

In situ experiments on the dissolved and colloidal state of iron in an acid bog lake¹

Jeffery P. Koenings²

School of Natural Resources, University of Michigan, Ann Arbor 48104

Abstract

A sampler and an analytical and characterization scheme were developed to investigate the chemical and physical state of iron in a highly stained acid bog lake (North Gate Lake). Iron fractions were chemically separated by reactivity to bathophenanthroline (BPN) after specific digestion procedures. Physical separation by anaerobic in situ filtration (450 nm) and in situ dialysis (4.8 nm) resulted in three size classes: particulate, colloidal, and dissolved.

Inorganic, nonreactive species of iron [e.g. $\text{Fe}(\text{OH})_3$] represent minor amounts of the total iron in North Gate Lake, in contrast to lakes of pH 6–8. In situ radiochemical analyses revealed that colloidal reactive ferric iron predominates in the oxygenated epilimnion, while dialyzable or dissolved ferrous iron increases with depth. Unlike iron, organic matter is present in a nontransient colloidal state. In acid (pH 4–5) bog lakes ferric iron may be colloidal not as an inorganic complex (OH^-) but as reactive Fe^{3+} by complexation with the colloidal organic acids.

After thermally induced mixing with anaerobic waters, ferric iron is reduced and dissolved; however some of the BPN reactive iron remains colloidal, suggesting the presence of a residual ferrous organic complex.

Inorganic iron may be present in the epilimnion of oxygenated lakes of pH 6–8 as $\text{Fe}(\text{III})$ hydroxides in the form of either a precipitate or a sol (Hutchinson 1957; Shapiro 1964). Shapiro (1964) showed that organic acids could hold iron in apparent solution above pH 5 as peptized sols. However, at lower pH, ionization of organic acids decreases, the rate of oxidation of iron becomes independent of pH, and the solubility of all ionic forms of iron increases. Low pH, combined with low oxygen tensions and a reducing environment containing colloidal organic matter (COM), may permit large amounts of ionic iron to be present without inorganic (hydroxyl ion) complexation in bog lakes. In addition, the low ionic strength of bog lake water, as indicated by the low conductivity ($20\text{--}30 \mu\text{mhos cm}^{-1}$ at 18°C), reduces the coagulation formation of particulate forms of iron. Under these conditions, solution size, oxidation state, and organic acid complexation of ferrous and ferric iron may be

quite different from those in lakes of neutral or basic pH.

Low dissolved oxygen, high CO_2 , low pH, and the presence of reducing organic and inorganic compounds all favor formation of ferrous iron. Decomposing organic residues (including "humic acid") can reduce ferric to ferrous iron or form ferrous-organic complexes (Bloomfield 1952). Shapiro (1966) showed that colored organic acids could reduce ferric iron from natural waters, and Hem (1960) showed that tannic acid reduced ferric iron in artificial laboratory systems. Divalent sulfur compounds (e.g. HS^-) in lake waters can also reduce ferric iron (Stumm and Morgan 1970). All the above are encountered in highly colored acid bog water (pH 4–5) and tend to increase the solubility of iron by favoring the ferrous state. Bog lakes therefore present complex systems for measurement of the physical and chemical states of iron. Sampling and analytical difficulties have created some uncertainties regarding the iron species at specific depths in the water column. My purpose here is to define more precisely the states of iron in acid bog lakes and to determine

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²Present address: Environ. Sci. and Eng., Univ. North Carolina, Chapel Hill 27514.

the in situ relationship of iron to COM in differentially oxygenated lake waters.

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Study area and methods

The experiments were done in North Gate Lake, a small, highly colored, meromictic lake in Section 37 of T45N, R42W, Gogebic County, Michigan. It is one of many bog lakes on a 2,225 ha reserve owned by the University of Notre Dame, has a surface area of about 0.4 ha, and a maximum depth of 8 m. The open water is surrounded by a *Sphagnum* mat which extends into a black spruce forest.

Measurements of the oxidation state and speciation of iron in lakes are difficult. The two oxidation states of iron and their various complexes may occur simultaneously at a given depth, both the oxidation state and coordination are very sensitive to dissolved oxygen, and the oxygen content of samples is easily altered during handling. Bathophenanthroline (BPN) was used to measure ferrous iron; it does not react with any other metal ion (including Fe^{3+}). BPN gives a colored complex that can be extracted by n-hexyl alcohol at pH 4.0 to isolate the colored complex from its aqueous solution, increase sensitivity, and extend the specificity to the point where there is no known interference by either metal cations or common anions (Smith et al. 1952). The analytical scheme is shown in Fig. 1. All samples were duplicated and each digestion procedure contained a blank. Solutions were read in a Klett-Sumerson colorimeter using the 4-cm cell. Standards were run with each experiment.

