

Influence of Organic Carbon and
Microorganisms on Iron and
Sulfide Concentrations in Groundwater

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INFLUENCE OF ORGANIC CARBON AND MICROORGANISMS ON IRON AND
SULFIDE CONCENTRATIONS IN GROUNDWATER

ABSTRACT

Twenty water supply wells in northern Missouri were sampled to determine the relationships between dissolved organic carbon and microorganisms on iron and sulfide concentrations in unpolluted ground water. Measurements of the pH, Eh, and bicarbonate and sulfide ion concentrations were done in the field as well as complexing and extracting ferrous iron. The concentrations of ferrous iron, sulfate, chloride, organic carbon, and major cations were determined in the laboratory. The bacterial populations of the water were sampled and keyed out using Bergey's Manual of Determinative Microbiology (1957).

Even though there was no evidence of coliform or streptococcus microorganisms (with one exception), none of the water samples were sterile. In each well, two to six genera of nonpathogenic bacteria were present, the vast majority being nitrate reducers. Sulfate-reducing bacteria were found in about half the waters sampled. Organic carbon and dissolved ferrous iron were readily measureable in all samples. Organic carbon was generally present in low levels (<2 mg/l) except in two samples in a geologic setting where natural organic acids were entering the ground water of shallow wells in alluvium.

The data suggest that there is not a good correlation between the redox potential and the organic carbon content of unpolluted ground water. The organic carbon content of the rocks is a far more important factor in controlling the redox potential due to the fact that many

solid organic compounds are readily digestible by bacteria in the presence of sulfate. The data for nitrate-ammonia and sulfate-sulfide indicate that many of the water samples are not in internal equilibrium with respect to oxidation-reduction reactions.

Considerable data was obtained on the chemical constituents and microorganisms in three areas characterized by high concentrations of dissolved organic carbon, ferrous iron, and hydrogen sulfide. Two of these areas were affected by leachate from sanitary land fill operations; the third was caused by the discharge of organic industrial wastes into a groundwater system. This investigation resulted in two discoveries which appear to be of considerable importance. The first of these is that landfill leachates have a very different total inorganic nitrogen (TIN) to total phosphorus (TP) ratio than sewage lagoon or septic tank effluent and that this ratio is apparently an effective method for distinguishing between these two sources of pollutants in groundwater. The second discovery is that there are microorganisms in groundwater other than members of the genus *Desulfovibrio* which are apparently capable of rapidly converting sulfate to hydrogen sulfide in the presence of total dissolved organic carbon concentrations exceeding 20 mg/l.

One of the major sources of organic carbon in ground water systems in Missouri is leachate from improperly located and/or improperly operated sanitary landfills. Several leachate samples were collected from eight landfill operations in Missouri and analyzed for twenty-one constituents including organic carbon, iron, sulfate, and hydrogen sulfide. The mean organic carbon content of the leachates studied was approximately 4,000 mg/l carbon. Preliminary calculations indicate that one gallon of this kind of liquid is potentially capable of

triggering the formation of hydrogen sulfide in as much as 2,000 gallons of typical Missouri ground water. These landfill leachates are typically about 40 times more potent than septic tank or sewage treatment plant effluent in terms of their relative ability to lower the redox potential of groundwater systems.

Percolation experiments were conducted to evaluate the capacity of the kaolinitic soils from central and southern Missouri to remove organic carbon from leachate. This study showed that less than 5 percent of the organic carbon is removed from the leachate by absorption or entrapment by this kind of treatment. This suggests that sanitary landfills located on residual soils in the Ozarks region of Missouri may pose a greater threat to groundwater quality than is presently suspected.

Data has also been obtained on the abundance of sulfate-reducing bacteria in seeps associated with landfills situated in abandoned strip coal mines. The abundance of *Desulfovibrio* may be as high as 2×10^4 /ml. Other sulfate-reducing organisms, apparently belonging to the genus *Desulfatomaclum*, have been found in domestic wastes and show a remarkable tolerance to pH's as low as 2.7. Laboratory experiments were completed which show that these organisms produce hydrogen sulfide at pH's as low as 4.0 and can induce the evolution of hydrogen sulfide gas from acid mine water enriched with organic carbon. These results indicate the sanitary landfill operations situated in old coal mining pits may produce some environmental problems related to the release of hydrogen sulfide which are not encountered in ordinary landfill operations.

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INTRODUCTION

Ground water from deep wells is widely used for domestic, industrial, and farm needs in northern Missouri. The most common complaints and comments about water quality in this region involve the unpleasant taste and odor from dissolved iron and hydrogen sulfide. The purpose of this investigation was to determine the effect of organic carbon in the water on controlling iron and sulfide concentrations in water supplies from selected sources in northern Missouri.

Regulations concerning surface water quality in recent years have caused many industries and municipalities to seek alternatives to discharging wastes into surface streams. The result has been an increase in land disposal of wastes such as in landfills and waste lagoons. This trend will inevitably lead to an increase in organic carbon levels in ground water with accompanying changes in water chemistry. It is hoped that once the role of organic carbon in natural systems is understood, a model can be developed to predict the effects of introducing organic pollutants into ground water.

BACKGROUND

Introduction to the Role of Organic Carbon, Oxidation-Reduction Reactions and Bacteria in Ground Water

Iron, sulfur, and manganese generally cause water quality problems only when the redox potential of the water is low. Reducing conditions favor the formation of hydrogen sulfide and increase the solubility of iron and manganese oxides. Because the redox potential and the pH determine the form and concentration of redox sensitive elements, it is important to determine the redox potential of groundwater systems and to determine which factors control the redox potential of these systems.

The oxidation of organic carbon has the effect of lowering the redox potential of ground water. Bacteria, most of which require organic carbon as a nutrient, catalyze many oxidation-reduction reactions. Thus it is apparent that organic carbon, bacteria, and oxidation-reduction reactions are all interrelated in controlling some of the chemical characteristics of ground water.

Organic Carbon in Groundwater Systems

Introduction: Because of the reduction of iron oxides and sulfate in the system by reducing agents, ground water containing enough iron or hydrogen sulfide to be detected by taste or smell always has a low redox potential. The predominant reducing agent in natural ground water is organic carbon (Carpenter, 1971). This organic carbon may be

present in dissolved or particulate form obtained by leaching organic material at the earth's surface, or as organic carbon contained within sedimentary rocks. The rate of various oxidation-reduction reactions is dependent on the kinds and amounts of organic carbon and bacteria present in the system (Carpenter, 1971).

Several investigators have suggested the use of dissolved organic carbon as an indicator of polluted water. Therefore, it is useful to review the normal levels of organic carbon in unpolluted ground waters and to note to what extent organic carbon in water may be used to recognize ground water contamination and pollution.

Normal Background Levels of Organic Carbon in Ground Water:

Leenheer, et al. (1974) collected 100 uncontaminated ground water samples in 27 states and found that the concentration of nonvolatile dissolved organic carbon (DOC) ranges from less than 0.1 mg/l to 15 mg/l, with a mean of 1.2 mg/l and a median of 0.7 mg/l. Robinson, Connor, and Engelbrecht (1967) found that the DOC concentrations in the ground water supplies of five small towns in Illinois ranged from 1.5 to 7.2 mg/l. The DOC concentrations of uncontaminated wells near Barstow, California ranged from 0.1 to 0.8 mg/l (Hughes et al., 1974). Shvets (1971) reported the average DOC of 308 ground waters in the USSR to be 3.6 mg/l. He also noted that water-soluble organic substances constitute only 7 to 22 percent of the total organic carbon in ground water, while the volatile organic compounds, averaging 24 mg/l (28 samples), predominate in ground water not associated with petroleum or gas deposits. In the Gulf Coast region, Buckley, Hocott, and Taggart (1958) found dissolved gas concentrations equivalent to 1,340 mg/l DOC in ground water obtained from depths down to 10,000 feet. Shvets (1971) stated that the volatile

organic compounds include fatty acids, ethers, low-molecular-weight alcohols, aromatic hydrocarbons, terpenes, and amines. The difficulties of sampling and measuring the volatile components have led most investigators to examine the concentrations of nonvolatile organic carbon, which Reuter and Perdue (1972) and Schnitzer (1971) have shown to be predominantly fulvic acid. The highest concentrations of organic compounds that Shvets (1971) found were in ground waters in direct contact with petroleum or gas where they reach 370 and 826 mg/l, respectively.

Factors Controlling the Concentration of Organic Carbon: Leenheer, et al. (1974) found that DOC levels increase with increasing specific conductance and alkalinity. They theorize that mineralized water may contain large amounts of alkali-metal carbonates which may react with insoluble organic acids to form soluble organic salts. In a study of source rock effects, Leenheer, et al. (1974) found the same median value of 0.7 mg/l of DOC for sandstone, limestone, and sand and gravel aquifers. Crystalline rock aquifers had a median between 0.4 and 0.5 mg/l DOC.

It would seem likely that shallow (<200 feet) sand and gravel aquifers would be more likely to be contaminated with organic carbon from the surface than deep (>200 feet) sand and gravel aquifers. However, Leenheer, et al. (1974) found that the median value for both deep and shallow sand and gravel aquifers was 0.7 mg/l DOC. Selected examples from their data, however, appear to demonstrate that the geologic setting of a well may cause the natural DOC to be higher than the average background levels. A shallow well receiving natural organic-rich recharge from a swampy area near Miami, Florida contained

15.0 mg/l DOC. These investigators suggest that the DOC levels of 6.9, 5.0, and 3.2 mg/l from specific locations in Illinois and Michigan may be higher than the median because the aquifers contain small amounts of oil, gas, or coal.

Use of Concentration of Organic Carbon as an Indicator of Organic Water Quality: Direct measurement of the amount of organic carbon in water by measuring the degree of absorbance of infrared light by the CO_2 produced by combustion of the organic carbon at 950°C is free from the difficulties which are inherent in the biological oxygen demand (BOD) and chemical oxygen demand (COD) methods. Because the background levels of dissolved organic carbon are typically very low, even small amounts of contamination can readily be detected. Organic contamination will often cause an increase in DOC of one order of magnitude or more over background levels. Values in excess of 5 mg/l DOC normally indicate contamination and pollution from infiltrating surface water or subsurface waste disposal operations (Leenheer, et al., 1974).

Bacteria in Groundwater Systems

Many oxidation-reduction reactions have activation energies which cause the reaction rates to be very slow or which effectively prevent the reaction from proceeding at all. Certain types of bacteria have been found to contain enzymes which catalyze the electron transfer in oxidation-reduction reactions, thereby obtaining energy for their life processes. The bacteria are said to mediate the reaction and in many cases are effective in overcoming activation energy barriers and increasing reaction rates. For example, at temperatures below 50°C ,

sulfate is not reduced to sulfide in sterile systems in time equivalents of 150 million years (Feely and Kulp, 1957; Martens and Berner, 1975; Orr, 1974). Sulfate-reducing bacteria, however, are known to be capable of producing hydrogen sulfide from sulfate at rapid rates; i.e., 1000 mg/l in 24 hours (Miller, 1949). Leathen, et al. (1956) found that the ferrous iron contained in acid mine waters in amounts of 200 mg/l was completely oxidized by a culture of iron-oxidizing bacteria in three days, whereas the chemical oxidation of a sterile solution of iron by atmospheric oxygen, at the same pH, required more than 2 years.

Since bacteria have the potential to greatly influence water chemistry, it is important to investigate the growth requirements of bacteria to understand if bacteria can survive in groundwater systems and if so, under what conditions. Because bacteria are approximately 1 μ in diameter, subsurface regions with sufficient porosity and permeability to transmit and store appreciable quantities of water have pores of sufficient size and quantity to be a potential microbial habitat.

