Iron Reactions in the Magothy and Upper Glacial Aquifers of Suffolk County, Long Island, New York

by

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ABSTRACT

Extremely high dissolved-iron concentrations are present in water from some wells on Long Island. High iron concentrations in ground water are of major concern to water suppliers and owners of private wells because of related well-encrustation problems and decreases in specific capacity; therefore, the sources of dissolved iron and factors that control iron dissolution and precipitation in the aquifer system are of growing interest. Preliminary data indicate that iron concentrations in Long Island aquifers are affected by several factors that can be grouped as processes that predominate in the upper glacial aquifer and those that predominate in the Magothy aquifer. Simulations with geochemical speciation and mass-balance models indicate that the dominant iron reactions along hydrologic flow paths are oxidative dissolution of pyrite in the Magothy aquifer and precipitation of iron hydroxides in the upper glacial aquifer. The effects of organic ligands on iron complexation and reductive dissolution can significantly increase dissolved iron concentrations in streams and shallow ground water. Bacteria are important in catalyzing these reactions.

INTRODUCTION

Iron in ground water is a concern with respect to water supply and water quality because iron can cause encrustation and corrosion of wells and iron staining; also, iron can control redox reactions that affect other constituents and contaminants. Iron is of particular concern in the Long Island ground-water system because the aquifer material contains few reactive minerals; as a result, the ionic strength of the ground water is extremely low. The geochemistry of the Long Island ground-water system is similar to that of other Atlantic Coastal Plain aquifer systems, including the Magothy aquifer in Maryland (Knobel and Phillips, 1988).

In a 1993 study by the U.S. Geological Survey (USGS), water-quality data for wells unaffected by iron encrustation were statistically compared with data for adversely affected wells to identify constituents that affect the encrustation process in wells and to define the spatial distribution of these constituents. Iron encrustation has resulted in decreased specific capacities of several public supply wells in Suffolk County. Most of the wells with decreased specific capacity were near ground-water-discharge zones and the well water contained high concentrations of iron and phosphate, and low concentrations of dissolved oxygen and nitrate, compared to water from wells in unaffected areas (D.A. Walter, U.S. Geological Survey, written commun., 1993).

Long Island is underlain by a sequence of upper Cretaceous and Pleistocene sediments that were deposited on a south-eastward dipping bedrock surface. The deposits thicken toward the southeast and reach a maximum thickness of about 2,000 feet in southeastern Long Island. The uppermost two aquifers, the Magothy (Cretaceous) and upper glacial (Pleistocene) represent the major sources of ground-water supply and are the focus of this paper.

Iron concentrations in Long Island aquifers are affected by several factors that can be grouped as reactions that predominate in the upper glacial and those that predominate in the Magothy aquifer. Native dissolved iron concentrations in the Magothy aquifer range from below detection limits to 8.8 µg/L (micrograms per liter), and in the upper glacial aquifer, from below detection limits to 40 µg/L (D.A. Walter, U.S. Geological Survey, written commun., 1993; deLaguna, 1964). Extremely high iron concentrations (up to 15,000 µg/L) in some localities indicates extensive dissolution of iron-bearing minerals, but detailed information on the iron sources and major reactions is lacking. Water-quality data (from the U.S. Geological Survey [USGS] National Water Information System database) from wells along a west-east transect in the Peconic River basin in eastern Long Island (fig. 1) were examined to identify geochemical changes that occur along flowpaths from recharge areas to points of discharge. The Peconic River, which is largely a gaining stream, flows eastward through a relatively pristine area of eastern Long Island before discharging into Flanders Bay.

This paper discusses the major iron reactions that occur within the upper glacial and Magothy aquifers of Suffolk County, Long Island. Geochemical mass-balance-modeling simulations were run to test evidence presented

