarily as dissolved organic carbon. Turbidity values range from near 10 nephelometric turbidity units (NTUs) during periods of minimum release to near 40 NTUs during periods of increased discharge. Manganese concentrations range from 3-4 mg · L⁻¹ in the releases during late stratification and are primarily dissolved and in the reduced form (Mn²⁺). Iron concentrations in the releases range from 4-6 mg · L⁻¹ with approximately 75% as particulate forms.

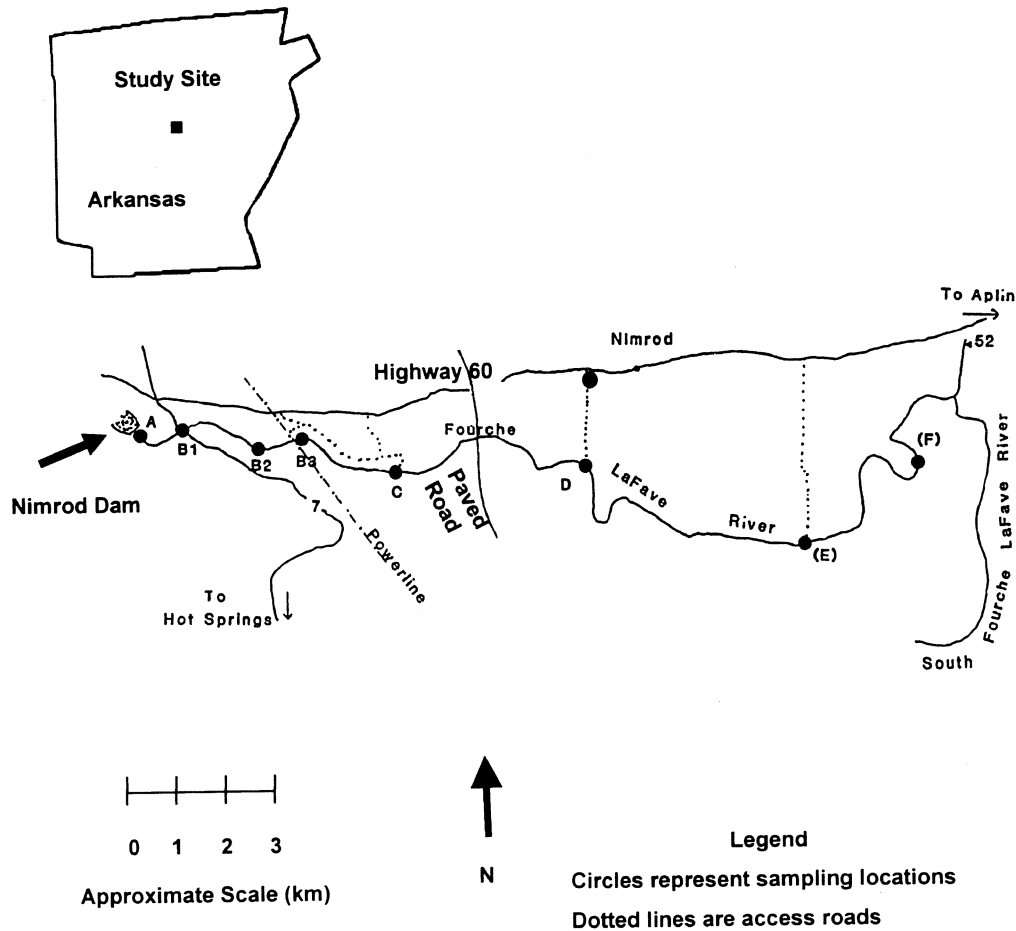


Figure 1.-Location of Nimrod Dam and Lake and tailwater sampling stations.

The depth of Nimrod Lake during summer is maintained near 14 m with some deviations for flood control or drought. The low-flow release is from the hypolimnion via Howell-Bunger valves. The centerline of the 3.6 m diameter penstock openings is approximately 7.6 m above the streambed elevation resulting in a withdrawal zone between the depths of 4 and 11 meters at normal summer pool elevations. The valves provide a discharge above the elevation of the tailwater, which falls approximately 7 m into a stilling basin. This type of discharge provides considerable aeration of the hypolimnetic release, which increases dissolved oxygen concentrations and affects iron dynamics.

Methods

Effects of Reservoir Operations

Iron dynamics in the tailwater as a function of reservoir operations were evaluated for two flow

regimes. Sampling design for the field studies was similar to previous studies conducted by Nix et al. (1991) for comparative purposes. Sampling was conducted at Stations A, B1, and B3 to describe conditions in the immediate tailwater and at Station D, to describe conditions further downstream (Fig. 1). These stations were selected since previous studies (Nix et al. 1991) indicated that iron processing was most pronounced between Stations A and B3 (visible formation of an orange floc) and downstream concentrations varied with flow.

Initial conditions of low flow (near $0.6 \text{ m}^3 \cdot \text{sec}^{-1}$ or $20 \text{ ft}^3 \cdot \text{sec}^{-1}$) represented typical late summer releases and were sampled prior to an increase in release to near $2.8 \text{ m}^3 \cdot \text{sec}^{-1}$ or $100 \text{ ft}^3 \cdot \text{sec}^{-1}$ (referred to as high-flow). The increase in flow was initiated at 1500 on August 22, 1995 and held constant until 1700 on August 23, 1995 to re-establish steady-state conditions for high-flow sampling. The increased discharge was about half the discharge of previous studies (near $5.6 \text{ m}^3 \cdot \text{sec}^{-1}$ or $200 \text{ ft}^3 \cdot \text{sec}^{-1}$) to provide an additional data set for evaluation under different flow conditions.