In regions of the zone of saturation where ground waters are highly mineralized, the availability of water to many organisms would be severely restricted because of high osmotic pressures. However, bacteria differ greatly in their ability to withstand and adapt to high osmotic pressures, and some have been found which will tolerate water containing up to 30 percent dissolved salts (Zajic, 1969).

Temperature is one of the most important environmental factors controlling the growth and survival of microorganisms. In general, the metabolic rate is roughly doubled for every 10⁰C increase in temperature until a temperature is reached where the rate of thermal denaturation of enzyme protein exceeds the thermal stimulation of enzyme reaction

rates. Depending on the resistance of their enzymes to thermal denaturation, different bacteria have varying optimum growth temperatures and limiting survival temperatures. Based on upper temperature limits of 80°C for growth and 100°C for survival (Dunlap and McNabb, 1973) and a geothermal gradient of 30°C per 100 m of depth, some bacterial activity should be possible to depths of 1800 m (5900 ft) and some bacteria should be able to exist to a depth of about 2500 m (8200 ft).

Dunlap and McNabb (1973) reviewed the literature on the response of microorganisms to hydrostatic pressure and concluded that hydrostatic pressures are not likely to exclude microbial activity in subsurface regions which are otherwise suitable as microbial habitats.

The oxidation-reduction conditions in which bacteria can grow have been cited by Vallentyne (1963) as ranging from an upper pe limit of 14.38 at pH 3 for iron bacteria to a lower pe limit of -7.62 at pH 9.5 for sulfate-reducing bacteria. The total exclusion of bacteria from a groundwater system as a result of unfavorable pH-pe conditions alone is most unlikely. However, since different species are usually able to live only within a relatively narrow range of redox values, the oxidation-reduction conditions in a given environment will determine what species can successfully inhabit that region and may determine the metabolic products of those microbes.

Finally, a microbial habitat must provide resident bacteria with the nutrients needed for protoplasm synthesis and for the generation of energy needed to conduct life processes. To produce protoplasm, a source of carbon, either carbon dioxide or organic carbon, is required, along with small amounts of nitrogen, phosphorus, and sulfur. As discussed in the previous section, organic carbon is present in sufficient quantity in the earth's crust and ground waters to support microbial growth.

The type of organic compound is very important, however, as some forms of carbon are utilized by microorganisms only very slowly and others may actually inhibit the growth of microorganisms.

The generation of energy by chemotrophic organisms requires 1) a suitable electron donor, such as oxidizable organic matter, or for chemolithotrophs, oxidizable inorganic compounds like molecular hydrogen, reduced sulfur compounds, ammonia, nitrite, and ferrous iron; and 2) suitable electron acceptors such as molecular oxygen, nitrate, sulfate, carbon dioxide, and simple organic compounds. These requirements are generally fulfilled in most ground waters.

Therefore, the requirements of space, availability of water, temperature, hydrostatic pressure, oxidation-reduction conditions, and nutrients will be met for at least some genera of microbes in most ground waters. Ground water should thus be a suitable habitat for bacteria and if so, the water chemistry may be greatly influenced by the particular bacteria present.

Oxidation-Reduction Reactions in Groundwater Systems

Measurement and Study of Redox Potential: The redox potential of a solution is a measure of the oxidizing or reducing tendency of a solution. Because oxidation and reduction are basically electrical processes, this tendency may be measured by an electrical potential called Eh. Traditionally, the determination of redox potential in ground water has consisted of measuring the potential produced by electron exchange at the inert surface of a platinum electrode compared to the constant potential of a calomel (Hg-HgCl_2) reference electrode. The Eh is related to the measured potential (Emf) as follows:

$$E_h = E_{mf} + E_{cal} \quad (1)$$

where E_{cal} is the potential of a saturated calomel electrode at the temperature of the solution being measured. Tabulated values of E_{cal} for various temperatures are available in the literature (Ives and Janz, 1961).

Truesdell (1968) explained the advantages of expressing the redox potential in terms of pe instead of Eh. Eh can be converted to pe by

$$pe = \frac{E_h \cdot F}{2.3 RT} \quad (2)$$

where F is the faraday constant, R is the gas constant, and T is the Kelvin temperature. Large positive values of pe represent strongly oxidizing conditions while small or negative values correspond to strongly reducing conditions.

The current of electrons produced by the reaction $ox + e^- \rightarrow red$ at the surface of the electrode is called the "cathodic exchange current," i_{cat} . The reaction $red \rightarrow ox + e^-$ produces a current of electrons called the "anodic exchange current," i_{an} . By convention, cathodic currents are negative and anodic currents are positive.

$$i = i_{cat} + i_{an} \quad (3)$$

where i is the net current passing through the electrodes. A redox reading free of drift can only be obtained when the net current is equal to zero.

The net current will only be zero for a reaction that is rapid and readily reversible (electroactive). According to Stumm (1967), with the exception of $Fe^{2+}-Fe^{3+}$ and possibly the manganese couple, none of the redox couples in natural systems (including $NO_3^- - NO_2^- - NH_4^+$, $SO_4^{2-} - H_2S$,

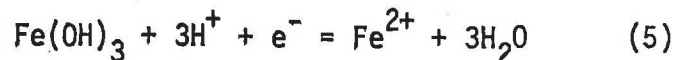
and most organic couples) are sufficiently electroactive to control the measured potential. Stumm (1967) stated that for any couple in solution, both the oxidized and reduced species must be present in concentrations greater than or equal to 10^{-6} M to ensure that sufficient current is produced to be detected at the surface of a platinum electrode. In the case of the iron couple, ferric iron oxide compounds are so insoluble that ferric iron concentrations exceed 10^{-6} M only in oxygenated acid mine water with a pH of less than 3. Berner (1963) has shown that the half-cell



can control platinum electrode redox potentials in H_2S -rich sediments. In this case, colloidal elemental sulfur acts in the same manner as a dissolved, electroactive chemical species.

One complication of electrode measurements is that the redox potential of natural systems can represent a mixed potential. The current is the sum of all the anodic and cathodic currents produced by all oxidation-reduction reactions taken together. The Eh is the potential at which this net current is zero, but it is not necessarily the equilibrium potential for any one redox couple.

In spite of the preceding difficulties, some environments isolated from the atmosphere at pHs above 4 yield measured Eh values that stabilize rapidly and reproducibly and appear to have thermodynamic significance (Langmuir, 1971a). This is probably a reflection of the forms of iron present under such conditions. At pHs above 4, many anoxic waters are in equilibrium with ferrous iron and ferric oxyhydroxides. Stumm (1967) found the reaction



is electroactive and can produce a stable and reproducible Eh at pH 7 for Fe^{2+} concentrations as low as 0.6 ppm.

Doyle (1968) found that if a film of ferric oxide forms on the electrode during measurement (by the reaction of Fe^{2+} with oxygen adsorbed on the surface of the electrode and/or sorption of colloidal ferric oxide) a stable potential can be measured even if the ferric ion activity is several orders of magnitude too low to sustain the minimum current required to maintain stable potential readings. The stable potentials approximate the Nernst potential for the reaction



Langmuir (1971a) states that Doyle's work shows that reaction (5) is catalyzed by the layer of ferric hydroxide which forms on the electrode. Therefore, he feels that because of reaction (5) and the reaction

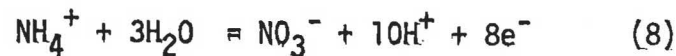


Eh measurements are sometimes possible which are consistent with the activities of iron species present.

Doyle (1968) states that if the electrode always becomes coated with ferric oxide in a solution of ferrous iron, it is hard to understand how the true redox potential of such a solution could be measured.

Stumm (1967) endorses the calculation of redox potentials from analytical information. This method has been fully described by Truesdell (1968), Stumm and Morgan (1970), and others. For example, if both nitrate and ammonia are present in a water sample, the pe can be calculated by the following steps:

1) Write the equation relating the two redox species.



2) Write the equilibrium constant expression for this reaction.

$$K_N = \frac{[\text{NO}_3^-] [\text{H}^+]^{10} [\text{e}^-]^8}{[\text{NH}_4^+]} \quad (9)$$

3) Take the log of this expression. Although aqueous solutions do not contain free protons and free electrons, it is nevertheless possible to define a relative electron activity ($\text{pe} = -\log [\text{e}^-]$) analogous to relative proton activity ($\text{pH} = -\log [\text{H}^+]$) (Stumm and Morgan, 1970).

$$\log K_N = \log \frac{[\text{NO}_3^-]}{[\text{NH}_4^+]} - 10 \text{ pH} - 8\text{pe} \quad (10)$$

4) Solve for pe.

$$\text{pe}_N = \frac{-\log K_N}{8} - \frac{\log \frac{[\text{NO}_3^-]}{[\text{NH}_4^+]}}{8} - 1.25 \text{ pH} \quad (11)$$

Using the same method, the pe can be calculated if both hydrogen sulfide and sulfate are measurable in the same sample:

$$\text{pe}_S = \frac{-\log K_S}{8} - \frac{\log \frac{[\text{SO}_4^{2-}]}{[\text{H}_2\text{S}]}}{8} - 1.25 \text{ pH} \quad (12)$$

Thorstenson (1970) used this analytical approach to determine redox potentials but found that in some instances widely differing redox potentials are calculated from different redox couples present in the same water samples. At the present time there does not appear to be any widespread agreement as to the best method of determining the redox potential in natural water systems. In fact, Carpenter (1971), has

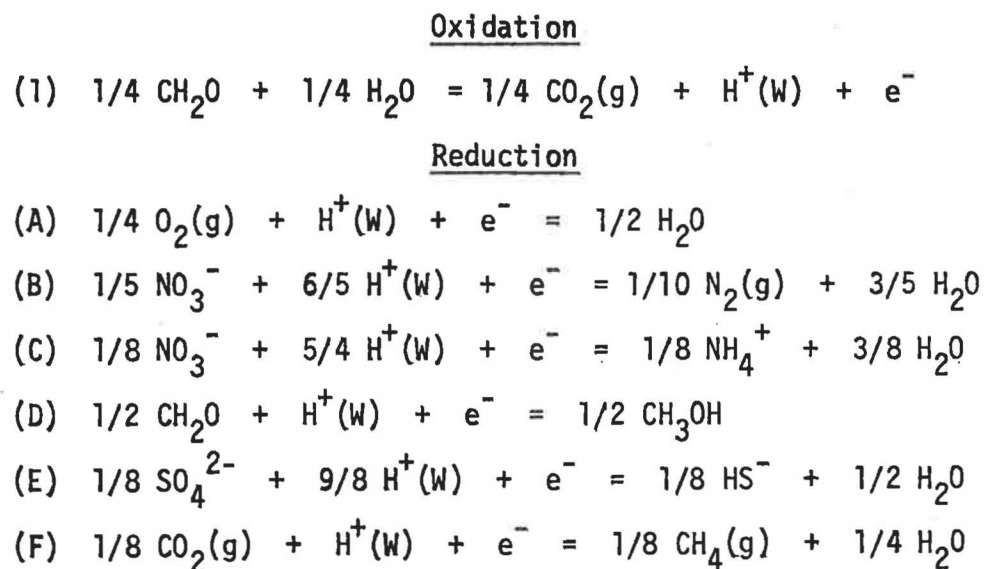
suggested that most natural waters may be sufficiently out of redox equilibrium that they cannot be said to have a unique redox potential.