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by earlier workers (Vecchioli and others, 1974; K.A. Pearsall, U.S. Geological Survey, written communication, 1993) which indicates that pyrite dissolution is a major source of iron in the aquifer system. Seasonal trends of dissolved iron in surface waters along the Peconic River indicate that organic complexation of iron can control iron solubility in surface waters and shallow ground waters.
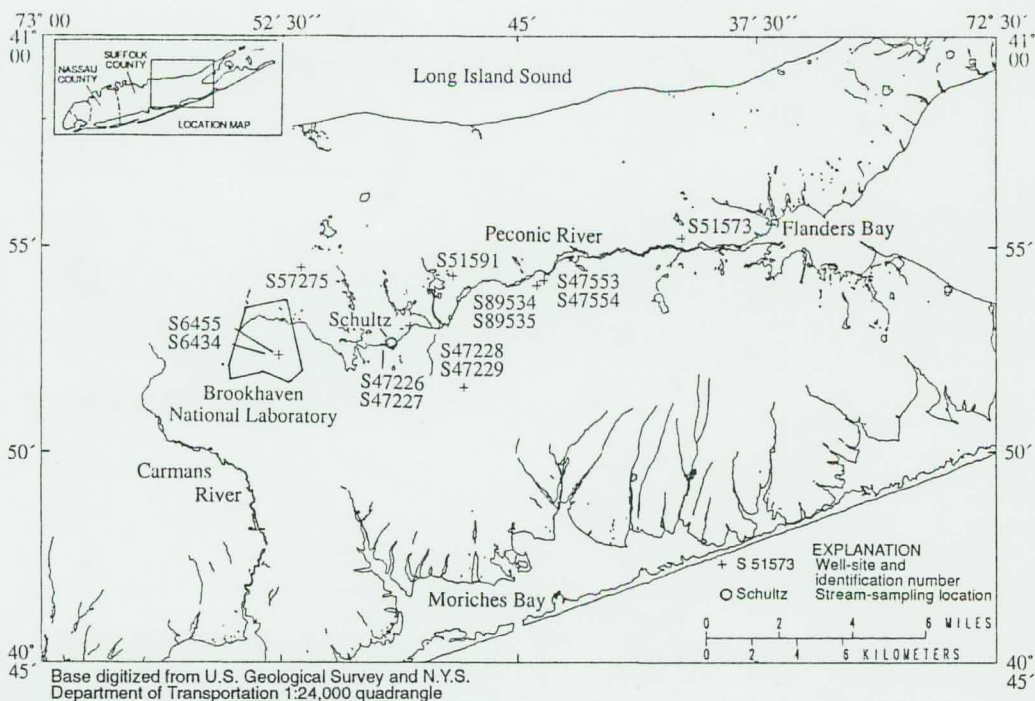

Figure 1. Location of wells along Peconic River.

IRON IN GROUND WATER

The major sources of the dissolved iron are iron oxides and hydroxides in the upper glacial aquifer, and pyrite and marcasite in the Magothy aquifer. Factors that strongly affect reaction rates along the ground-water flow paths are redox conditions and pH; other factors include biological controls, such as organic complexation and bacterial activity. Dissolved iron is assumed to increase progressively with travel distance as a result of (1) mineral weathering, and (2) changes in dissolved-oxygen (DO) concentrations and redox conditions. The decrease in redox conditions with depth is a major factor in the iron-dissolution process, and redox conditions control the reactions of the dominant iron-mineral phase. Stability relations (Eh-pH) for the iron minerals of the Magothy aquifers (fig. 2) indicate that the length of the flow path and, consequently, the redox conditions and pH, have a significant effect on iron chemistry. Water samples from wells along selected flowpaths and sediment cores from the various geochemical environments can provide information on changes in iron chemistry and redox conditions as ground water moves toward areas of discharge.