Sampling was conducted at each station based on

estimated travel time to describe water quality conditions of a parcel of release water over time during steady-state conditions. Time of travel was determined based on estimates from the TWQM, previous measurements using fluorescent dyes (Nix et al. 1991), and physical observations of neutrally buoyant floats (Table 1). Temperature, dissolved oxygen, pH, and specific conductivity were monitored with Hydrolab® data sondes at each site to describe steady-state conditions. An in-lake profile of temperature, dissolved oxygen, pH, specific conductivity, and oxidation-reduction potential was conducted in the forebay (near-dam) region of the lake during the study to describe vertical gradients and verify the presence of anoxic conditions. One water sample was collected with a Van Dorn sampler from near the lake bottom for analysis of oxidized and reduced iron in the hypolimnion. This sample verified that measurable concentrations would occur in the release but did not describe initial release concentrations, which could vary with discharge and the withdrawal zone. Samples from Station A were used to describe initial conditions in the tailwater region.

Evaluation of Field Techniques

Evaluation of filtration, selected colorimetric methods, and on-site reduction as a field technique to distinguish iron species (total, soluble, and Fe²⁺ iron) was conducted on samples filtered through filters with selected pore sizes. Three one-liter samples were collected at each tailwater location. One aliquot was analyzed without filtration while the remaining sample was vacuum-filtered through a 0.45 µm filter. This filtered sample was then filtered separately (not sequentially) through 0.4, 0.2, and 0.1 µm filters with in-line syringe holders to evaluate the effects of selected filter pore sizes. Colorimetric methods which utilize ferrozine (monosodium 3-(2-pyridyl)-5,6-bis(4-phenylsulphonic acid)-1,2,4-triazine, monohydrate, (FerroZine®), see Stookey (1970) and Gibbs (1976)) and a,a',-dipyridyl (see Müller 1932) to analyze for ferrous iron (Fe²⁺) iron

concentrations were evaluated in separate laboratory studies (Faulkner et al. 1996). Faulkner et al. (1999) also found that ferrous iron determination using 1, 10 Phenanthroline for color development was comparable to using ferrozine but reported a greater recovery of ferrous iron in hypoxic and oxic conditions. The ferrozine method was selected for use in this study since recovery was greater under conditions expected in reservoir releases and color development appeared to be more stable with time, which would improve field analytical techniques.

During both the low- and high-flow releases, ferrous iron was determined in both filtered and unfiltered samples using the ferrozine method, which employs the use of ferrozine in 50 mM Hepes free acid to make a color-developing reagent. Five milliliters of each sample were added to 1.0 ml of ferrozine reagent. This was diluted to 10 ml total volume with distilled, deionized water and read at 565 nm on a Milton Roy Mini 20 spectrometer. Total iron in each sample was determined on site using the same procedure with the addition of 1.0 ml 10% NH₂OH · HCl prior to adding the ferrozine to allow for reduction to ferrous iron on-site. Ferric iron was calculated by difference using mean values.

Two replicate samples were collected in 20-ml scintillation vials at each station, and from the reservoir near-bottom sample, for in situ filtration and subsequent laboratory analyses typically conducted with field studies that do not utilize on site analytical techniques (e.g., colorimetric methods). Total and total soluble (filtered with 0.45 µm filters in the field) samples were preserved with 3 drops of nitric acid to reduce the pH to at least 2. The samples were transferred to the Wetland Biogeochemistry Institute (WBI) at Louisiana State University for analysis using a Jarrell-Ash Atom Comp Series 800 Inductively Coupled Plasma (ICP) instrument.

Evaluation of Oxidation Rates

Two related studies were conducted to evaluate

Table 1.—Distance and travel times (for the 2 flow regimes) for the study reach.

Station	Distance from Dam (km)	Cumulative Travel Time (hrs) at 0.6 m ³ · sec ⁻¹	Cumulative Travel Time (hrs) at 2.8 m ³ · sec ⁻¹
A	0.2	3	1.4
B1	1.1	16.7	5.1
B3	3.2	41.9	13.4
D	7.5	138.4	35.4

factors other than analytical techniques that could contribute to poor prediction of iron oxidation, photochemical reduction of ferric iron and poor estimates associated with travel time determined in field studies. The potential for photochemical reduction of ferric iron was evaluated with light and dark bottle incubations using six 1-liter samples (3 in clear bottles and 3 in foil-wrapped bottles) collected at Station A. Incubation was from 1000 hours to 1800 hours in open sunlight and at ambient temperatures. Several samples were collected at intervals during the period of incubation and analyzed for ferrous iron. Following the 8-hour incubation period, the samples were acidified to pH 3 (from an initial pH between 6.8 and 7.2) with concentrated nitric acid (to convert ferric to ferrous iron) and measured for ferrous iron.

To obtain more precise oxidation rates, laboratory studies were conducted in recirculating raceways with streambed substrate (cobble, sand, and sediment) from the tailwater of the field site. Substrate was added to all three sections of one raceway and allowed to acclimate for a four-month period. The raceways were filled with approximately 3000 liters of deionized water that was amended with approximately 50 liters of water from the tailwater and leaf packs with material collected at the field site added as a source of organic carbon (near $3 \text{ mg} \cdot \text{L}^{-1}$) and nutrients. The pH was near 7 standard units.

The recirculating raceway system consisted of two fiberglass raceways, each with three compartments, that represent shallow, high velocity (< than 0.08 m deep), deep, low velocity (~1 m deep), and intermediate depth, low velocity (~0.5 m deep) stream reaches. The raceways were configured such that the flow originates in the shallow section, passes through the deepest section then through the intermediate depth section where it is pumped to the second raceway and travels the same route. Total length of the system is 16.5 m. The time of travel was measured with a dye tracer and was approximately 0.4-0.5 hours.