Sequence of Microbially Mediated Oxidation and Reduction Reactions: Living organic matter is composed of reduced carbon compounds with high-energy bonds. Once a living entity dies, its organic carbon is subject to oxidation which releases energy and thus makes the organic matter thermodynamically more stable. Several oxidizing agents may be available in natural waters. The oxidizing agent which will yield the most energy from the oxidation reaction will be preferred while less energy-yielding oxidizing agents will be repressed.

Stumm and Morgan (1970) presented a model for the oxidation of an excess of carbohydrate (CH_2O). Table 1 shows some possible oxidation and reduction reactions and the energy yields for oxidation of the carbohydrate by various oxidizing agents. The $\Delta G^0(W)$ expresses the free energy change in kcal per electron at pH 7. The $\Delta G^0(W)$ value for aerobic respiration is the most negative which shows that oxidation of carbohydrate by oxygen yields the most energy and thus it is likely that oxygen will be consumed first in the oxidation process. When the oxygen is gone, nitrate will react as the oxidizing agent and fermentation, sulfate reduction, and methane fermentation reactions will follow in order. Since the reactions considered are biologically mediated, the chemical reaction sequence is accompanied by a succession of microorganisms from aerobic heterotrophs to denifiers, fermenters, sulfate reducers, and methane bacteria.

Dissolved Oxygen: It is possible to calculate the theoretical partial pressure of oxygen gas (P_{O_2}) in a particular system for a given

TABLE 1.
Reactions Involved in Oxidizing an Excess of Carbohydrate¹



Sequence of Microbial Mediation

	<u>Combination</u>	<u>$\Delta G^0(\text{W})$</u> <u>kcal</u>
Aerobic respiration	(1) + (A)	-29.9
Denitrification	(1) + (B)	-28.4
Nitrate reduction	(1) + (C)	-19.6
Fermentation	(1) + (D)	-6.4
Sulfate reduction	(1) + (E)	-5.9
Methane fermentation	(1) + (F)	-5.6

¹From Stumm and Morgan (1970)

pe and pH as shown below:



$$\text{Log } K = \text{Log } P_{\text{O}_2} - 4\text{pH} - 4\text{pe} \quad (14)$$

$$\text{Log } P_{\text{O}_2} = \text{Log } K + 4\text{pH} + 4\text{pe} \quad (15)$$

P_{O_2} values are related to pe and pH as shown in Figure 1. The pe-pH diagram in Figure 1 also shows the position of the analytical detection limit for dissolved oxygen (0.1 mg/l). This O_2 concentration coincides with the point where it has been suggested that anaerobic biologic processes become predominant over aerobic ones (Carpenter, 1971).

Nitrogen Reactions and the Nitrogen Cycle: The earth's reservoir of nitrogen to meet the protein synthesis requirements of all organisms is the N_2 gas of the atmosphere. Nitrogen gas is inert to most organisms but a small group of blue-green algae and nitrogen-fixing bacteria assimilate atmospheric nitrogen and release ammonia. Upon the death of these microorganisms additional nitrogen is released by decomposition as free amino acids and as ammonia. The ammonia can be used as a nutrient or it may be oxidized to nitrite and then to nitrate. In addition, the nitrite may react with the ammonia to produce N_2 gas and H_2O . This process completes the nitrogen cycle shown in Figure 2.

Problems in breaking the strong bonding in the N_2 molecule cause a kinetic barrier to reactions between N_2 and NO_3^- , NO_2^- , and NH_4^+ . In natural water systems, N_2 essentially acts as an inert species. Therefore, it is useful to consider a system in which NO_3^- , NO_2^- , and NH_4^+ are treated as active participants in redox reactions and to ignore potential reactions involving N_2 . The predominance fields of these species are shown in Figure 3 and have been calculated from thermodynamic data in Wagman, *et al.* (1968).

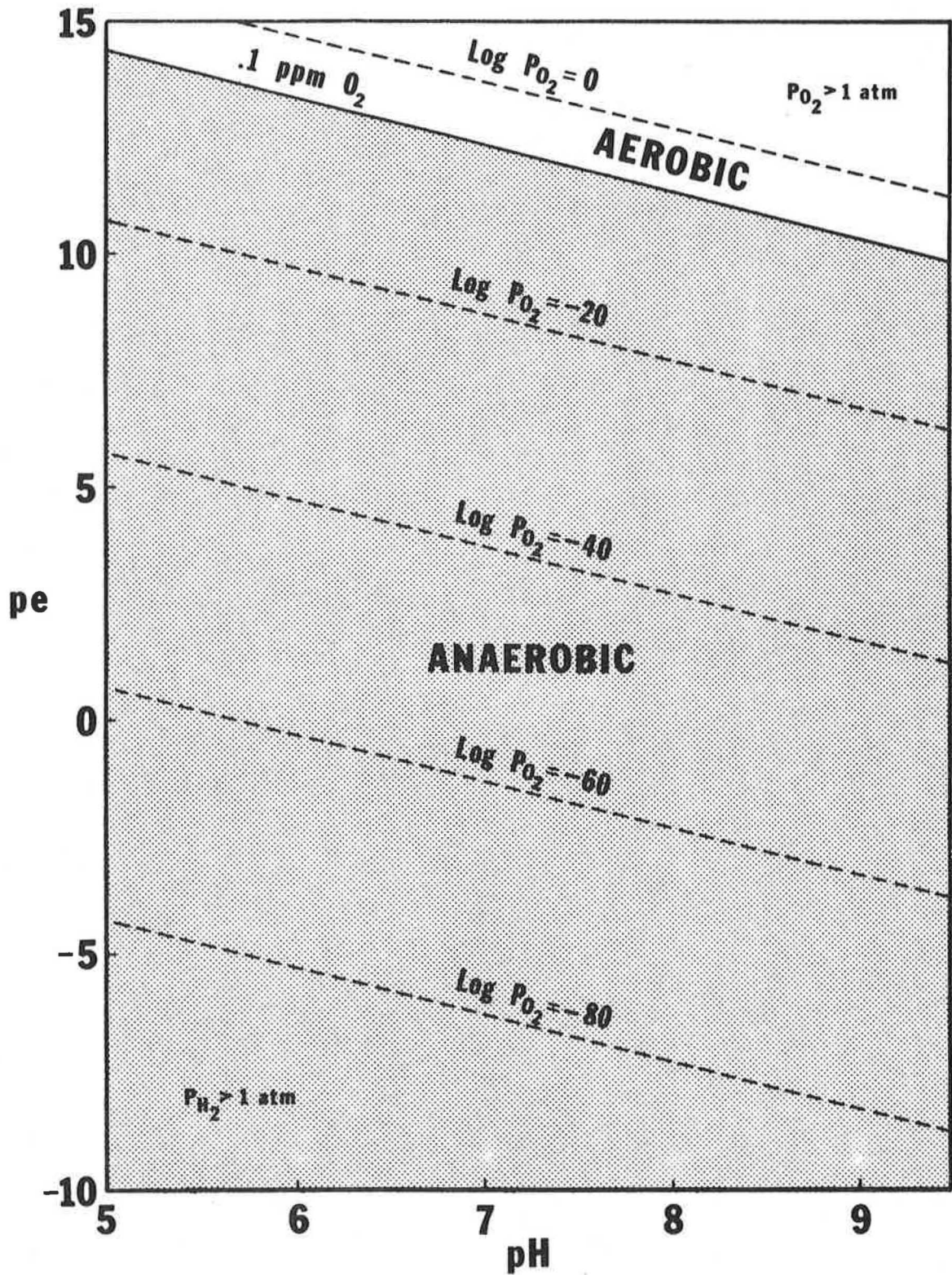


Figure 1. Relationship of $\log P_{O_2}$ to pH and pe at 25°C and 1 atm.

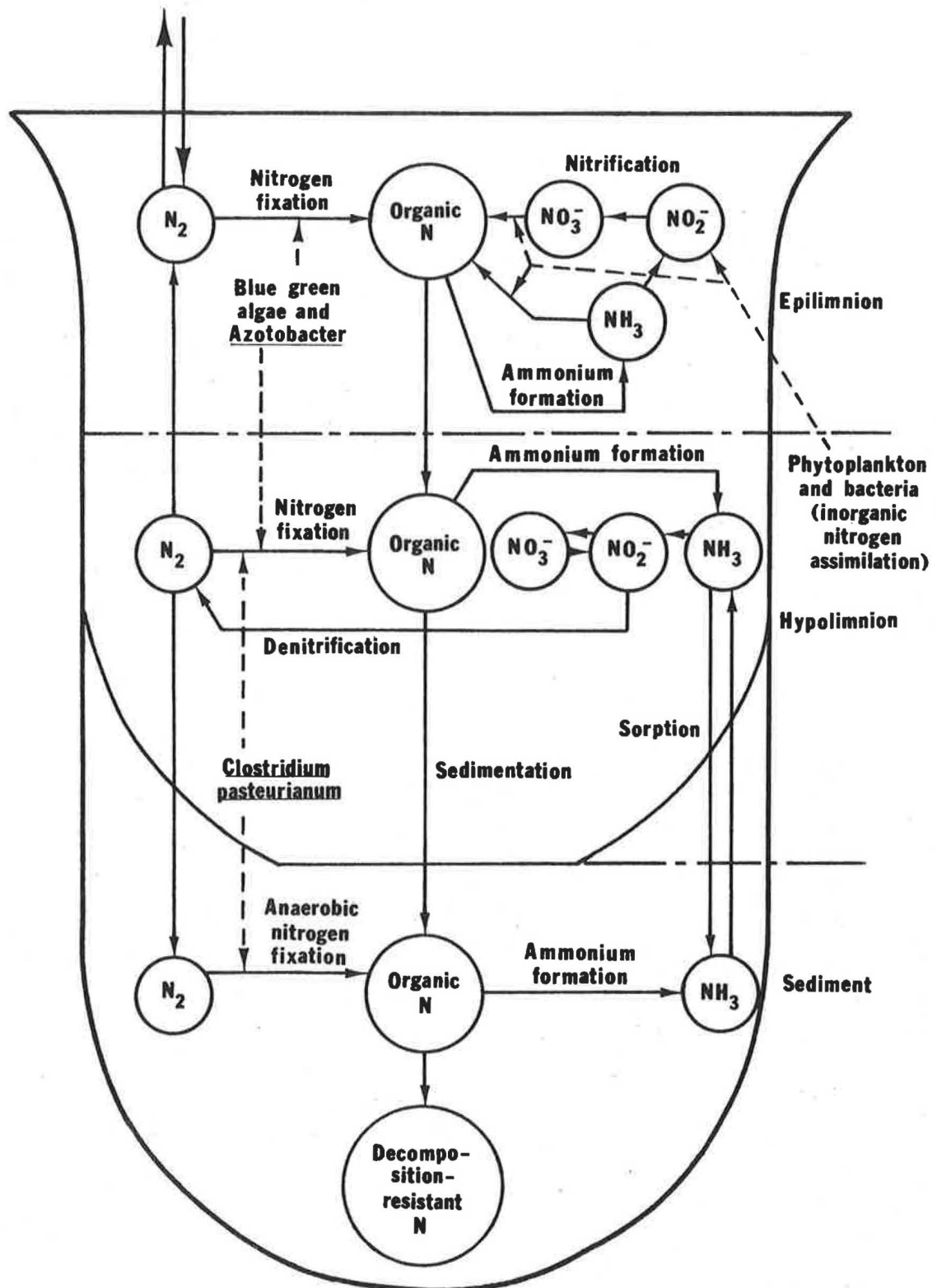


Figure 2. Nitrogen cycle reactions in an idealized stratified lake. After Brezonik (1972) as adapted from Kuznetsov (1959).