Iron Dissolution

Dissolution of iron-bearing minerals increases iron concentrations in ground water. Mineral dissolution can occur through several processes including (1) the proton-promoted reaction, which involves the association of hydrogen ions with oxygen ions at the mineral surface and subsequent polarization and rupture of the adjacent metal-oxygen bonds; (2) the ligand-promoted reaction, which involves coordination of ligands to metals at the mineral surface and the rupture of the underlying, hydrolyzable bonds (as mentioned above); and (3) the oxidative and reductive reactions, which involve a net change in oxidation state and the subsequent rupture of the metal-oxygen bond (Casey and others, 1993).
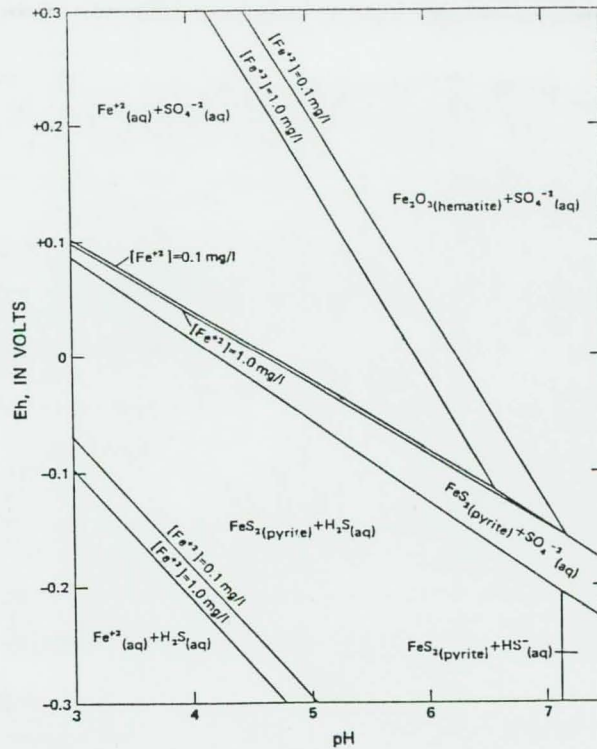
Figure 2. Eh-pH diagram for the system Fe-S from the Magothy aquifer at Bay Park, Long Island showing stability relations of iron oxides and sulfides, at 15°C, 1 atmosphere of pressure and sulfur species activity of 4.2 mg/L as SO_4^{2-} (Modified from Vecchioli and others, 1974, fig. 13).

Detachment of metal species from the surface of crystalline material into solution is generally slow for slightly soluble minerals and, thus, is rate limiting (Berner, 1981; Casey and others, 1993). Weathering of iron-bearing minerals, such as pyrite, hematite, magnetite, hornblende, and iron hydroxides, is significantly enhanced by redox reactions, and dissolution of these minerals has been shown to be surface controlled under field conditions (Berner, 1978).

The spatial distribution of dissolved-oxygen and iron concentrations in a vertical section along the Peconic River in eastern Suffolk County are depicted in figures 3A and 3B, respectively. Iron concentrations in the shallow system along the Peconic River range widely depending on the vertical extent of the flow path and on the residence time. Elevated iron concentrations (up to 15,000 µg/L) were measured in ground water in the vicinity of wells S47226 through S47229 (fig. 3B), which indicates extensive dissolution of iron-bearing minerals. Hydraulic heads at these wells indicate an upward hydraulic gradient in these localities, suggesting that ground water has moved upward along flow paths through the Magothy aquifer and (or) the lower part of the upper glacial sediments.

Iron-bearing minerals in the Magothy aquifer include pyrite, ilmenite, garnet, staurolite, and, locally, epidote and chlorite (Faust, 1963; Perlmutter and Todd, 1965). In addition, lignite is present as beds and (or) particles dispersed in the sediments; pyrite and marcasite are commonly associated with lignite. The presence of low pH and high concentrations of dissolved iron (which result from pyrite dissolution, table 1, eq. 5) in some areas along the southern shore of Long Island is evidence that pyrite is a likely source of dissolved iron in the Magothy aquifer (K.A. Pearsall, U.S. Geological Survey, written commun., 1988). Geochemical modeling with the computer programs PHREEQE (Parkhurst and others, 1990) and NETPATH provides further evidence that pyrite dissolution is a major source of dissolved iron. A simulation in which ground water typical of Magothy aquifer chemistry was exposed to pyrite and oxygen resulted in the dissolution of 10^{-6} M (moles per liter) of Fe^{2+}, but the dissolution of pyrite did not account for the entire reaction (see Colabufo and Schoonen, this Proceedings). Pyrite dissolution alone results in low pH (table 1, eq. 1a or 1b) that is not prevalent throughout the Magothy; thus, a proton acceptor and donor, such as Fe^{3+} (for example, hematite, table 1, eq. 3) or possibly lignite, must be present to act as a buffer (table 1, eq. 5; Pearson and Friedman, 1970). In some areas along the southern shore of Long Island, however, the pH of ground