Since $\text{Fe}(\text{II})$ is unstable in the presence of oxygen, samples are usually preserved at the time of collection. Preservation with acid accelerates the reduction of $\text{Fe}(\text{III})$ to $\text{Fe}(\text{II})$, releases iron from organic complexes, and dissolves inorganic ferrous salts (McMahon 1967; O'Connor et al. 1965). Thus, only total ferrous iron is measurable.

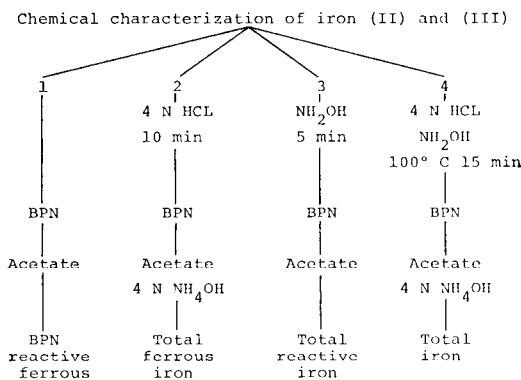


Fig. 1. Analytical scheme used to characterize iron species in North Gate Lake. Duplicate samples (25 ml) were carried through each procedure (1-4). After neutralization to pH 4.0 with NH_4OH , the red BPN- $\text{Fe}(\text{II})$ complex was extracted into n-hexanol, diluted with 95% ethanol, and the absorbance measured at 540 nm. (See Golterman and Clymo 1969.)

Sunlight also interferes with the determination of ferrous iron by differentially reducing $\text{Fe}(\text{III})$ compounds.

To circumvent these problems I used a plastic in situ filtration sampler which yielded 200 ml of a $0.45\text{-}\mu$ membrane-filtered sample (Fig. 2). Samples were collected with four airtight, light-proof samplers from the surface (0-5 cm), the top of the thermocline (2 m), the middle of the anaerobic hypolimnion (5 m), and the monimolimnion (7.5 m). Sampler containers were filled with a mixture of helium (99.05%) and isobutane (0.95%) and then transferred in a pressurized condition to the lake. A container was attached to a $0.45\text{-}\mu$ membrane-filtering apparatus and to filtration tubing connected to a vacuum pump. The apparatus was then lowered to the desired depth and filled with lake water by vacuum filtration. Sampler cylinders were returned to the laboratory under a slight negative pressure and a gas-filled balloon was fitted to the upper stopcock. Gas from the balloon entered the cylinder during the removal of subsamples from the lower stopcock.