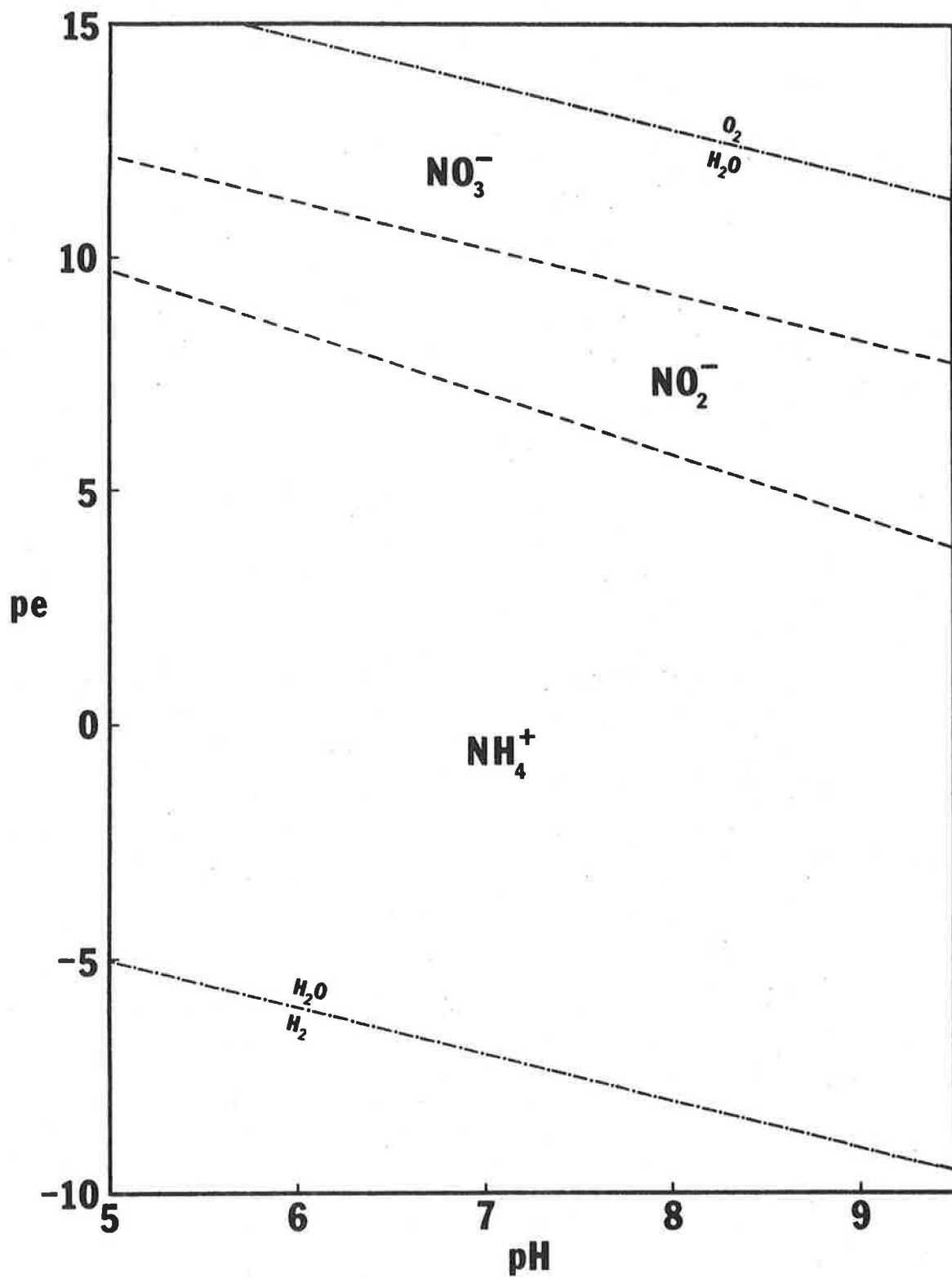
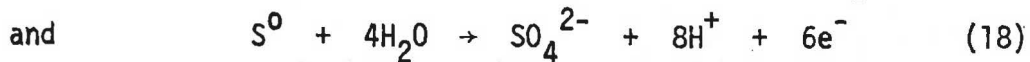
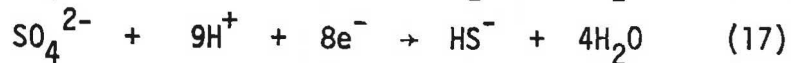
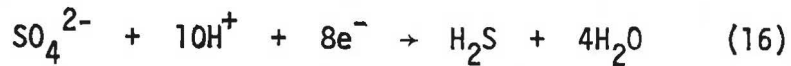


Figure 3. Predominance fields of the aqueous nitrogen species at 16°C and 1 atm.

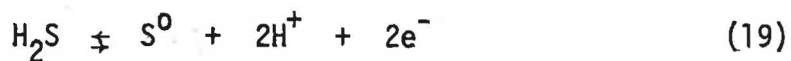
Sulfur Reactions and the Sulfur Cycle: Valensi (1950) showed that SO_4^{2-} , H_2S , and HS^- are the sulfur species which predominate between pH 5 and 9.5 (Figure 4).

The reaction pathways between the dominant sulfur species are shown schematically in Figure 5. It is important to notice that the reactions



are not reversible in sterile systems at temperatures less than 100°C and bacterial mediation is required for the reverse reactions to proceed.

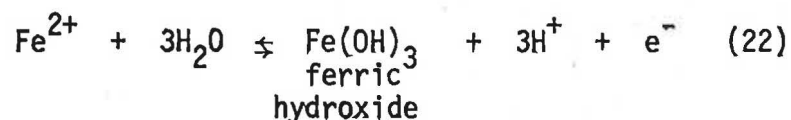
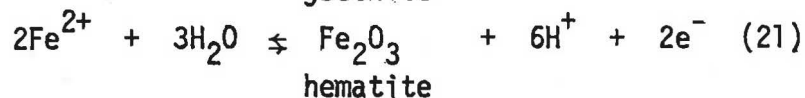
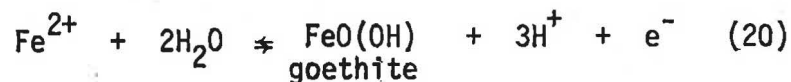
The reaction



does proceed rapidly and reversibly in sterile systems although some bacteria mediate this reaction also.

Iron: The range of predominance of various aqueous iron species in terms of pe and pH (Figure 6) is such that Fe^{2+} is the only significant species in solution at the pH and pe normally encountered in natural groundwater systems.

Under normal groundwater conditions, Fe^{2+} is derived from the reduction of iron oxide minerals, probably goethite, hematite, or ferric hydroxide:



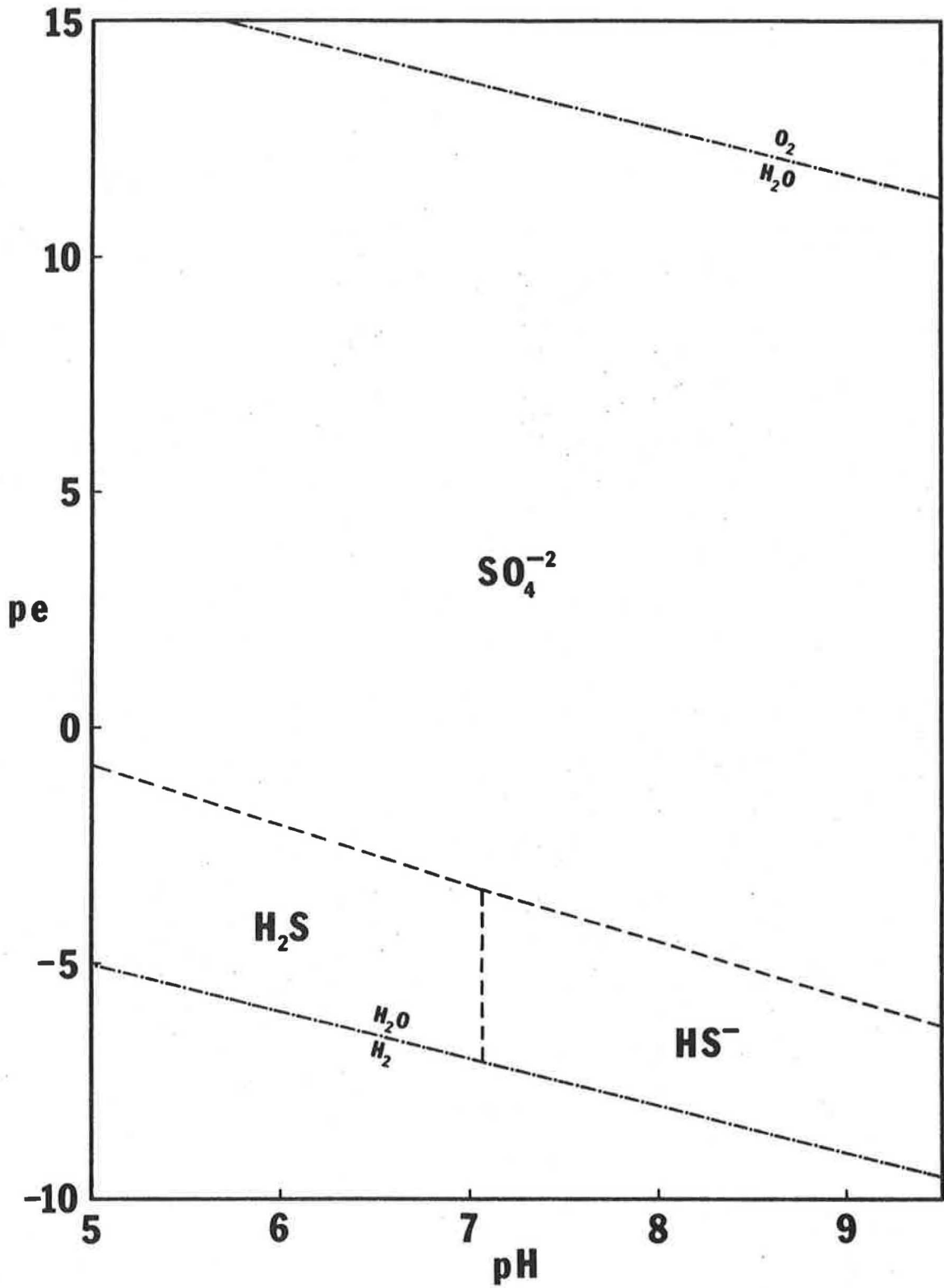


Figure 4. Predominance fields of the aqueous sulfur species at 16°C and 1 atm.

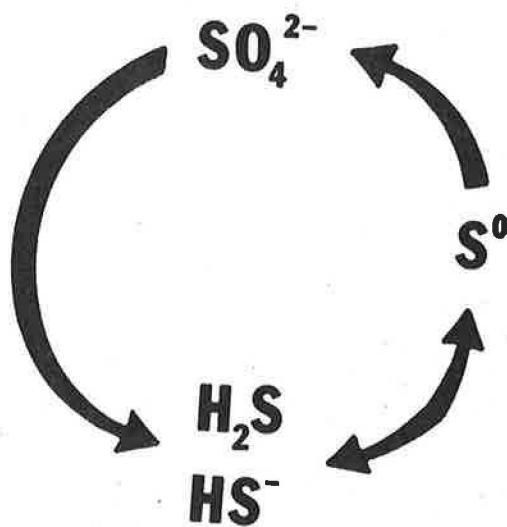


Figure 5. The sulfur cycle.