water is less than 5.0 and iron concentrations are high (greater than 500 µg/L), indicating that pyrite dissolution without significant buffering is occurring. The geochemical mass-balance model, NETPATH, was used to interpret net geochemical mass-balance reactions between initial and final waters along generalized hydrologic flow paths through the Magothy and upper glacial aquifers of the Peconic River basin (figs. 1 and 3). Results of model simulations show undersaturation (suggesting dissolution) with respect to pyrite and supersaturation (suggesting precipitation) with respect to iron oxide (goethite).
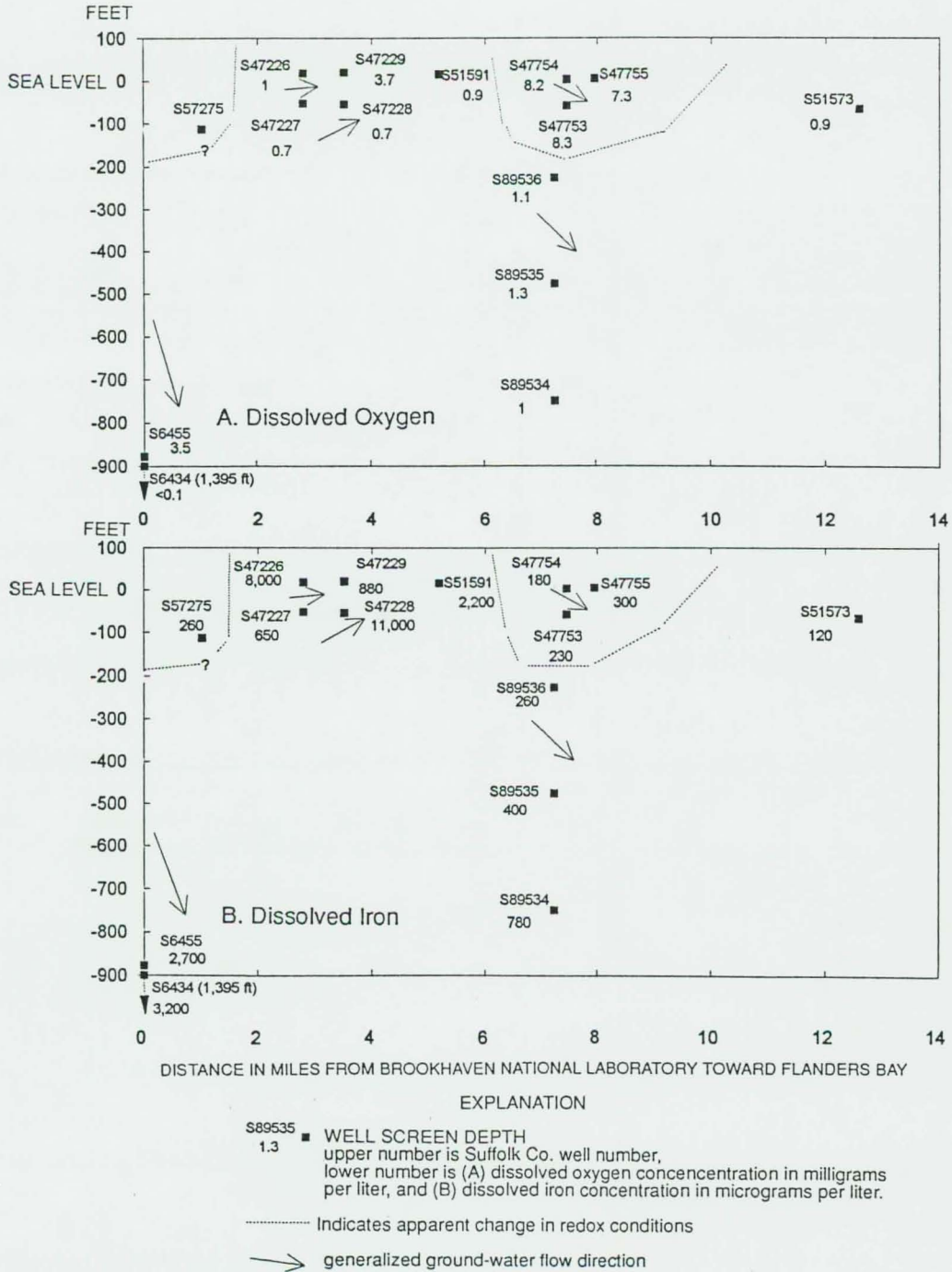

Figure 3. Dissolved oxygen (A) and iron concentrations (B) in water samples from observation wells along the Peconic River in eastern Long Island. (Location is shown in fig. 1.)