Four analyses were performed on duplicate 25-ml samples from a series of depths

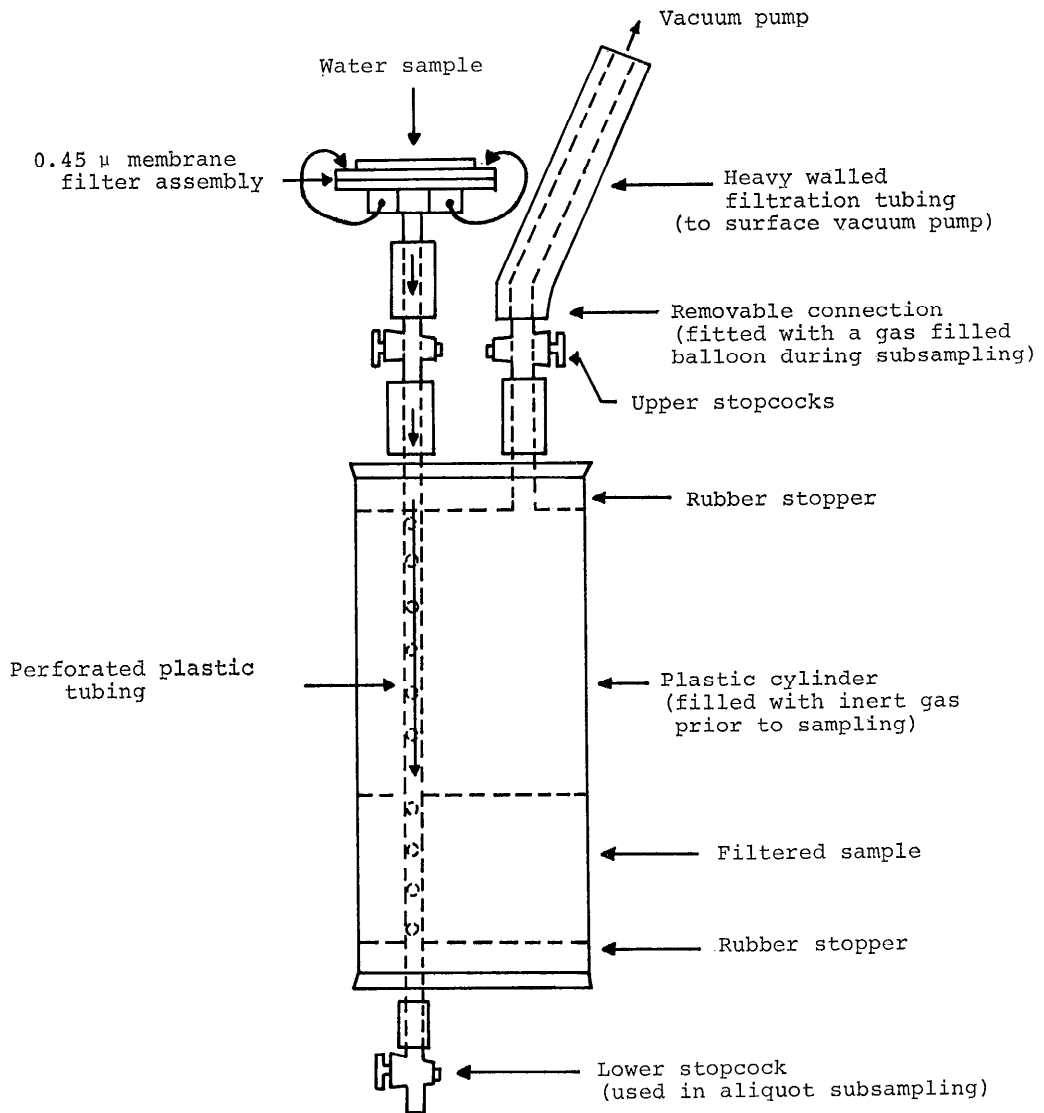


Fig. 2. In situ filtration device used to take 0.45- μ membrane-filtered samples from four depths in North Gate Lake without interference from oxygen.

(Fig. 1, 1-4). Two of these included acid digestion, two did not. All were done within 20 min of time of collection. Analysis 1 consisted of the addition of BPN directly to a sample, followed by color development and hexanol extraction (McMahon 1969b). Since acid dissolves insoluble ferrous salts (O'Connor et al. 1965), and releases Fe(II) from organic complexes (McMahon 1969a), the addition of BPN

without acid measures only the BPN reactive form of ferrous iron (Fe^{2+}). Analysis 2 measured total ferrous iron (acid + BPN). Analysis 3 consisted of adding only a reducing agent, hydroxylamine hydrochloride (NH_2OH), followed by BPN, color development, and extraction. This measured total reactive iron, which includes BPN reactive ferrous iron, in addition to reactive ferric iron, which requires reduction

alone to bring it to the BPN reactive state. The term nonreactive ferric iron is used here to describe all forms of iron that require hot acid digestion plus reduction for release to the BPN reactive state. This is similar to the procedure used by Stumm and Lee (1961) to measure colloidal ferric oxyhydroxide. Analysis 4 measured total iron (reductant + acid + heat) (Golterman and Clymo 1969).

Results from these four analyses were used as follows in calculations of iron species—

- analysis 1 = BPN reactive ferrous iron;
- analysis 2 - analysis 1 = nonreactive ferrous iron;
- analysis 3 - analysis 1 = reactive ferric iron (result A);
- analysis 4 - analysis 2 = total ferric iron (result B);
- result B - result A = nonreactive ferric iron.

These categories can be described as dissolved, colloidal, etc. if the water has been appropriately pretreated. The effectiveness of the above characterization scheme in differentiating between dissociated and undissociated iron as well as between ferrous and ferric iron was tested by analyzing freshly prepared iron standards of known concentration. These compounds do not exist in nature, but they do demonstrate the reactivity of known forms of iron to the proposed reaction scheme, from which natural lake iron was later classified. The replicability of the BPN method was excellent. Eight samples containing 10 μg of iron were analyzed for total iron with a standard error of 0.02 μg .