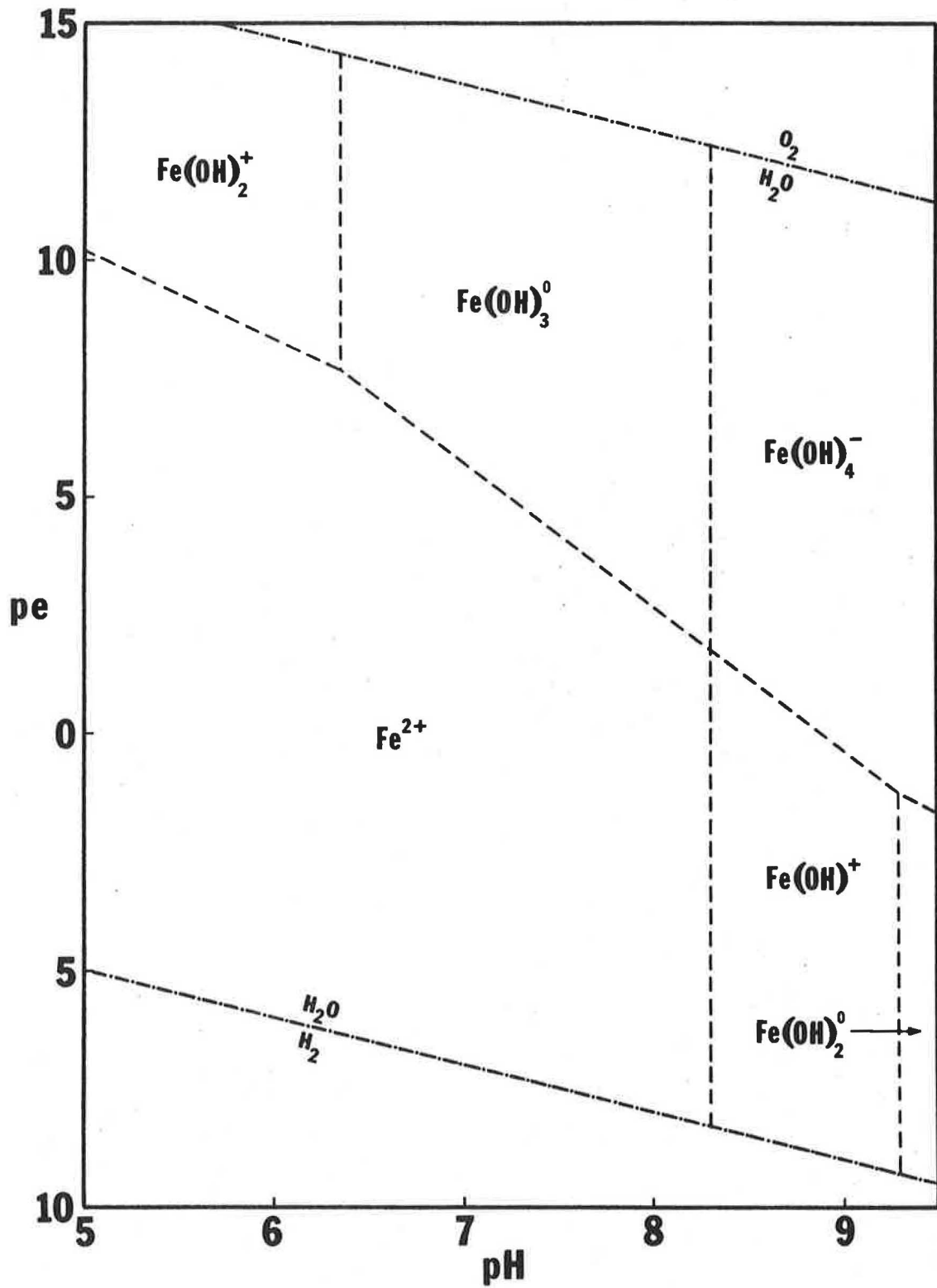
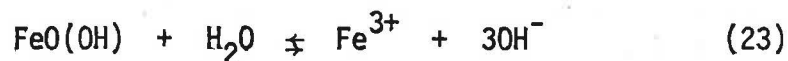


Figure 6. The predominance fields of the aqueous iron species at 25°C and 1 atm. calculated using data from Langmuir (1971b). After Carpenter (1974).

Therefore, the stability of the ferric oxyhydroxide mineral(s) present is a very important factor influencing the amount of iron in solution. Because goethite, hematite, and ferric hydroxide all have different compositions, their free energies of formation can not be used directly as indicators of relative stability. Also, Langmuir and Whittemore (1971) have shown that the stability of these minerals is quite variable and depends on the degree of crystallinity and particle size.

However, Langmuir and Whittemore (1971) showed that equations can be written to obtain Fe^{3+} and OH^- from each of the three iron minerals of interest as follows:



which in turn makes it possible to calculate their relative stability.

The negative logarithm of the thermodynamic activity product expressions for these reactions can be written as

$$p^Q\text{Fe(OH)}_3 = -\log [\text{Fe}^{3+}] [\text{OH}^-]^3 \quad (26)$$

or

$$p^Q\text{Fe(OH)}_3 = p[\text{Fe}^{3+}] + 3(pK_w - \text{pH}) \quad (27)$$

The $p^Q\text{Fe(OH)}_3$ is an index of relative stability which reflects the crystal structure, degree of crystallinity, and the particle size of the mineral.

In nearly all field situations, the concentration of dissolved ferric iron is well below analytical detection limits. Consequently, the value of $p[\text{Fe}^{3+}]$ is calculated from data on $p[\text{Fe}^{2+}]$ and p_e from the equations



$$\text{Log } K = p[\text{Fe}^{2+}] - p[\text{Fe}^{3+}] - p_e \quad (29)$$

$$p[\text{Fe}^{3+}] = -\text{Log } K + p[\text{Fe}^{2+}] - p_e \quad (30)$$

Langmuir and Whittemore (1971) report occurrences of $p^Q\text{Fe}(\text{OH})_3$ in natural waters ranging from 37.1 (most soluble) to 43.5 (most stable). If the p^Q of the ferric oxide in equilibrium with a water system is known, one can predict the activity (or alternatively the concentration) of Fe^{2+} in the water at a particular pH and p_e (Figure 7). It should be noted, however, that the effectiveness of this prediction depends on the ability to measure p_e , both for the initial determination of p^Q and subsequently for determining the nature of a particular water sample. In view of the present uncertainty about the validity of measuring the redox potential of natural waters the results of these types of calculations must be used with a great deal of caution.

Manganese: Hem (1963) showed that Mn^{2+} is the only significant dissolved manganese species below pH 10. Figure 8 shows the stability fields of the manganese oxide minerals commonly found in nature relative to specific concentrations of Mn^{2+} .

In spite of the high solubility of the manganese oxides at $P_{\text{O}_2} < 10^{-10}$ atm, analyses of ground waters from water supply wells rarely report dissolved manganese in excess of 0.1 mg/l. One factor affecting this occurrence is that manganese is not very abundant in the earth's crust--about .10 weight percent compared to nearly 5.0 percent for iron (Hem, 1963). In a few places the absence of manganese-containing minerals may limit the amount of Mn^{2+} in ground water. However, minor amounts of manganese-containing minerals are relatively common in soils and sedimentary rocks.

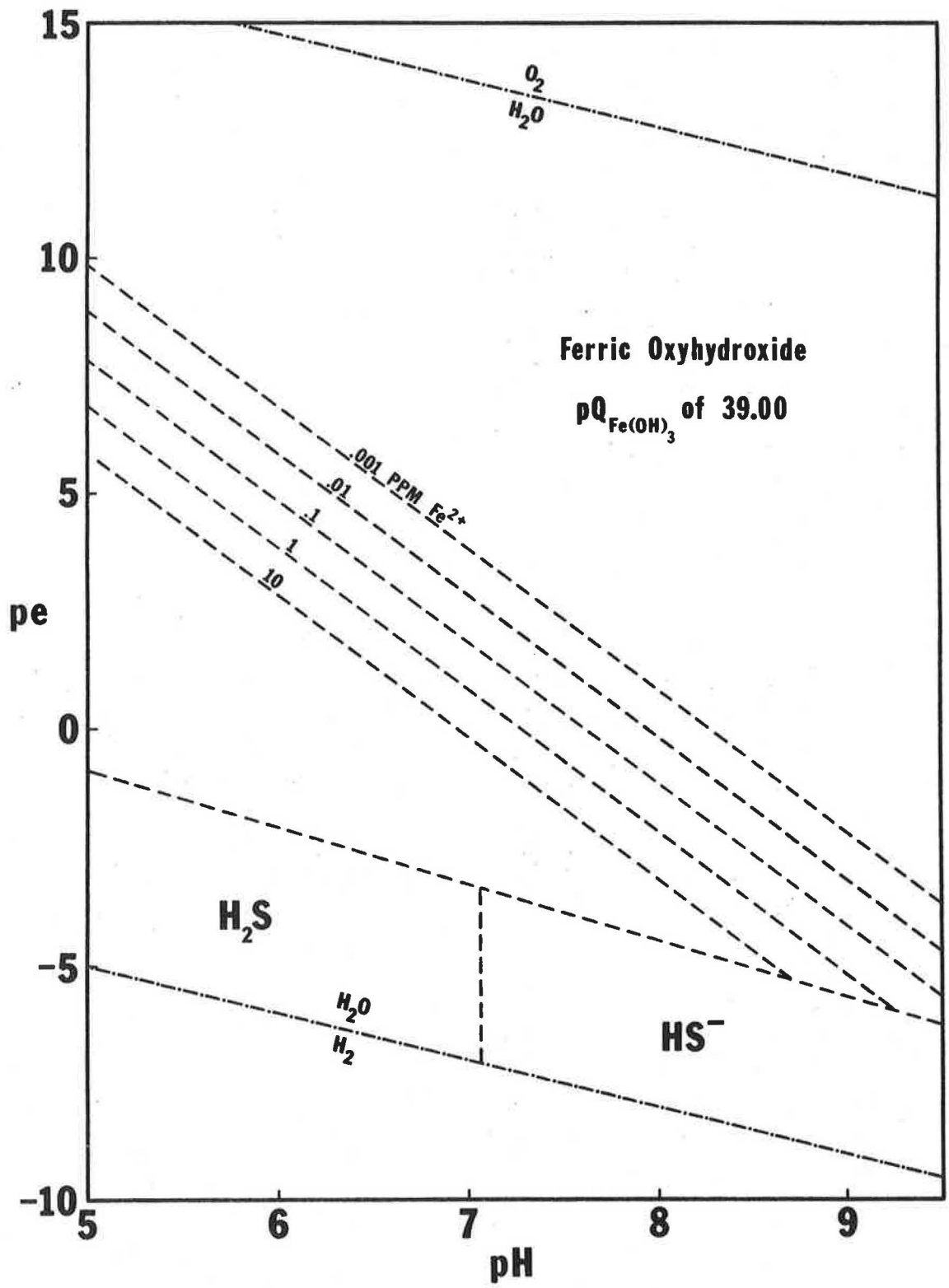


Figure 7. Predicted concentrations of Fe^{2+} in relation to pe and pH with $pQ_{Fe(OH)_3} = 39.0$.