Table 1. Major iron-related reactions in Suffolk County, Long Island.

Mineral	Reaction
Pyrite	
Dissolution	(1a) $FeS_{2(s)} + H_2O + 7/2O_{2(aq)} \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$
	(1b) $FeS_{2(s)} + 14 Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$
	(1c) $Fe^{2+} + 1/4O_{2(aq)} + H^+ \rightarrow Fe^{3+} + 1/2H_2O$
Formation	(2a) $2CH_2O_{(s)} + SO_4^{2-} + H^+ \rightarrow HS^- + 2H_2O + 2CO_2$
	(2b) $Fe^{2+} + HS^- \rightarrow FeS + H^+$
	(2c) $FeS_{2(s)} = FeS + 1/2S_{2(g)}$
Hematite	(3) $1/2Fe_2O_{3(s)} + 3/2H_2O = Fe^{3+} + 3OH^-$
Fe(OH)₃	(4a) $2Fe^{2+} + 5H_2O + 1/2O_{2(aq)} = 2Fe(OH)_{3(s)} + 4H^+$
(with organic ligand)	(4b) $CH_2O_{(s)} + 8H^+ + 4Fe(OH)_{3(s)} \rightarrow 4Fe^{2+} + 11H_2O + CO_2$
Lignite	(5) $CH_2O_{(s)} + O_{2(aq)} \rightarrow H + HCO_3^-$

Analytical data from the hypothetical flow path along the Peconic River (fig. 3) show a general decrease in dissolved oxygen concentration and an increase in dissolved-iron concentration seaward with distance along the flow path, indicating a decrease in redox potential over travel distance. Thus, the Magothy aquifer may contain a redox front, beyond which mineral grains contain less oxide cement and surface coating than mineral grains in areas near the point of recharge. In Nassau County, the Magothy aquifer is reported to have an Eh range of -0.03 to -0.10 volts and a pH range of 5.2 to 7.2 (Ragone and others, 1975).

In addition to redox, pH, mineral reactivity, and grain surface area, ground-water residence time affects the extent of dissolution of iron-bearing minerals. Most studies of dissolution kinetics in natural aquifer systems derive a mass-transfer value directly from the difference in solution chemistry between two points along a ground-water flow path, then divide this difference by the ground-water residence time to obtain element fluxes (Rowe and Brantley, 1993). Studying the aquifer minerals and their dissolution features (which include etch pits) can provide additional information on relative contributions of iron minerals and element fluxes.

The weathering of pyrite has not been studied in detail under natural conditions. In laboratory experiments, Fe(III) has been found to be the preferred oxidant of pyrite (McKibben and Barnes, 1986; Moses and others, 1987) (Table 1, eq. 1a and 1b), but DO is required for conversion of Fe(II) to Fe(III) (table 1, eq. 1c). McKibben and Barnes (1986) fitted the oxidation-rate data to square-root rate laws for both DO and Fe(III) and found that the Fe(III) rate law is inversely proportional to the square root of H+ concentration. Given the apparent abundance of pyrite in the Magothy aquifer (Suter and others, 1949) and the low DO in many locations, this oxidative dissolution pathway is likely to prevail in the Peconic River area. Pyrite may be precipitating in deep, highly reducing parts of the Magothy aquifer where sulfate reduction is occurring.

Organic And Bacterial Reactions

In areas of ground-water recharge and shallow flow, organic acids formed from decomposition of organic matter could promote iron dissolution and mobility through ligand complexation (Crerar and others, 1981). Iron concentrations measured in ponds, streams, and shallow ground water in the Peconic River basin appear to be seasonally affected by the availability of organic ligands (fig. 4) derived from the decay of organic matter. Seasonal fluctuations in dissolved-iron concentration were also observed in the New Jersey Pine Barrens, an area that is hydrogeochemically similar to the pine barrens within the Peconic River basin, are attributed to complexation with organic ligands (Crerar and others, 1981). Rates of reductive dissolution can also be increased by the presence of

organic ligands (Johnson and Hochella, 1993); humic, fulvic, and tannic acids occur naturally in shallow ground water and can promote iron-bearing-mineral dissolution. Grandstaff (1986), for example, found that the organic ligand ethylenedinitrilo-tetraacetic acid (EDTA) increased olivine-dissolution rates about 110-fold and that the rate of dissolution is proportional to the square root of free-ligand concentration.