Oxidation of ferrous iron (added as ferrous ammonium sulfate, i.e., Fe^{2+}) in the raceways was evaluated by measuring total iron and Fe^{2+} concentrations. Replicate samples were collected for total, total soluble (<0.45 μm), and ferrous iron determinations (Ferrozine method, HACH Company, 1992 and colorimeter (Bausch and Lomb Spec 20)) at a time series sufficient to describe concentration changes for approximately 2 days or approximately 1.2 km of tailwater.

Results and Discussion

Conditions for the field study were determined by

in-lake water quality data, which may be inferred from sampling in the forebay or downstream region of the lake. Profiles of temperature indicate a stratified system with temperatures ranging from 31.3°C in the surface to 24.7°C in the bottom (Fig. 2A) resulting in an anoxic hypolimnion (Fig. 2B). Specific conductivity displayed maximum concentrations ($110 \mu\text{mhos} \cdot \text{cm}^{-1}$) near the bottom, and relative oxidation-reduction values (the instrument was not calibrated for oxidation-reduction potential) decreased in the hypolimnion coincident with anoxia (Figs. 2C and 2D, respectively). Values of pH ranged from 9.0 in the surface water to 8.0 in the bottom.

Iron dynamics in the release from Nimrod Dam and Lake (as a function of operations) were evaluated with two approaches. These approaches describe 1) oxidation states during the low-flow release at stations A, B1, and B3 on filtered and unfiltered samples and 2) total and total soluble fractions at both the low-flow and high-flow releases. Each of these approaches provides different information. Evaluation of changes in oxidation states, in conjunction with time-of-travel sampling, describes kinetics of iron in the release water as it travels downstream. Differentiation of total and total soluble fractions, in conjunction with time-of-

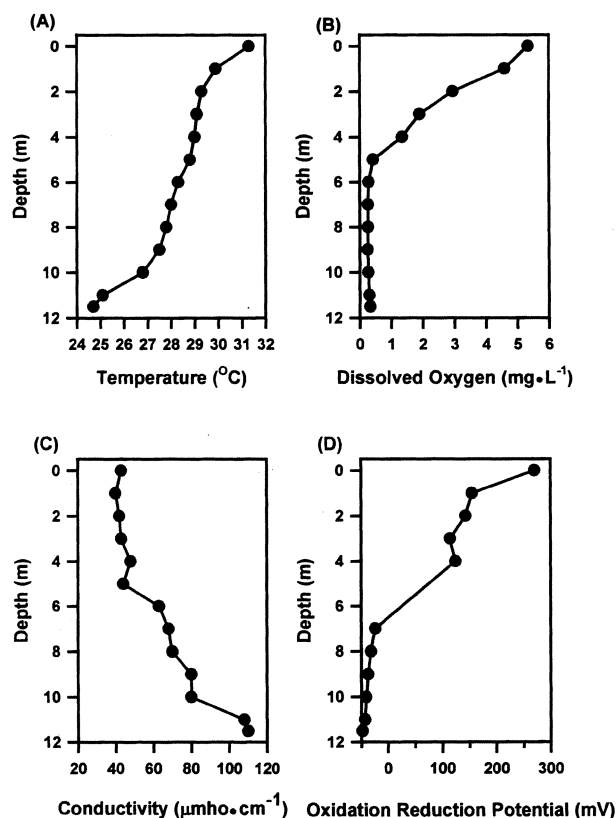


Figure 2.-Water quality in the forebay of Nimrod Lake during the field study.

travel, allows description of particulate formation and comparison with concentration changes observed for soluble or dissolved size fractions typically measured in field studies. Sampling during the low-flow also provides information on particulate formation with increased residence time in the channel.

For the two flow regimes, steady-state conditions in the tailwater were described with continuous monitoring of temperature, dissolved oxygen, pH, and specific conductivity. Conditions at station A remained relatively constant with dissolved oxygen values near $7 \text{ mg} \cdot \text{L}^{-1}$, pH values near 6.5, specific conductivity near $60 \mu\text{mhos} \cdot \text{cm}^{-1}$, and temperatures between 27 and 28°C . At station B1, dissolved oxygen and conductivity were similar to observations at station A, however, diurnal effects were observed for temperature with maximum values near 30°C occurring mid-afternoon and higher pH values near 7.0 occurring late afternoon.

Temperature at station B3 also reflected diurnal effects but pH, specific conductivity, and dissolved oxygen remained relatively constant (near 6.5 for pH, $60 \mu\text{mhos} \cdot \text{cm}^{-1}$ for specific conductivity, and $6.0 \text{ mg} \cdot \text{L}^{-1}$ for dissolved oxygen) after arrival of the high-flow release.

Iron in the reservoir bottom water was in the reduced ferrous (Fe^{2+}) form at a concentration near $17 \text{ mg} \cdot \text{L}^{-1}$ prior to release from the reservoir (Fig. 3). Concentrations were higher in the unfiltered sample but there was relatively good agreement in measurements of total and ferrous forms on samples filtered through different pore sizes. Slightly higher concentrations of ferrous iron were within 2 standard deviations, except for the sample filtered through the $0.1 \mu\text{m}$ filter, and considered acceptable for the purpose of determining sufficient concentrations of ferrous iron available for reservoir releases. Concentrations at