Samples were taken on 19 and 21 July by *in situ* anaerobic filtration at the four sampling depths in the center of the lake, and on 24 July and 24 August with a modified Hale sampler with acid-washed 300-ml BOD bottles, transported to the laboratory with minimal exposure to light or atmospheric oxygen, filtered through 0.45- μ membranes in the presence of air, and the analytical and characterization schemes described above were applied. Conductivity, pH, alkalinity, temperature, dissolved oxy-

gen, and total iron were monitored continuously from 12 May to 10 August. These parameters did not change after 1 June. A stable thermocline (2 m) develops early in North Gate Lake with chemical and physical parameters remaining nearly constant until the fall overturn of the mixolimnion. Day-to-day variations were small, permitting comparison of samples collected in the same location but analyzed with different procedures on successive dates. Duplicated experiments agreed very well and were averaged to show the naturally existing species of iron in different strata of the lake and the effects of aeration (aerobic filtration) on the species of iron present.

To determine both the natural physical state and the movement of iron in acid bog waters, $^{59}\text{Fe}-\text{FeCl}_3$ (1.0 mCi) was carefully added to the surface (7.0 cm) of a column of lake water contained in a polyethylene cylinder 1 m in diameter and 8 m deep. The tracer increased the amount of iron in the surface water by less than 1%. An evacuated bottle was used to draw samples from a series of glass sampling tubes spaced at 1-m intervals down the center of the tube, through connecting tygon tubing; a volume of water equal to that of the tubing volume was discarded before sampling. Samples were taken to the laboratory, filtered, and total and filterable activity was measured by drying triplicate 5-ml subsamples on planchets and counting on a low background beta counting system. Rates of movement of the tracer were equal to the slope of the least squares regression estimate for the change in ^{59}Fe activity with time after correcting for isotopic decay. A total radioactive iron budget was calculated for the plastic cylinder to determine any loss of tracer out of the epilimnion during the experiment.

To characterize further the physical state of the iron, I installed sealed sections of acid-cleaned (10% HCl) cellulose dialysis tubing (pore diameter of 4.8 nm, or molecular weight cutoff for proteins of >12,000) containing distilled water inside the cylinder, at 1-m intervals, 5 days after the tracer was introduced. After another 5 days triplicate 5-ml samples were withdrawn from

Table 1. Iron standards characterized by the proposed analytical scheme showing the separation of differentially reactive iron species. (Values are in percent of total iron.)

	Iron Standards			
	BPN reactive ferrous iron	Non-reactive ferrous iron	Reactive ferric iron	Non-reactive ferric iron
(1) ferric oxyhydroxide	0.0	0.0	16.0	84.0
(2) ferric chloride	0.0	0.0	16.0	84.0
(3) ferric NH_4 sulfate	0.0	0.0	12.0	88.0
(4) ferric perchlorate	0.0	0.0	100.0	0.0
(5) ferric citrate	0.0	0.0	100.0	0.0
(6) ferric EDTA	0.0	0.0	100.0	0.0
(7) ferrous NH_4 sulfate	95.0	5.0	0.0	0.0

inside the tubing, evaporated to dryness, and counted. I determined the period of 5 days for quantitative equilibrium of the dialysate with the surrounding water using ^{59}Fe - FeCl_3 and FeCl_3 standard solutions at 20° and 5°C.

The fractions were defined as: materials $>0.45 \mu$, particulate; those $<0.45 \mu$, but $>4.8 \text{ nm}$, were colloidal; those $<4.8 \text{ nm}$, truly soluble or dissolved.

Results

Standard iron solutions—All solutions were analyzed at pH 4–5 with 400–500 μg liter⁻¹ of iron present. Ferrous ammonium sulfate reacted as ferrous iron (100%) and as BPN reactive ferrous iron (95%) (Table 1); $<5\%$ reacted as nonreactive ferrous iron. Ferric ammonium sulfate, ferric chloride, and most important, ferric oxyhydroxide, all reacted as ferric iron (100%) and were calculated to be nonreactive ferric iron compounds (84–88%). These ferric compounds, unlike the ferrous iron, did not react as free dissociated (hydrated) iron but required acid digestion plus reduction to be reactive to BPN. The ability of ferric iron to form incompletely dissociated inorganic complexes with sulfate and chloride is well known (Cooper 1937; Rabinowich and Stockmayer 1942; Stumm and Lee 1960). The results given are from freshly prepared standards. Aged solutions (3–5 days) of ferric chloride and ferric oxy-

Table 2. Size classification of ^{59}Fe activity following addition of tracer to a water column enclosed in a plastic cylinder in North Gate Lake (A), and stable iron distribution in North Gate Lake using in situ dialysis (B).