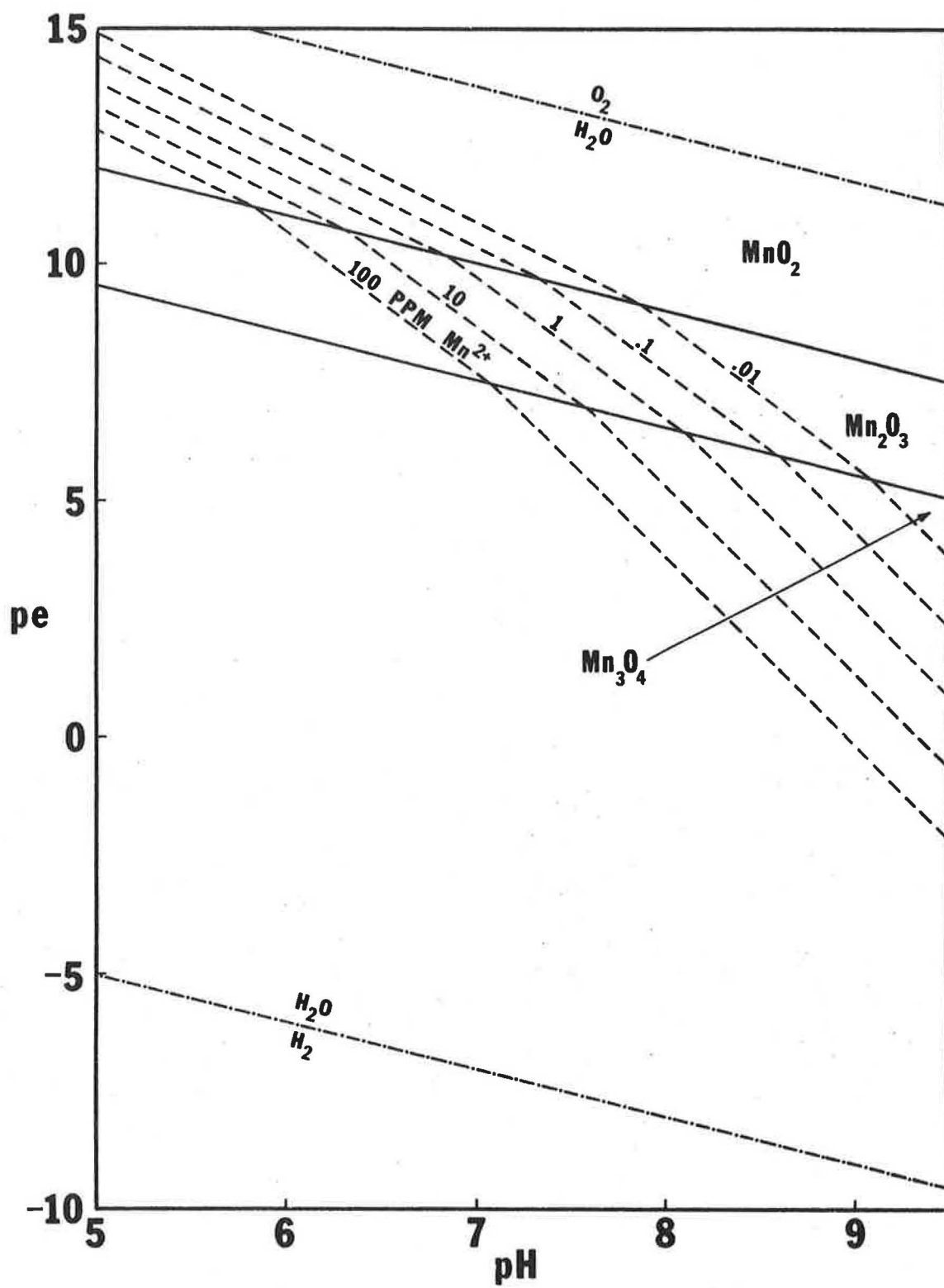


Figure 8. Manganese concentrations in equilibrium with manganese oxide minerals at 16°C and 1 atm.

The coprecipitation of manganese in calcium carbonate as calcite appears to be the most important factor limiting the concentration of manganese in natural waters (Figure 9; Carpenter, 1975).

Methanogenic Reactions: Claypool and Kaplan (1974) calculated energy yields to show that sulfate-reduction and methane formation should be mutually exclusive in marine sediments. They suggest, as have Nissenbaum et al. (1972) and Zobell (1947), that the most important mechanism for methane formation in the marine environment is reduction of CO₂ by biologically produced hydrogen



The experiments of Martens and Berner (1974) have shown that methane production does not begin until dissolved sulfate is completely exhausted. They propose that upward diffusion of methane or methane production in sulfate-free microenvironments can explain why sulfate and methane sometimes occur together in the upper parts of anoxic sediments.

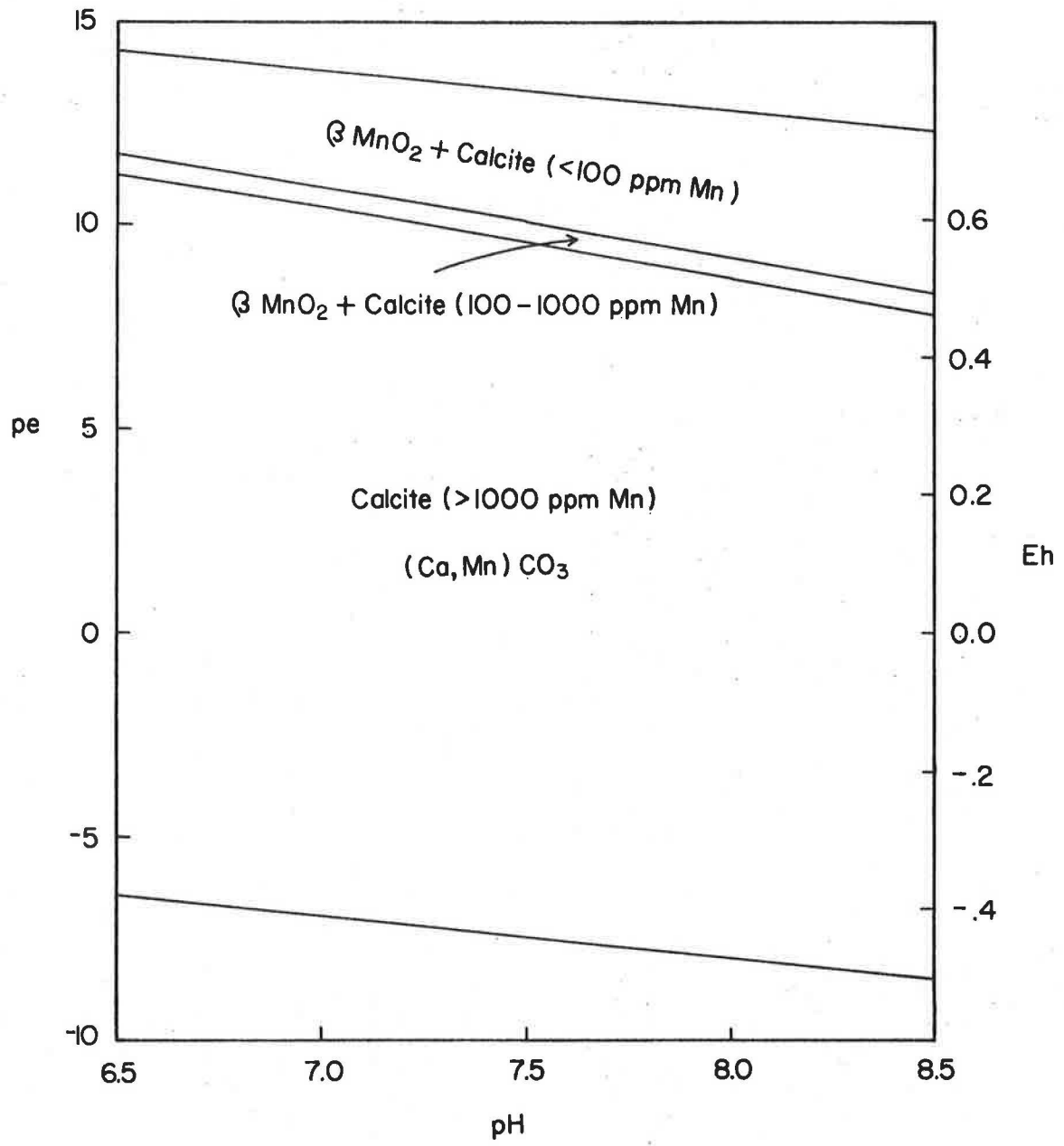


Figure 9. Manganese concentrations in equilibrium with manganese oxide minerals and calcite at 25°C and 1 atm.

METHODS OF STUDY

General Geology of Study Area and Criteria for Selection of Well Sites

The area selected for study is located within the northern third of Missouri (Figure 10). Six of the seven geohydrologic units of Missouri described by the United States Geological Survey (Meisch, 1971) are present in this area, either on the surface or in the sub-surface. These units include 1) unconsolidated stratified sands, silts, and clays of Quaternary alluvium; 2) unconsolidated glacial drift composed of generally unstratified sands, gravels, silts and clays; 3) Pennsylvanian consolidated sandstone, shale, limestone, and coal; 4) Mississippian limestone; and 5) Cambrian and 6) Ordovician dolomite and sandstone. Average elemental and mineralogic compositions for each of these units have been described elsewhere (Meisch, 1971). The bedrock geology is shown schematically in Figure 10.

The major aquifers in the study area are the Upper Ordovician St. Peter Sandstone, the Lower Ordovician Roubidoux Formation, glacial drift, and Quaternary alluvium.

Wells were selected which appeared likely to exceed the United States Public Health Service drinking water standards (USPHS, 1962) for at least one of the following: iron, hydrogen sulfide, sulfate, chloride, or total dissolved solids. It was anticipated that these wells would contain some of the species of interest to this investigation in readily measureable concentrations.