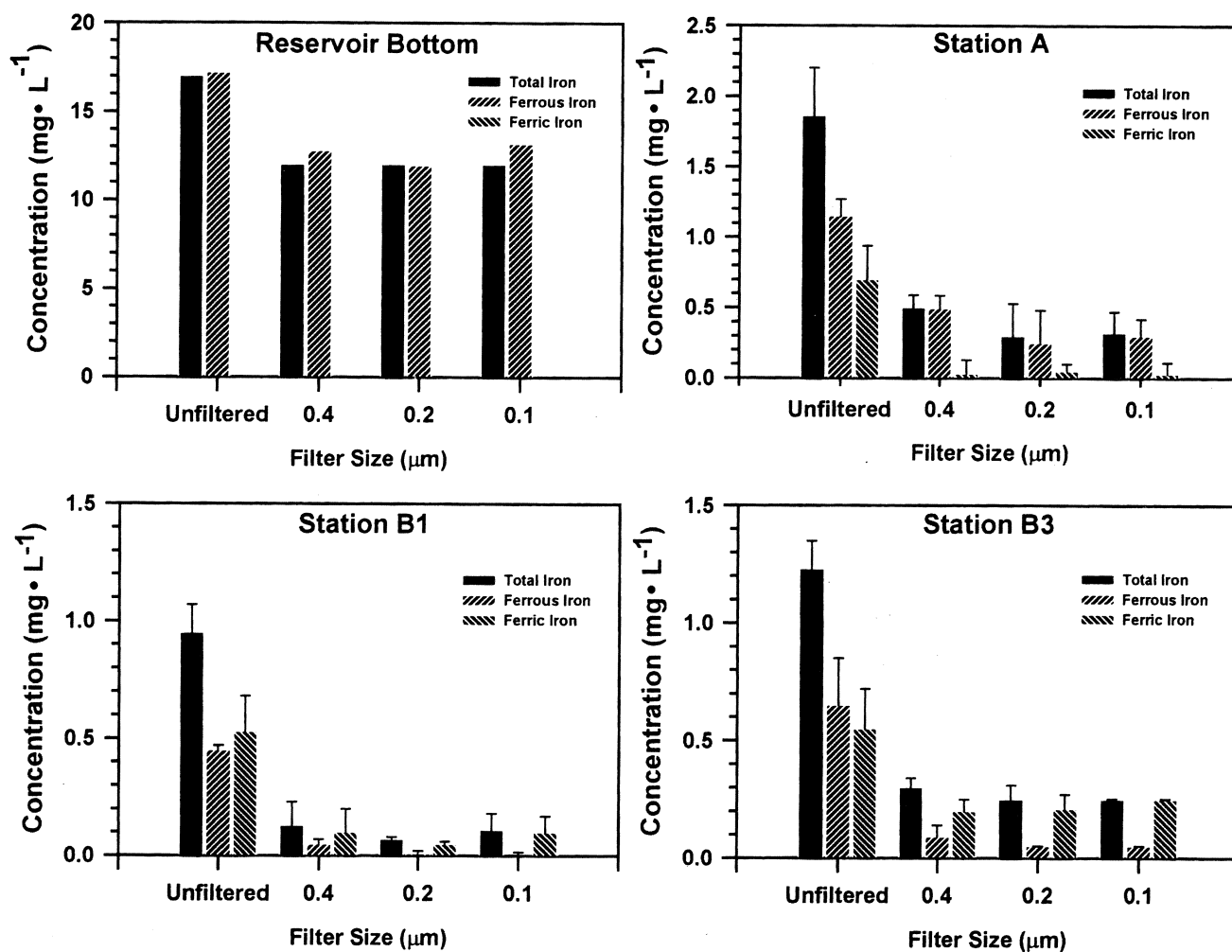


Figure 3.—Total, ferrous, and ferric iron concentrations in selected size fractions at selected sites downstream from Nimrod Dam (error bars = 1 standard deviation).

station A were considerably lower (near $1.8 \text{ mg} \cdot \text{L}^{-1}$) than those observed for the reservoir bottom water (Fig. 3) and ferric (Fe^{3+}) concentrations accounted for nearly 40% of the total in the unfiltered sample indicating rapid oxidation of the ferrous iron. Differences in concentrations between the reservoir bottom water sample and the sample from station A may be attributed to dilution of withdrawal water during release (as a function of vertical concentration gradients and density layers) and possible loss of iron in the reach from the dam to station A. Concentrations in the 0.1 and $0.2 \mu\text{m}$ filtered samples were similar but lower than concentrations in the $0.4 \mu\text{m}$ filtered samples suggesting some size fractionation. However, most of the iron in all filtered samples at Station A was in the ferrous form. Differences in total iron (and ferrous iron) in the unfiltered and filtered samples suggest that particulate ferrous iron was present and represented 50% or more of the total ferrous iron. Greater concentrations of ferrous iron in the unfiltered sample suggest that filtration as a means to differentiate oxidation states may significantly underestimate ferrous concentrations.

At station B1, total iron concentrations decreased to near $1 \text{ mg} \cdot \text{L}^{-1}$, indicating removal of nearly 50% of the total iron from the release water between stations A and B1 (Fig. 3). The channel between these two stations may be characterized as a pool with decreased velocities that could contribute to settling of particulate iron during low flow conditions. Concentrations in the unfiltered sample were nearly equally represented by ferrous and ferric forms and were considerably greater than concentrations in filtered samples suggesting particulate fractions were predominant. A similar pattern was observed at station B3 except that concentrations were slightly greater at station B3 and ferric iron in the filtered samples was greater than ferrous concentrations (Fig. 3). Differences in concentrations between stations B1 and B3 may be related to time-of-travel or resuspension associated with change in flow since station B3 is immediately downstream from a riffle zone that could contribute to resuspension of settled, particulate material. Perhaps the best information is obtained in evaluation of the percentage of ferrous iron relative to the total in the unfiltered sample at each station. At station A., ferrous iron represents about 62% of the total, and approximately 50% of the total at stations B1 and B3 suggesting limited oxidation occurs between these two stations.