Depth	A		B	
	Tracer iron filterable*	dialyzable*	Stable iron filterable*	dialyzable*
Surface	91-100	14-15.5	90-100	8
1 m	84-92	22-25	-	-
2 m	80	55-63	99	45-60

*Values in percent of total iron.

hydroxide yielded recoveries as nonreactive ferric iron of 96%.

Ferric perchlorate reacted as reducible ferric iron and was entirely reactive ferric iron that required reduction alone to react with BPN. The perchlorate anion does not form an inorganically bound complex with iron to the degree of sulfate, chloride, or hydroxide. Thus, reactive ferric iron represents iron more in the completely dissociated Fe^{3+} state. However, reactive ferric iron need not be in the free state, as iron organically complexed (e.g. ferric EDTA and ferric citrate) also was present in the reactive state. Lake iron in the ferric reactive state is therefore primarily dissociated iron (Fe^{3+}) present either free (hydrated) or organically complexed. Since free (hydrated) ferric iron would be dialyzable, reactive iron in bog lake waters of colloidal size could exist as COM-bound iron rather than an inorganic colloid. If colloidal and reactive, the iron may be present in an organic complex with COM, but if colloidal and nonreactive, the iron is more likely to be present as an inorganic colloid, e.g. ferric oxyhydroxide.

The rationale is, then, that although dissociated iron will react with BPN without acid, inorganically complexed iron will not react until the appropriate acid digestion procedure renders the iron reactive. The above classification scheme, together with size separation by in situ filtration and dialysis, yielded a characterization scheme for acid bog lake iron.

Lake iron—Levels of iron in North Gate Lake were in the highest range of values for similar lakes found by Juday et al. (1938). Many of the lakes of this region

Table 3. Distribution of the natural species of filterable iron in North Gate Lake following in situ (0.45 μ) filtration (A), and the distribution of filterable iron species in the same strata following aerobic (0.45 μ) filtration (B). (Values are in $\mu\text{g liter}^{-1}$.)

Depth (m)	BPN reactive		Nonreactive		Reactive		Nonreactive		Total	
	Fe(+2)		Fe(II)		Fe(+3)		Fe(III)		A	B
	A	B	A	B	A	B	A	B		
0 (surface)	73	42	46	19	119	93	26	140	264	294
2 (metalimnion)	426	182	36	16	84	241	49	168	595	607
5 (hypolimnion)	634	366	3	126	8	160	32	24	677	676
7.5 (monimolimnion)	1073	610	4	228	0	279	79	37	1161	1154

are highly stained. In North Gate Lake yellow colloidal organic matter comprises up to 85% of the total organic carbon, and 90–100% of the total iron is 0.45- μ membrane filterable (Table 2). This large fraction of filterable iron suggests that the presence of 30–40 mg liter⁻¹ COM, combined with low pH and conductivity, prevents formation of large iron polymers. Total filterable iron increased from 264 $\mu\text{g liter}^{-1}$ at the surface to 1,161 in the monimolimnion, and BPN reactive ferrous iron, measured after in situ filtration, increased from 28 to 93% of total iron (Table 3). Since oxygen was absent below 2 m, it is not surprising that iron was present almost exclusively as BPN reactive ferrous iron. However, it is interesting that reactive ferric iron on the dates sampled represented 78–90% of the ferric iron in the surface water, in turn an average of 45% of the total iron, and that I did not find large amounts of nonreactive Fe(III) (e.g. ferric oxyhydroxide) at any depth sampled. These values represented <10% of total iron. BPN reactive Fe(II) and reactive Fe(III) (i.e. from acid-free analysis), which increased from 73% in the epilimnion to 95% in the hypolimnion, thus represented a majority of the iron present. The small remaining fractions in these two strata were acid-digestible nonreactive iron [Fe(II) and/or Fe(III)].

The reducing COM in the hypolimnion does not form a complex with ferrous iron more stable than the BPN-Fe²⁺ complex. The predominant form of Fe(II) was BPN reactive, contrary to the suggestion of Gjesing (1964) that Fe(II) in highly colored, pH 4–6 Norwegian waters existed as organic complexes reactive only after hot

acid digestion. The oxygenated epilimnion contains principally reactive ferric iron (84% of ferric iron) and little ferric oxyhydroxide. The 2-m stratum, with 0.50 mg liter⁻¹ dissolved oxygen, also contains reactive ferric iron and appears to be the zone in which the downward-diffusing dissolved oxygen first oxidizes the Fe(II) diffusing upward from the anaerobic hypolimnion.