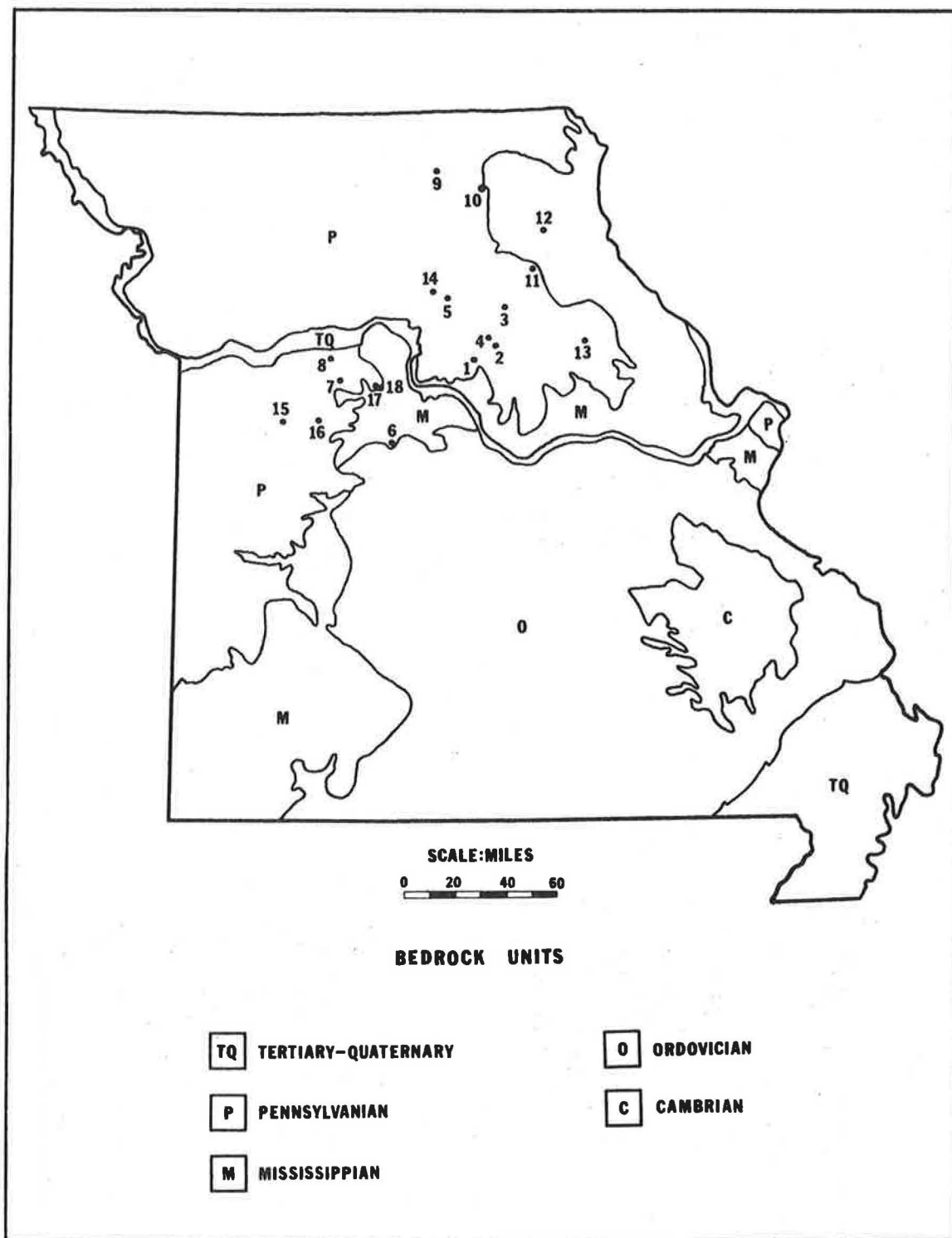


Figure 10. Generalized geologic map of Missouri showing bedrock geology and sample locations. The sample localities are described in Table 2.

TABLE 2.
Description of Water Sample Localities

Sample No.	Well owner and location	Depth (ft.)	Casing (ft. from surface)	Rock units open to well	Thickness of Penn. sedimentary rocks (ft.)	Date of collection	Temp. (°C)	Rate of prod.	Odor	T.D.S.
1	City of Harrisburg Boone Co. Sec 11 T50W R14W	1100	0-585	Devonian ls., dol. -Roubidoux Fm.	42	7-17-74	18.2	140	H ₂ S	1370
2	City of Sturgeon Boone Co. Sec. 5 T51N R12W	1051	0-535	St. Peter Fm.- Roubidoux Fm.	115	7-19-74	17.9	130	H ₂ S	1210
3	City of Madison Monroe Co. Sec 14 T54N R12W	680	0-175 418-463	Burlington Fm.- Chouteau Fm., Dev- onian-St. Peter Fm.	125	7-22-74	17.2	48	None	568
4	City of Clark Randolph Co. Sec 23 T52N R13W	750	0-612	Cotter Fm.	0	7-23-74	17.5	95	None	919
5	B. Kertz Randolph Co. Sec 5 T54N R15W	487				7-24-74	15.6		H ₂ S	11000
6a	City of Otterville Cooper Co. Sec 3 T45N R19W	815	0-210 705-751	Cotter Fm.- Eminence Fm.		9-14-74	18.0	75	None	258
6b	J. Wright Cooper Co. Sec 3 T45N R19W					9-14-74	22.0		H ₂ S	264
7	R. Arni Saline Co. Sec 3 T49N R23W	560	0-238	Burlington Fm.- St. Peter Fm.		9-21-74	16.2		H ₂ S	1850
8	W. Finkeldei Lafayette Co. Sec 12 T50N R24W	600		Cotter Fm.- Jeff. City Fm.		9-21-74	16.1		H ₂ S	4070

Table 2. Continued

Sample No.	Well owner and location	Depth (ft.)	Casing (ft. from surface)	Rock units open to well	Thickness of Penn. sedimentary rocks (ft.)	Date of collection	Temp. (°C)	Rate of prod.	Odor	T.D.S.
9	City of Novinger Adair Co. Sec 29 T63N R16W	40		Glacial drift	0	9-28-74	14.7		None	291
10	City of Brashear Adair Co. Sec 29 T62N R13W	64	0-37	Pennsylvanian	32	9-28-74	13.5	35	None	353
11	V. Buckman Shelby Co. Sec 10 T56N R10W	675			39	10-5-74	15.8		H ₂ S	7590
12	L. Coon Shelby Co. Sec 25 T59N R10W	557				10-5-74	16.0		H ₂ S	1840
13a	City of Farber Audrain Co. Sec 21 T52N R6W	1235			70	10-19-74	18.0		H ₂ S	1100
13b	City of Farber Audrain Co. Sec 21 T52N R6W	632	0-255 273-400 450-632	Chouteau Fm., Kimmswick Fm.	70	10-19-74	17.1	13	H ₂ S	1090
14	Prairie Hill School Chariton Co. Sec 32 T55N R16W	410	0-220	Warsaw Fm.- Keokuk Fm.	115	10-26-74	17.3	20	H ₂ S	10700
15	E. Bullington Johnson Co. Sec 16 T46N R26W	663	0-257	Burlington Fm.- Jeff. City Fm.	240	11-2-74	17.2		H ₂ S	756
16	T. Morgan Lafayette Co. Sec 21 T48N R24W	525				11-2-74	15.5		None	586
17	T. Davis Saline Co. Sec 18 T49N R20W	565	0-148	Chouteau Fm.- Jeff. City Fm.		11-9-74	14.3	25	None	927
18	E. Yaegle Saline Co. Sec 29 T49N R20W	440	0-273	Burlington Fm.- Jeff. City Fm.		11-9-74	13.6	25	H ₂ S	1100

TABLE 2. Continued

<u>Sample</u>	<u>Remarks</u>
2	The Pennsylvanian here consists of 45 ft. of shale, 15 ft. of sandstone, and 15 ft. of limestone.
3	The topmost 90 ft. of the section is composed of Warrensburg-Moberly (Penn.) channel sandstone.
4	The glacial drift is 170 feet thick.
5	Quite turbid water suggests a possible leak in the casing.
6b	Sample from house faucet in distribution system for well 6a.
7	The water turned black (FeS) during collection and measurement. This water is very corrosive to bathroom fixtures.
8	Some iron sulfides in water. Owner reported a recent change in taste.
9	On Chariton R. floodplain.
10	On Chariton R. floodplain. A plastic pipe in the water plant had been reduced in I.D. from 3" to 2.25" with iron oxide scale in 2 years.
13a	Well no. 4 at Farber.
13b	Well no. 2 at Farber. Black iron sulfide particles were visible in the water. The Penn. contains 30 ft. of clay overlain by 10 ft. of shale.
14	90 ft. of glacial drift. The pump has to be replaced every two years due to severe corrosion by the water.
15	The water sample turned black after standing 15 min.

Several considerations entered into the selection of specific wells. All of the wells sampled were deep wells (> 200 feet) except for two shallow wells known to be very high in iron. Deep wells were chosen because they were most likely to be free from contamination by organic carbon from the surface and were most likely to contain no dissolved oxygen. High-yield wells that are in constant use were selected whenever possible to minimize contamination from oxygenated water standing in the casing. Whenever possible, municipal wells were sampled because they have large capacities, are built to meet state specifications, have well logs that are generally available at the Missouri Division of Geological Survey and Water Resources, and because the information gained would benefit a relatively large number of people.

Sample collection localities were limited by the distance from Columbia and by the relative scarcity of wells in northern Missouri. Because of the generally poor water quality, county extension agents and the Missouri Geological Survey have discouraged well drilling in the area for many years.

Methods of Water Sampling and Analysis

The collection of water samples for this investigation was carried out from July, 1974 to November, 1974.

An Orion 407 expanded scale pH meter and standard 5-inch Beckman combination electrodes were used for all pH measurements. Eh measurements were made with a Beckman platinum thimble and calomel reference electrodes and an Orion 401 meter. Immediately before each measurement, the platinum surface on the Eh electrode was polished with either powdered toothpaste or 200-mesh powdered glass.

The electrodes were calibrated in buffers brought to within one degree of the sample temperature by being immersed in flowing sample water. The pe measurements were made after calibrating the platinum and reference electrode pair with Zobell solution. The electrodes were then placed in an air-tight lucite pH-Eh measurement chamber modeled after Back and Barnes (1961), through which sample water flowed continuously. The electrodes were left in the chamber for approximately one hour to flush all oxygen from the system and to allow the water and electrodes to equilibrate before the pH and Eh measurements were taken.

The bicarbonate ion concentration was determined in the field by titration with standardized sulfuric acid to a pH of 4.0. The end point for each water sample was determined from these data by the method of Barnes (1964, p. H16). The sulfide ion concentration was determined in the field by the methylene blue visual color matching method (APHA, 1971).

An aliquot of sample water that had been filtered through a 0.025 μ membrane filter was immediately acidified, the ferrous iron complexed with bathophenanthroline, buffered to pH 4 with sodium acetate, and extracted with n-hexyl alcohol in the field. This sample was then placed in an ice-filled cooler and the determination of ferrous iron was done in the laboratory within 16 hours.

At each locality, two 250 ml samples for the determination of nitrate, ammonia, calcium, magnesium, sodium, potassium, iron, and magnesium were filtered through a .025 μ membrane filter by applying pressure to a syringe filled with sample water. These samples were immediately acidified to pH 2 with concentrated HCl and placed in an ice filled cooler. One sample was used for the determinations of

nitrate and ammonia which were completed within 48 hours. The other sample was refrigerated until the analyses of the cations were completed in 2-5 months.

Two 2.5 liter unfiltered samples were collected and acidified to pH 2 with 5 ml of concentrated HNO_3 for the laboratory determinations of total iron, chloride, and sulfate. These analyses were completed 2 to 5 months after sampling.

One 250 ml sample was obtained directly from a tap at the pump and was placed on ice and refrigerated until the determination of total organic carbon was completed in 1-4 months.

A summary of the procedures used in the chemical analyses of the water samples is given in Table 3.

The organic carbon concentration of the samples was measured without filtering and thus is total organic carbon. The water was not filtered because in some instances, dissolved organic constituents have been found to sorb onto the surface of plastic membrane filters (Malcolm and Leenheer, 1973). Also, there is a thin film of organic detergent on filters of this type which may dissolve and contaminate samples for dissolved organic carbon analyses (Malcolm and Leenheer, 1973).

Several problems occurred with the determination of total organic carbon with a Beckman model 915 Carbon Analyzer. The microsyringe used in injecting the samples has a tip diameter of 170μ , which excludes larger particles. For samples containing particulate sediment of silt size or larger, the precision may vary due to inclusion or exclusion of large sediment particles coated with organic material (Malcolm and Leenheer, 1973). Only two water samples had particulates visible on a

TABLE 3.
Methods of Chemical Analysis

<u>Parameter</u>	<u>Method</u>	<u>Reference</u>
Fe ⁺⁺	Bathophenanthroline	Shapiro (1966)
Ca*, Mg*, Mn*, Total Fe*	Atomic Absorption	Brown <u>et al.</u> (1970)
Na*, K*	Flame Emission	Pickett and Koirtyohann (1969)
Cl*	Automatic coulometric titration	Cotlove (1964)
SO ₄	Gravimetric	APHA (1971)
Total Sulfide	Methylene Blue	APHA (1971)
NH ₃	Nesslerization	APHA (1971)
NO ₃	Brucine	U.S. Dept. of Interior (1969)
HCO ₃	Titration with standard sulfuric acid	Barnes (1964)
Total Organic C	Beckman Model 915 Carbon Analyzer	Goerlitz and Brown (1972)
TDS	Calculated	
pH	Electrode	Barnes (1964)
Eh	Electrode	(see text)
Temperature	Tele-Thermometer	Yellow Springs Instrument Co., inc.