Iron bacteria can mediate iron oxidation and reduction and have a major effect on the dissolution and precipitation of iron-bearing minerals. Singer and Stumm (1970) concluded that the rate of oxidative dissolution of pyrite by natural weathering exceeded the laboratory rate by a factor larger than 10^6 because bacteria in the field catalyze one or more steps in the overall reaction.

The bacterially-mediated oxidation of pyrite and subsequent precipitation as iron hydroxides on well screens in areas of ground-water discharge necessitates a costly treatment program for water-supply companies. The most common species of iron bacteria in Suffolk County public-supply wells is *Gallionella ferruginea* (D.A. Walter, U.S. Geological Survey, written commun., 1993), and analysis of sediment cores from replacement wells and test borings indicates that iron bacteria are ubiquitous throughout the aquifer system of Suffolk County.
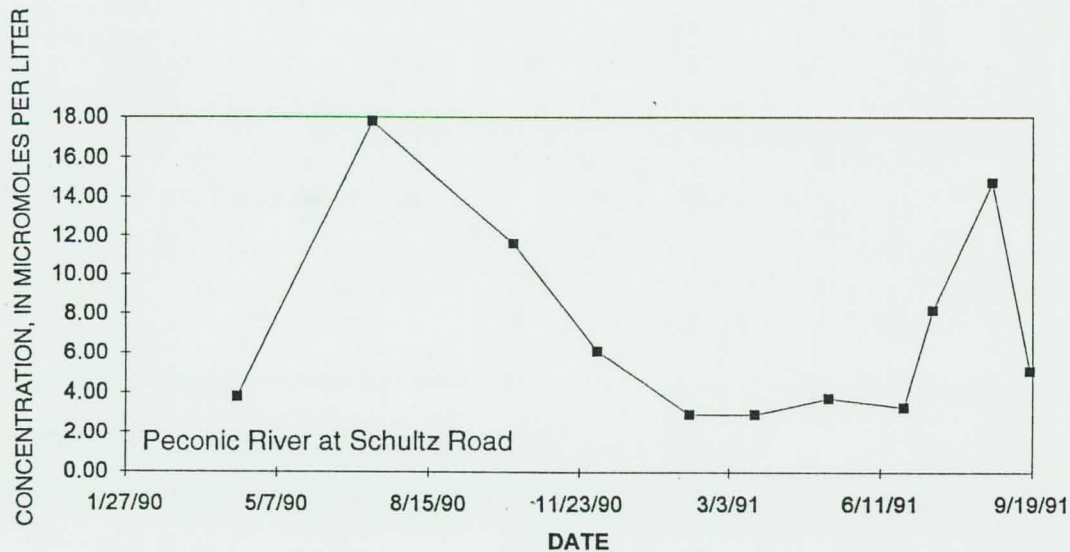

Figure 4. Dissolved iron concentration in the upper Peconic River January 27, 1990 through September 19, 1991) at Schultz Road (C.J. Brown and M.A.A. Schoonen, SUNY-Stony Brook, written communic., 1993). Location shown in fig. 1.

CONCLUSIONS

Definition of iron reactions within the ground-water system requires data on the occurrence, spatial distribution, and weathering rates of the major iron-bearing minerals. These data can, in turn, be related to geochemical evolution and differences in water chemistry at monitoring wells along ground-water-flow paths. The major source of iron within the Long Island aquifer system is probably pyrite, which weathers through oxidative dissolution to form Fe(II). Organic and (or) bacterial interactions, including ligand-promoted dissolution and organic complexation, are key factors in the iron reactions within the shallow system and, to some extent, within the deep system. Definition of these processes would entail study of aqueous ferrous and ferric iron species and dissolved organic carbon over a range of particle-size fractions. Research into these aspects could provide data on iron-bearing mineral dissolution rates, optimal well siting, and heavy-metal complexation in the Long Island aquifer system.

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