In the low pH range (4–5) of the surface water of North Gate Lake, the reactive form of Fe(III) is the predominant form of iron. However, even though environmental conditions in these waters allow Fe(III) to exist chemically in a reactive state, the stable iron analysis and radiochemical data presented below indicate that this is in colloidal form.

Labeling experiment—Working on highly stained lake waters from Alaska, Barsdate (1970) found that 80% of the cobalt and 68% of the manganese (in addition to the organic acids) were retained by dialysis bags. He believed that this was due to the formation of complexes and associations between metals and the highly dispersed organic colloids. To make an in situ test of this hypothesis in North Gate Lake, ⁵⁹Fe-FeCl₃ was carefully added to the surface water in the polyethylene cylinder in the lake after thermal equilibrium had been established with the surrounding water (Fig. 3). Slow exchange with the 1-m stratum took place until cool weather and wind mixed the upper two layers (day 5). Slow vertical leakage then occurred from the 1-m layer through the thermocline for the rest of the 11-day experiment.

Marshall and LeRoy (1972) showed that ⁵⁹Fe equilibrated with the particulate

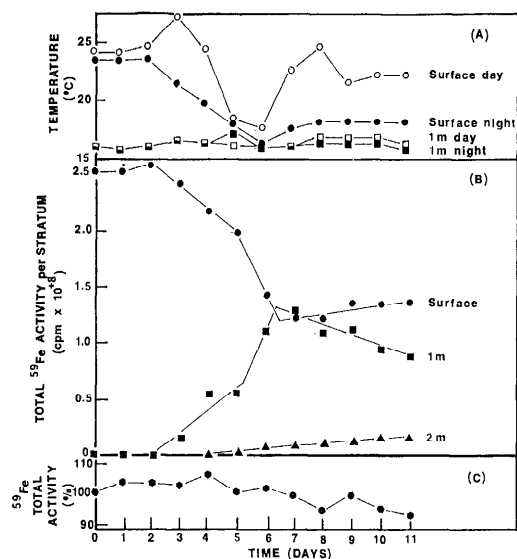


Fig. 3. Tracer (^{59}Fe) cylinder experiment in which the changing thermal regime of the lake water (A) caused the movement of ^{59}Fe added to the surface stratum to lower strata (B), and the total tracer budget for the epilimnion of the cylinder (C).

inorganic iron of a South Carolina reservoir within 24 h, and that on the average 65% of the iron was particulate. In the surface waters of North Gate Lake, 91–100% of the total activity was filterable and only 15.5% of the filterable activity was dialyzable after 11 days, but at 2 m, up to 63% of the total activity was dialyzable. The percentage increase in the dialyzable activity fraction from the surface to 2 m was similar to but lower than the increase in BPN reactive ferrous iron (28 to 72%) between these two strata and reflects increasing reduction and release of colloidal to dissolved iron with increasing depth (Tables 2 and 3).

Colloidal Fe(III) of the surface water moved down in the cylinder and was reduced to dissolved iron [Fe(II)]. This movement was caused by cooling of the the surface water and thermal equilibration between the 1-m and surface strata (Fig. 3). During the cooling period (days 2–5) the rate of loss ($-0.210 \times 10^{+8}$ cpm d^{-1}) of activity from the surface agreed well

with the increase of $+0.185 \times 10^{+8}$ cpm d^{-1} at 1 m before mixing. These rates increased to $-0.546 \times 10^{+8}$ cpm and $+0.576 \times 10^{+8}$ cpm during mixing (days 5–6). The combined rate of loss of tracer from the surface ($0.756 \times 10^{+8}$ cpm d^{-1}) agreed with the increase at 1 m ($0.759 \times 10^{+8}$ cpm d^{-1}). On day 6, the recovery of added tracer was 102%. After thermal equilibration (day 6) no further tracer was lost at the surface layer through day 11, when ^{59}Fe activity at the surface layer represented >50% of the added iron. After mixing, activity was lost from the 1-m stratum at the rate of $-0.0953 \times 10^{+8}$ cpm d^{-1} , a significantly lower rate than the rate of loss at the surface (days 2–5). However, unlike the surface to 1-m mixing, the loss was not balanced by the total rate of ^{59}Fe increase at other depths (2 m, $+0.0190 \times 10^{+8}$ cpm; surface, $+0.0346 \times 10^{+8}$ cpm; 3 m, $+0.0012 \times 10^{+8}$ cpm), suggesting that 42% of the loss from 1 m either was held in strata which were not sampled or had become concentrated between 1 and 2 m. The unaccounted for loss of tracer from 1 m, $-0.0405 \times 10^{+8}$ cpm d^{-1} for the 5-day period following mixing equals $-0.2025 \times 10^{+8}$ cpm, is 8% of the total ^{59}Fe added. This loss, possibly held at the top of the thermocline, appears to be responsible for the slight underrecovery (92%) calculated for the total iron budget at the end of the cylinder experiment.