Measurements of iron on unfiltered and filtered samples using ICP analyses provide additional information on iron dynamics at the two different release levels (Fig. 4). Total iron concentrations measured by ICP analyses were much higher at all stations, i.e., $2\text{--}6 \text{ mg} \cdot \text{L}^{-1}$ compared to less than 2 when measured with ferrozine after reduction. Concentrations of total

soluble iron (DFe), while in closer agreement with unfiltered samples analyzed with ferrozine, were still greater suggesting an iron fraction detectable with ICP analyses that is not detected with ferrozine and the reduction method used in this study. Steady-state conditions were assumed for each flow regime but the samples were collected a few hours apart for the two methods described above precluding additional rigorous comparisons.

Effects of flow were apparent with total iron concentrations decreasing downstream during low-flow, while total soluble concentrations fluctuated between 1 and $2 \text{ mg} \cdot \text{L}^{-1}$. Concentrations of both total and total soluble remained relatively constant during the high-flow release with the exception of a slight increase in total soluble iron at station B3. Concentration increases downstream were also observed by Nix et al. 1991 and have been observed for other systems as well, Ashby et al. (1999). The decrease of total iron during

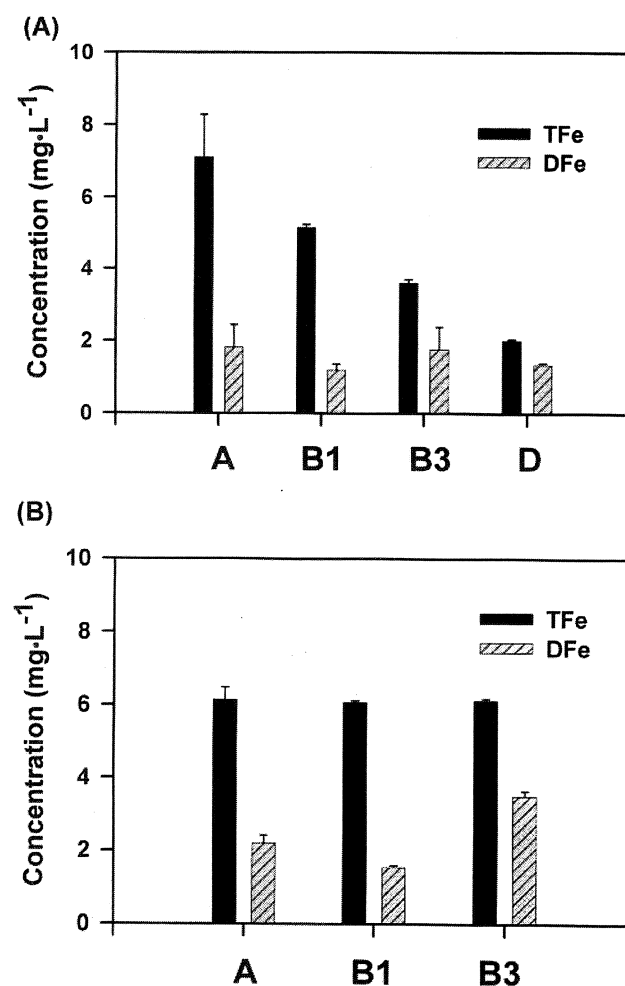


Figure 4.—Total and dissolved iron in the reservoir release from Nimrod Lake at low (A) and high (B) releases, August 1995 (error bars = 1 standard deviation).

low-flow followed a first order removal function. The removal or loss of iron may be the result of oxidation, particulate formation (including ferrous iron complexes, co-precipitation, or sorption to colloids), and subsequent precipitation (orange, flocculent turbidity observed visually). At higher flows, precipitation may be inhibited by increased velocities, and/or aggregation of very fine ($<0.45 \mu\text{m}$) particulates may be inhibited, and particulates are transported a greater distance downstream. Mechanisms contributing to fluctuations in total soluble concentrations are less readily apparent and may include sampling artifacts or size fractionation during oxidation and particulate formation.

Results of the evaluation of photochemical reduction of ferric iron indicated that photochemical reduction was not occurring at ambient pH (Fig. 5). After six hours of incubation and subsequent acidification, an increase in ferrous iron was observed. The increase was much greater for the samples exposed to sunlight than those kept in the dark and is consistent with observations of photochemical reduction of iron in oxic water at lower pH values (near 4) and in the presence of organic matter (Collienne 1983). These results indicate that although photochemical reduction is possible, it is not a significant process in the Nimrod Dam release waters.

Iron concentrations in the raceway study indicated a rapid change in oxidation states within the first 15 minutes since less than $2 \text{ mg} \cdot \text{L}^{-1}$ of the total (near $7 \text{ mg} \cdot \text{L}^{-1}$) was in the soluble form after 15 minutes (TFe and DFe, UFz, and Fz, Fig. 6). Removal or loss of total iron was described with a logarithmic equation (R-square = 0.96) while removal or loss of DFe is best described by a power function (R-square = 0.79). Sample replication for assessing analytical variability resulted in very low standard deviations (mostly $<0.02 \text{ mg} \cdot \text{L}^{-1}$).

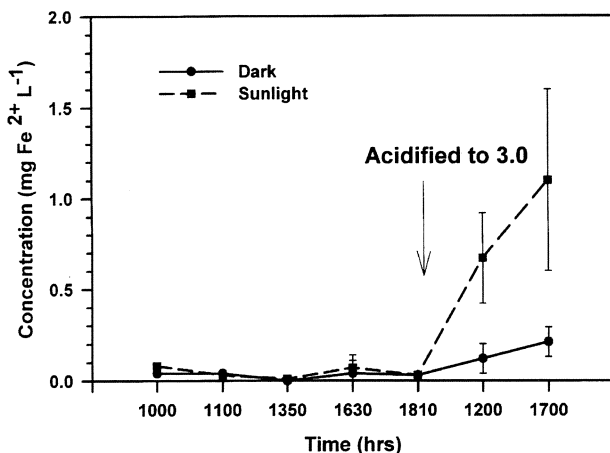


Figure 5.-Photochemical reduction assessment for the release water at Nimrod Lake, Arkansas (error bars = 1 standard deviation).