During the entire experiment, 80–100% of the tracer was filterable at all depths sampled. In this acid bog lake particulate polymers of iron constituted a minor fraction of the total iron and iron was not removed from the epilimnion by precipitation and sedimentation. The predominant form of ferric iron is colloidal. As the colloidal ferric iron moved to deeper layers, it was reduced to dissolved ferrous iron. However, a colloidal form of BPN reactive iron (II) also appeared to be present: at 2 m 72% was BPN reactive ferrous iron and only 63% dialyzable ferrous iron.

In summary, the organic matter in North Gate Lake does not require sorption to colloidal inorganic ferric iron to be nondialyzable. Along with the COM, the iron of the

surface waters was primarily colloidal, but did not react as an inorganic colloid. The iron species of the surface waters [primarily reactive Fe(III)] thus may be colloidal due to complexation with COM. Although at 2 m ferrous iron shows significantly less affinity for the colloidal state and appears to be in a dissolved ionic state, a small fraction of COM bound ferrous iron may also be present.

Comparison with aerobic filtered samples—Aerobically filtered (0.45- μ membrane) samples were characterized by the same reaction series used for in situ filtered samples (Table 3). Since these samples were not and could not be subsamples of the anaerobic samples, but were from the same water layer, exact microgram per liter comparisons are not valid. However, I feel that the relative forms of iron can be compared, as shown by the high degree of similarity between the iron species and the total iron within each of the replicated aerobic (24 July and 24 August) and anaerobic (19 July and 21 July) experiments. Although the results within the replicated experiments were similar, large differences between the aerobic and anaerobic results cannot be attributed to spatial or temporal variations in the depths sampled.

Exposure to air during filtration (1–5 min) results in major shifts in iron species. In the oxygenated waters of the epilimnion, aerobic filtration caused BPN reactive Fe(II), nonreactive Fe(II), and reactive Fe(III) to decrease and nonreactive Fe(III) (perhaps ferric oxyhydroxide) to increase. These changes indicate that the filterable iron in the surface water is in a chemical state which is changed by further aeration. In the partially oxygenated water at 2 m, filtration brought about a decrease in BPN reactive Fe(II) and nonreactive Fe(II) and an increase in reactive Fe(III) and in nonreactive Fe(III). Aerobic filtration of completely deoxygenated water from 5 and 7.5 m resulted in similar responses (Table 3). In the anaerobic monimolimnion (7.5 m), 41% of BPN reactive Fe(II) was lost by aeration, 20% appeared as nonreactive Fe(II), and 24% appeared as reactive Fe(III). Nonreactive Fe(III)

was not formed. In the two equally deoxygenated strata (5 and 7.5 m), the percentage of BPN reactive ferrous iron lost by aeration was identical (43%) and the percentages of nonreactive Fe(II) and reactive Fe(III) that appeared were very close. Since responses to aeration in these strata were similar, whereas the response of strata with different oxygen content (surface and 2 m) differed considerably, the in situ oxygen content seems to regulate changes that take place on aeration. Apparently the overall trend is successive conversion of iron to a more oxidized and nonreactive state on aeration of samples from different depths. However, on aeration of the anaerobic lake water, a major increase occurred in reactive Fe(III), suggesting that COM may retard the formation of nonreactive Fe(III). This may also happen in natural lake water since the former state of iron predominates in the surface waters of North Gate Lake.

Discussion

When lake stratification is destroyed, any dissolved Fe^{2+} in the hypolimnion is oxidized and if the pH is greater than 6.0, the Fe^{3+} ions that are formed precipitate as $Fe(OH)_3$. Thus, in the oxygenated epilimnion of neutral to basic pH lakes, ferrous iron is not detectable and iron cannot be in true solution above 17 μg liter⁻¹. Since lakes contain iron above this level, Shapiro (1967) proposed, and demonstrated in laboratory studies, the capacity of concentrated or chemically extracted organic acids or their salts to hold large amounts of iron in apparent solution. He concluded that the mechanism of "solubilization" of iron at high pH and redox potential is the formation of a protected sol of colloidal inorganic ferric iron. Peptized sol formation has become widely accepted as the mechanism through which organic matter complexes with iron (Hutchinson 1957; Stumm and Morgan 1970).