Although observations in the tailwater where the unfiltered samples (UFz) yielded higher concentrations of Fe^{2+} than filtered samples (Fz) when measured with the ferrozine method (see Fig. 3), the change in concentration with time observed in the raceways was described with similar equations and comparable to that for soluble iron (Fig. 6).

Ferrous iron concentrations in the tailwater were highly variable at the upstream sites and varied with distance or time during the low-flow sampling (Fig. 7, Fe^{2+} Tailwater). As observed by Nix et al. (1991), concentrations increased at some of the downstream sites. When compared to observations of total soluble iron (DFe) reported in Nix et al. (1991), removal rates of ferrous iron in the tailwater appear to be similar but did not resemble removal rates observed for total or ferrous iron in the laboratory raceway studies. Obviously, more complex interactions were occurring in the tailwater than in the raceway.

The challenge in using oxidation states to describe iron kinetics is compounded by analytical methods and contributing environmental factors. Singer and Stumm (1970) showed that the oxidation rate of ferrous iron in water at $\text{pH} > 4.5$ may be defined by the equation:

$$-d[\text{Fe}^{2+}]/dt = k[\text{Fe}^{2+}]P_{\text{O}_2}[\text{OH}^-]^2$$

where $k = 8.0 \pm 2.5 \cdot 10^{13} \text{ mol}^2 \text{ atm}^{-1} \text{ min}^{-1}$ at 20.0°C . At a constant pH and P_{O_2} , a pseudo first-order rate constant can be defined to estimate the minimum abiotic oxidation rate:

$$k^* = kP_{\text{O}_2}[\text{OH}^-]^2$$

Comparing the actual ferrous concentrations with the predicted concentrations derived from the average ($8.0 \cdot 10^{13}$, theoretical k value) and a pH of 7.0 and P_{O_2}

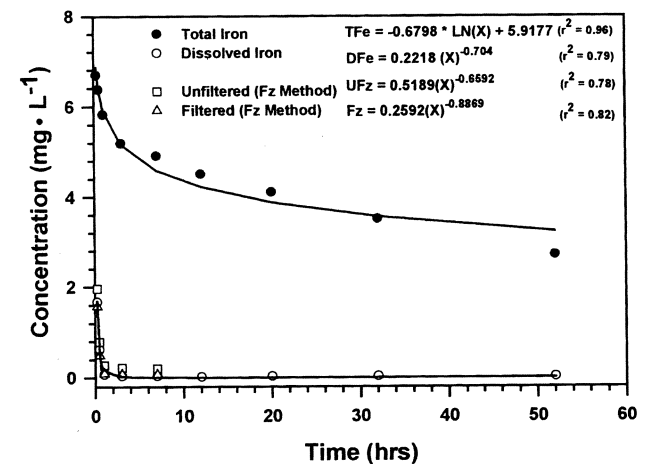


Figure 6.-Loss of total, dissolved, and ferrous iron in the raceways.

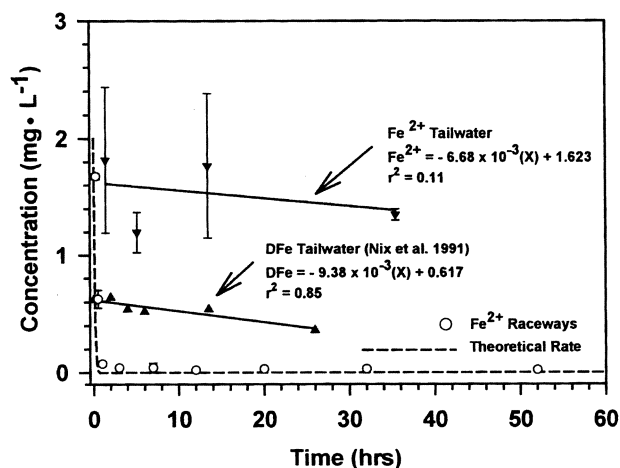


Figure 7.-Loss of dissolved and ferrous iron in the raceways and tailwater of Nimrod Dam (error bars = 1 standard deviation).

= 0.2, it is apparent that the observed rates are much slower for tailwaters yet are well described in the raceways by the theoretical rate (Fig. 7).

Several possible mechanisms exist that could contribute to discrepancies in field and laboratory studies. Dortch et al. (1992) and Nix et al. (1991) speculated that colloidal-sized ferric iron precipitates may have passed through the 0.45 μm filter causing erroneously high ferrous values. Conversely, greater concentrations of Fe^{2+} in unfiltered samples suggest that some complexation, co-precipitation, or sorption to colloids may occur, resulting in particles greater than 0.45 μm and an underestimation of oxidation rates. However, no size partitioning was observed down to the 0.1- μm filter sizes. Knocke et al. (1994) also found no differences in ferrous concentrations between unfiltered and 0.2- μm filtered in laboratory samples prepared with dissolved organic carbon (DOC). The use of ferrous-specific colorimetric indicators provides a more detailed assessment of oxidation states in conjunction with size fractions and offers a method of *in situ* estimation of oxidation rates.

Another potential explanation is the combined effects of pH and complexing anions. The second-order dependence on $[\text{OH}^-]$ causes the oxidation rate to increase 100 times for every unit increase in pH. Additionally, 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 et al. 1991), these anions may be causing some of the discrepancies between the ferrous oxidation model and the actual downstream concentrations. However, concentrations of these anions were relatively low and therefore, would likely not be a major contributing factor at this site.

A more likely explanation is the complexation of iron with DOC (Aiken and Leenheer 1993, Jones et al. 1993, Shaw et al. 2000) in the tailwaters. Theis and Singer (1974) outlined the likely mechanism of this interaction between DOC and iron. The DOC can cause high steady-state ferrous concentrations in two ways. One, it reduces the ferrous oxidation rate (Theis and Singer 1974, Knocke et al. 1994) when complexed with ferrous iron. Another mechanism is the photochemical reduction of ferric-organic complexes, which generates ferrous iron and oxidized organic matter. However, photochemical reduction may also occur in low-DOC waters with inorganic ferric species (Madsen et al. 1986, McKnight et al. 1988). Photochemical reduction was not detected with the incubation experiment in the field studies.

Conclusions

Iron dynamics in reservoir releases were described for two flow regimes using methods for determining different forms (e.g., dissolved and different oxidation states) with filtration and colorimetric methods applied in field and laboratory studies. Iron removal varied with flow (e.g., suspension of flocs and resuspension of settled material) in the study reach indicating that retention time and discharge rates are important in the iron removal process. Greater retention during the low flow release resulted in a greater removal rate, probably due to increased oxidation/complexation of ferrous iron and increased settling of particulate iron. Increased flow, which resulted in increased concentrations downstream, may also provide a transport mechanism for iron complexes, including those deposited during low-flow periods and available for resuspension. For example Ashby et al. (1995 and 1999) observed an increase in total iron concentrations associated with the leading edge of the hydrograph during hydropower generation at two reservoir tailwaters. Varied responses of total, particulate, and iron species suggest that opportunities for management of iron turbidity and flocs in reservoir tailwaters exist via reservoir release operations. For example, knowledge of floc formation processes and travel time of various discharges would allow scheduled releases of appropriate magnitudes to avoid floc formation or deposition in critical areas. Observations indicated that knowledge of the morphometry and hydrodynamics of the tailwater is required for accurate description and prediction of iron dynamics in reservoir release.

Effects of filtration, analytical methods, and

discharge were apparent and results demonstrated the difficulty in describing iron dynamics in the field. Ferrous iron concentrations in unfiltered samples were greater than concentrations in filtered samples (which were generally similar regardless of filter size) indicating that filtration as a method to differentiate ferrous and ferric iron is not appropriate. This finding is consistent with results of earlier studies (Stumm and Morgan 1981, Laxen and Chandler 1982, Danielsson 1982). Study results suggest that a more feasible (i.e., easily implemented) method for measurement of iron concentrations at different oxidation states can be accomplished with field determination of ferrous iron with a colorimetric reagent (e.g., ferrozine) on an unfiltered sample. Total iron should be measured via laboratory analysis using instrumentation such as an atomic absorption or emission spectrophotometer. Ferric iron can then be determined by difference. Samples collected for total iron analysis should be preserved with sulfuric or nitric acid to a pH near 2 when collected. Colorimetric analytical techniques are subject to interferences (e.g., interactions with organics) and additional research is needed to look at analytical recovery of ferrous iron under various conditions common to field sites.

While techniques used were sufficient for controlled, laboratory studies, and results were comparable to theoretical predictions, the same techniques used in the field produced results that were dissimilar to theoretical predictions. Possible influences of complexation processes on oxidation rates suggest that theoretical kinetics alone are not adequate to develop rigorous predictive models. Deviations from theoretical oxidation rates of iron, as observed in field studies, may be attributed to chemical flocculation and complexation processes perhaps associated with organic carbon, anions, and cations. Greater concentrations of ferrous iron in unfiltered samples in the field studies suggests that this material is transported in the reduced (ferrous) form and oxidizes at a slower rate than theoretical predictions. However oxidation rates observed in laboratory studies were comparable to theoretical rates. Lower concentrations of organic carbon in the laboratory studies could be a possible mechanism for differences observed in the field and laboratory. Clearly, additional research is needed to evaluate the effects of cations, anions, and organic compounds on iron oxidation and solubility.