Acid bog lakes are different from the systems on which a majority of the iron studies have been done. The presence of a large amount of COM, high CO_2 levels,

low conductivity and alkalinity, and an acid (4–5) pH may result in iron species and relationships different from those previously reported. Elder (1975) demonstrated in theory that an acid pH alone may drastically de-emphasize the importance of hydroxyl ion as a ligand for metal ions. A tenfold change in the hydroxide concentration of the water can produce changes in species of several orders of magnitude, even for iron, whose nonhydroxyl coordination is commonly considered negligible. Thus, in acid bog lakes ligands other than hydroxyl ion may be important in complexing iron when dissolved Fe^{2+} is oxidized to Fe^{3+} ions.

My *in situ* stable and radiochemical studies support the laboratory findings of a colloidal form of iron only in those oxygenated epilimnetic waters where ferric iron predominates. In acid bog lakes, colloidal iron consists of many reactive species of iron II and III, and ferric iron reacting as a colloidal inorganic complex [e.g. sol of $\text{Fe}(\text{OH})_3$] is notably lacking. By chemical reactivity about 84% of ferric iron is potentially dialyzable reactive $\text{Fe}(\text{III})$. Since the reactive ferric iron is not dialyzable, the colloidal size of this species can be explained by complexation with pre-existing COM. The ligands present in COM appear to be important in complexing reactive iron at the low pH values encountered in bog lake waters. Although colloidal reactive ferric iron is the major form of iron in aerobic strata, ferrous iron is also present, not in trace amounts, but up to 45% of the total iron. High amounts of ferrous iron can be maintained in partially oxygenated water by photoreduction of complexed reactive Fe^{3+} . Other organic reactive Fe^{3+} compounds (ferric citrate and ferric EDTA) can be photoreduced to moderately stable ferrous compounds if not subjected to oxidizing conditions (Jones and Long 1952).

In summary, the forms of ferric and ferrous iron prevalent in North Gate Lake were those not requiring acid digestion to be reactive to BPN, an indication of a lack of inorganic [$\text{Fe}(\text{III})$ and $\text{Fe}(\text{II})$] iron

polymers. The hydroxyl ion concentration in North Gate Lake is up to 10,000 times less than that in pH 8 lakes from which most of the published iron data have been derived. In these low pH lakes, ferric iron is in a colloidal reactive state through complexation with the colloidal-sized organic ligands (COM) rather than through inorganic (OH^-) complexation and nonreactive ferric iron [i.e. $\text{Fe}(\text{OH})_3$] is present in minor quantities. Instead of organic matter sorbing at the surface of colloidal inorganically complexed iron [sol of $\text{Fe}(\text{OH})_3$] as in lakes of pH 8, iron in the reactive state (Fe^{3+}) is complexed by COM in highly stained bog lakes of pH 4–5. This form of iron once reduced could account for the residual Fe^{2+} -colloidal BPN reactive iron found in strata that had recently become anaerobic.

I feel that in lake waters of pH 4–5 the iron species present and their reactivities are not adequately explained by sol formation. The chemical environment of stained (COM) acid bog lakes differs from lakes of pH 6–8 in which iron is soon precipitated as an acid-digestible inorganic complex [$\text{Fe}(\text{OH})_3$] and ferrous iron is not usually present. I, therefore, propose two mechanisms for the binding of iron to organic matter. The first predominates in highly colored bog waters (pH 4–5) where the colloidal nature of iron is imparted by the high molecular weight organic acid (or organic sol) with its bound reactive $\text{Fe}(\text{III})$ and $\text{Fe}(\text{II})$. A second mechanism predominates in nonstained lake waters (pH 7–9), where the colloidal particle may be a nonreactive iron sol [e.g. $\text{Fe}(\text{OH})_3$] maintained in apparent solution by sorption of organic acids to the iron colloid. The changes in organic matter and, in particular, in iron with changes in pH (i.e. the OH^- ligand) allow for a differential binding of iron to organic acids above and below pH 6–7.

Thus, by determining the physical and chemical states of iron in natural waters, pH in combination with the type and quantity of organic matter may control the relative roles of iron and organic matter in lake

waters. Since flocculation and subsequent precipitation of iron has been linked to phosphate elimination from trophogenic waters of neutral to basic lakes, the interaction of iron to phosphate might also differ in acid bog lakes.

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