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References

- Aiken, G. and J. Leenheer. 1993. Isolation and chemical characterization of dissolved and colloidal organic matter. *Chem. Ecol.* 8:135-151.
- Ashby, S. L., R. H. Kennedy and W. E. Jabour. 1995. Water quality dynamics in the discharge of a southeastern hydropower reservoir: Response to peaking generation operation. *Lake and Reserv. Manage.* 11(3):209-215.
- Ashby, S. L., J. L. Myers, E. Laney, D. Honnell and C. Owens. 1999. The effects of hydropower releases from Lake Texoma on downstream water quality. *J. Freshwat. Ecol.* 14(1):103-112.
- Barillier, A., J. Garnier and M. Coste. 1993. Experimental reservoir water quality release. Impact on the water quality on a river 60 km downstream (Upper Seine River, France). *Wat. Res.* 27(4):635-643.
- Barry, R. C., J. L. Schnoor, B. Sulzberger, L. Sigg and W. Stumm. 1994. Iron oxidation kinetics in an acidic alpine lake. *Wat. Res.* 28(2):323-333.
- Brendel, P. J. and G. W. Luther, III. 1995. Development of a gold amalgam voltammetric microelectrode for the determination of dissolved Fe, Mn, O₂, and S(-II) in porewaters of marine sediments. *Environ. Sci. Technol.* 29:751-761.
- Chen, R. L., D. Gunnison and J. M. Brannon. 1983. Characterization of Aerobic Chemical Processes in Reservoirs: Problem Description and Model Formulation. Techn. Rep. E-83-16. U.S. Army Eng. Wat. Exp. Sta., Vicksburg, MS.
- Collienne, R. H. 1983. Photoreduction of iron in the epilimnion of acidic lakes. *Limnol. Oceanogr.* 28(1):83-100.
- Danielsson, L. G. 1982. On the use of filters for distinguishing between dissolved and particulate fractions in natural waters. *Wat. Res.* 16:179-182.
- Dortch, M. S., D. H. Tillman and B. W. Bunch. 1992. Modeling water quality of reservoir tailwaters. Techn. Rep. W-92-1, U.S. Army Eng. Wat. Exp. Sta., Vicksburg, MS.
- Faulkner, S. P., R. P. Gambrell and S. L. Ashby. 1996. Analytical methods for iron and manganese determinations in reservoir tailwaters: Laboratory Investigations. *Wat. Qual. Techn. Note*, PD-01. U.S. Army Eng. Wat. Exp. Sta., Vicksburg, MS.
- Faulkner, S. P., P. E. Hintze and S. L. Ashby. 1999. Evaluation of colorimetric methods for measuring reduced (ferrous) iron. *Wat. Qual. Techn. Note*, PD-02, U.S. Army Eng. Wat. Exp. Sta., Vicksburg, MS.
- Florence, T. M. 1982. The speciation of trace elements in water. *Talanta.* 29:345-364.
- Gerhardt, A. and F. Westermann. 1995. Effects of precipitations of iron hydroxides on *Leptophlebia marginata* (L.) (Insecta: Ephemeroptera) in the field. *Arch. Hydrobiol.* 133(1):81-93.
- Gibbs, C. R. 1976. Characterization and application of ferrozine iron reagent as a ferrous indicator. *Anal. Chem.* 48(8):1197-1201.
- Gordon, J. A., W. P. Bonner and J. D. Milligan. 1984. Iron, manganese, and sulfide transformations downstream from Normandy Dam. *Lake and Reserv. Manage.* 58-62.
- HACH Company. 1992. *Water analysis handbook*, 2nd ed. Loveland, CO.
- Horowitz, A. J., K. A. Elrick and M. R. Colberg. 1992. The effect of membrane filtration artifacts on dissolved trace element concentrations. *Wat. Res.* 26(6):753-763.
- Jones, R. I., P. J. Shaw and H. De Haan. 1993. Effects of dissolved humic substances on the speciation of iron and phosphate at different pH and ionic strength. *Environ. Sci. Technol.* 27:1052-1059.
- Knocke, W. R., H. L. Shorney and J. D. Bellamy. 1994. Examining the reactions between soluble iron, DOC, and alternative oxidants during conventional treatment. *J. Amer. Wat. Works Assoc.* 117-127.
- Laxen, D. P. H. and I. M. Chandler. 1982. Comparison of filtration

- techniques for size distribution in freshwaters. *Anal. Chem.* 54:1350-1355.
- Mathur, D., E. S. McClellan and S. A. Haney. 1988. Effects of variable discharge schemes on dissolved oxygen at a hydroelectric station. *Wat. Resour. Bull.* 24(1):159-167.
- Madsen, E. L., M. D. Morgan and R. E. Good. 1986. Simultaneous photoreduction and microbial oxidation of iron in a stream in the New Jersey Pinelands. *Limnol. Oceanogr.* 31:832-838.
- McKnight, D. M., B. A. Kimball and K. E. Bencala. 1988. Iron photoreduction and oxidation in an acidic mountain stream. *Science*, 240:637-640.
- Müller, H. 1932. Die Verwendung von α - α' -Dipyridyl zur Bestimmung von Ferro- und Gesamteisen in natürlichen Wässern. *Mikrochemie*, 12:307-314.
- Nix, J. 1986. Spatial and temporal distribution of sulfide and reduced metals in the tailwater of Narrows Dam (Lake Greason), Arkansas. Tech. Rep. E-86-14, prepared by Ouachita Baptist University, Arkadelphia, AR, for the U.S. Army Eng. Wat. Exp. Sta., Vicksburg, MS.
- Nix, J., D. E. Hamlin-Tillman, S. L. Ashby and M. S. Dortch. 1991. Water quality of selected tailwaters. Tech. Rep. W-91-2, U.S. Army Eng. Wat. Exp. Sta., Vicksburg, MS.
- Pehkonen, S. O. 1995. Determination of the Oxidation States of Iron in Natural Waters - A Review. *Analyst*, 120:2655-2663.
- Rasmussen, K. and C. Lindegaard. 1988. Effects of iron compounds on macroinvertebrate communities in a Danish Lowland River System. *Wat. Res.* 22:1101-1108.
- Shaw, P. J., R. I. Jones and H. De Haan. 2000. The influence of humic substances on the molecular weight distributions of phosphate and iron in epilimnetic waters. *Freshwat. Biol.* 45:383-393.
- Singer, P. C. and W. Stumm. 1970. Acidic mine drainage: The rate-determining step. *Science*, 167:1121-1123.
- Stookey, L. L. 1970. Ferrozine - a new spectrophotometric reagent for iron. *Anal. Chem.* 42:779-781.
- Stumm, W. and J. J. Morgan. 1981. *Aquatic Chemistry*. John Wiley and Sons, New York, NY.
- Sung, W. and J. J. Morgan. 1981. Oxidative removal of Mn(II) from solution catalyzed by the FeOOH (lepidocrocite) surface. *Geochimica et Cosmochimica Acta*, 45:2377-2383.
- Suzuki, Y., K. Kuma, I. Kudo, K. Hasebe and K. Matsunaga. 1992. Existence of stable Fe(II) complex in oxic river water and its determination. *Wat. Res.* 26(11):1421-1424.
- Theis, T. L. and P. C. Singer. 1974. Complexation of iron (III) by organic matter and its effect on iron (II) oxygenation. *Environ. Sci. Technol.* 8:569-73.
- Webb, B. W. and D. E. Walling. 1993. Temporal variability in the impact of river regulation on the thermal regime and some biological implications. *Freshwat. Biol.* 28:167-182.