*Analyses performed by the Environmental Trace Substances Center,
University of Missouri-Columbia

.025 μ filter so this problem was quite limited. After being acidified, the organic carbon samples were bubbled with nitrogen to purge carbon dioxide. This process probably also drives off some of the volatile organic carbon compounds.

Methods of Bacteriological Sampling and Identification

Field Sampling: At each locality, a 4-liter water sample was obtained through a weighted sterile rubber tube. One milliliter of the sample was delivered aseptically to each of two glass test tubes in which iron sulfite agar had been melted with a Coleman propane stove. These tubes were spun to spread a thin coating of the mixture on the wall of each tube. The tubes were incubated for 21 days and then examined for the presence of black colonies which would indicate the presence of sulfate-reducing bacteria. In addition, 10 ml of water were inoculated into each of two evacuated bottles, one containing 100 ml of trypticase soy medium and the other containing 100 ml of brain heart infusion medium. This method was designed to culture both obligate and facultative anaerobes. One ml of sample was streaked onto a blood agar plate and then placed in a sealed Torbal jar which was immediately filled with H_2 and CO_2 by using a BBI gas pack. Duplicate samples were plated aerobically. This procedure is designed to detect the more fastidious anaerobes. In a fourth step, the microorganisms from one liter of water from the sterile flask were concentrated on a .45 μ Millipore filter and the filter was transferred to an iron sulfite agar plate in the anaerobic Torbal jar. The filter plate was used to determine the number of sulfate-reducing bacteria per milliliter of water.

Identification: In the laboratory, the trypticase soy and brain heart infusion media were streaked onto blood agar plates for isolation.

Isolates from all the media were keyed to genera using Bergey's Manual of Determinative Bacteriology (1957). Determinations were based on colony morphology, color, spore formation, and gram stain as well as standard biochemical tests including tests for motility, nitrate reduction, sugar fermentation, citrate utilization, and production of hydrogen sulfide. The identification of the microorganisms was carried out by C. Dorsey and G. Tarka using facilities at the Dalton Research Center.

DATA

The analytical chemical data from water samples collected from water supply wells are presented in Tables 4 and 5. The data on bacteria identified in the samples are presented in Table 6.

Calculation of the charge balance is a method commonly used to determine the validity of a water analysis. Calculations for the percent departure from electrical neutrality (% error) were carried out according to the equation:

$$\% \text{ Error} = \frac{\Sigma(+)\text{ meq} - \Sigma(-)\text{ meq}}{\Sigma(+)\text{ meq} + \Sigma(-)\text{ meq}} \times 100 \quad (32)$$

and are listed in Table 4.

TABLE 4.
Major Chemical Species in Groundwater Samples (mg/l)

Sample No.	Total Fe	Total Mn	Ca	Mg	Na	K	HCO ₃	SO ₄	Cl	pH	Eh	TDS	Percent Error
1	1.65	<.01	110.	50.6	(328.)*	12.8	380.	114.	(548.)*	7.08	.139	1360.	0.5
2	1.12	.02	156.	74.6	130.	19.8	398.	607.	25.0	6.97	.104	1210.	0.6
3	1.08	.03	33.8	24.7	159.	6.9	494.	77.	20.	7.51	.290	568.	2.6
4	<.1	<.01	124.	60.2	110.	18.0	427.	286.	107.	6.98	.300	919.	1.3
5	<.1	.04	402.	230.	3370.	69.8	317.	1280.	5490.	6.95	-.015	11000.	0.3
6a	<.1	<.01	54.4	23.0	6.90	2.24	313.	12.	3.4	7.36	.339	258.	-4.8
6b	1.86	<.01	54.6	27.4	9.50	2.28	313.	9.	4.8	7.23	.176	264.	0.0
7	7.88	.03	46.1	29.5	600.	18.3	384.	59.	905.	7.61	-.087	1850.	-2.7
8	8.86	.02	84.1	63.1	1320.	37.2	332.	144.	2260.	7.51	.140	4070.	-3.3
9	53.4	3.35	32.0	8.44	11.0	1.44	188.	80.	9.3	6.00	.181	291.	-2.4
10	14.1	1.88	54.3	16.2	40.0	1.28	358.	35.	13.	6.33	.162	353.	-4.7
11	14.6	.08	251.	139.	2300.	49.0	357.	1050.	3620.	7.56	.005	7590.	-1.7
12	<.1	<.01	112.	58.6	470.	13.8	490.	438.	500.	6.98	.190	1840.	-0.1
13a	.47	<.01	79.2	40.4	248.	18.4	471.	288.	188.	7.19	.089	1100.	-1.3
13b	33.0	.06	71.2	45.9	250.	18.4	469.	290.	176.	7.35	.210	1090.	0.0
14	8.21	.04	375.	212.	3210.	68.5	324.	1260.	5400.	7.13	-2.88	10700.	-1.7
15	.29	<.01	38.6	21.5	221.	9.30	337.	22.	275.	7.90	-.086	756.	-0.7
16	.10	<.01	63.2	33.5	110.	9.50	269.	43.	192.	7.70	.259	586.	1.0
17	.92	.02	160.	60.4	46.3	12.2	490.	397.	6.7	6.85	.257	927.	-3.8
18	2.31	.02	162.	74.1	79.9	13.9	497.	481.	42.	6.73	-.073	1100.	-3.5

*Analyses taken from Missouri Department of Natural Resources (1973)

TABLE 5.
 Minor Chemical Species in Groundwater Samples (mg/l)

Sample No.	Filterable Fe	Fe ²⁺ ¹	Filterable Mn	NO ₃ -N	NH ₃ -N	Sulfide as H ₂ S	Total Org. Carbon	pH	pe
1	1.51	n.a.	<.01	.10	.55	.25	2.9	7.08	2.41
2	.73	n.a.	<.01	.00	1.08	<.05	1.6	6.97	1.80
3	<.1	n.a.	.03	.14	.56	<.03	1.6	7.51	5.04
4	<.1	n.a.	<.01	.30	.54	<.03	1.7	6.98	5.21
5	2.61	n.a.	.04	.13	9.08	3.00	1.5	6.95	-0.26
6a	<.1	.02	<.01	.07	.33	<.03	1.2	7.36	5.87
6b	.71	.13	<.01	.08	.16	<.05	2.1	7.23	3.00
7	2.00	.48	.05	.00	1.33	7.50	2.5	7.61	-1.52
8	<.1	.26	.02	.01	3.44	3.00	1.5	7.51	2.44
9	51.3	5.68	3.58	2.40	7.30	<.03	4.1	6.00	3.17
10	12.7	3.56	1.74	.63	2.15	<.03	4.0	6.33	2.84
11	13.0	2.14	.09	.65	7.70	.30	1.4	7.56	0.09
12	<.1	.02	.01	.48	2.42	.17	2.5	6.98	3.31
13a	.24	.08	<.01	.04	3.58	.15	1.5	7.19	1.54
13b	1.23	.36	.05	.08	1.60	.75	1.7	7.35	3.65
14	7.96	1.40	.04	.28	6.85	.45	2.1	7.13	-5.00
15	<.1	.04	<.01	.00	1.42	1.61	1.8	7.90	-1.49
16	<.1	.03	<.01	.02	1.19	<.03	1.7	7.70	4.53
17	.48	.11	.03	.31	1.08	<.03	2.6	6.85	4.51
18	1.96	.43	.03	.39	1.70	.05	1.7	6.73	-1.29

¹Bathophenanthroline iron; n.a. not analyzed

TABLE 6. Bacteria Present in Water Samples

Sample	Bacillus	Pseudomonas	Enterobacteriaceae	Corynebacterium	Achromobacter	Clostridium	Staphylococcus	Proteus	Alkaligenes	Desulfovibrio	No. of NO ₃ ⁻ reducing genera	Bacteriologist
1	X						X		N		1	T
2									N,X		1	T
3				X					N		1	T
4	N			X			N		X		2	T
5	N								N		2	T
6a	X				X						0	T
6b				N							1	T
7	N			N	X						2	T
8	N			N						S	2	T
9	N										1	T
10	N				N		X				2	T
11	X	N									1	T
12	X	N									1	T
13a	P	P									0	D
13b	P	P									0	D
14		X						P		S	0	D
15		N	N								2	D
16	N	N									2	D
17	N										1	D
18	N									S	1	D

SYMBOLS

P present, data not available on nitrate reduction
 N present, reduces nitrate
 X present, negative test for nitrate reduction
 S present, reduces sulfate

T Bacterial identification by Gene Tarka
 D Bacterial identification by Christa Dorsey

DISCUSSION

Organic Carbon

The data in Table 5 shows that organic carbon was detectable in all samples although the concentrations were very low; there was little variation between samples. All the samples contained between 1.2 and 3.0 mg/l organic carbon except for two shallow wells which contained 4.0 mg/l carbon. These samples are believed to be higher in organic carbon because they were collected from a geologic setting (floodplain) where natural organic acids from decaying organic matter were probably entering the ground water. All of the organic carbon values obtained in this study are comparable to the data obtained by Leenheer et al. (1974) discussed above.

Because most of the organic carbon measured was presumably in solution, it is probably biodegradable. Nonbiodegradable organic matter in rocks is mostly in the form of a complex polymer called kerogen, which is not soluble even in organic solvents. If the organic carbon in the samples is indeed biodegradable, it should be adequate to support bacterial growth. Zobell et al. (1942, 1943) observed marine bacteria growing readily at concentrations of organic substances lower than 0.1 mg/l.

The log P_{O_2} for each sample was calculated as described in the section on dissolved oxygen. These values were compared with the organic carbon concentrations to see if the calculated P_{O_2} in ground water is

related to the amount of organic carbon in the water. A scattergram of these variables is shown in Figure 11. Because the data is not strictly normally distributed, the Spearman rank correlation coefficient is considered the best indicator of a relationship. In this method, the data for each variable must be expressed in terms of ranks. From the difference between each pair of ranks (d) and number of data pairs (n), the Spearman rank correlation coefficient (r_s) (Snedecor and Cochran, 1967) is calculated by the formula

$$r_s = 1 - \frac{6 \sum d^2}{n(n^2 - 1)} \quad (33).$$

The r_s between ppm organic carbon and $\log P_{O_2}$ is $-.096$, where 1 indicates perfect correlation and 0 indicates no correlation. There is therefore no correlation between these two variables, at least with the range of organic carbon occurring in these water samples. A generalization about the relationship between $\log P_{O_2}$ and any organic carbon concentration cannot be made because the degree of heterogeneity of the samples influences the size of a correlation coefficient. If a correlation exists between two variables, a wide range in data values will produce a larger correlation coefficient. Since the range of ppm organic carbon happened by chance to fall within a small range, this may have some effect on the size of the correlation coefficient. However, because r_s is so low it is doubtful that a more heterogeneous group of samples would show a statistically significant relationship. As more data becomes available from other areas, this problem may be resolved.

The lack of correlation between the organic carbon concentration and P_{O_2} is reflected in the lack of relationship between the concentration of organic carbon and the concentrations of H_2S and ferrous iron

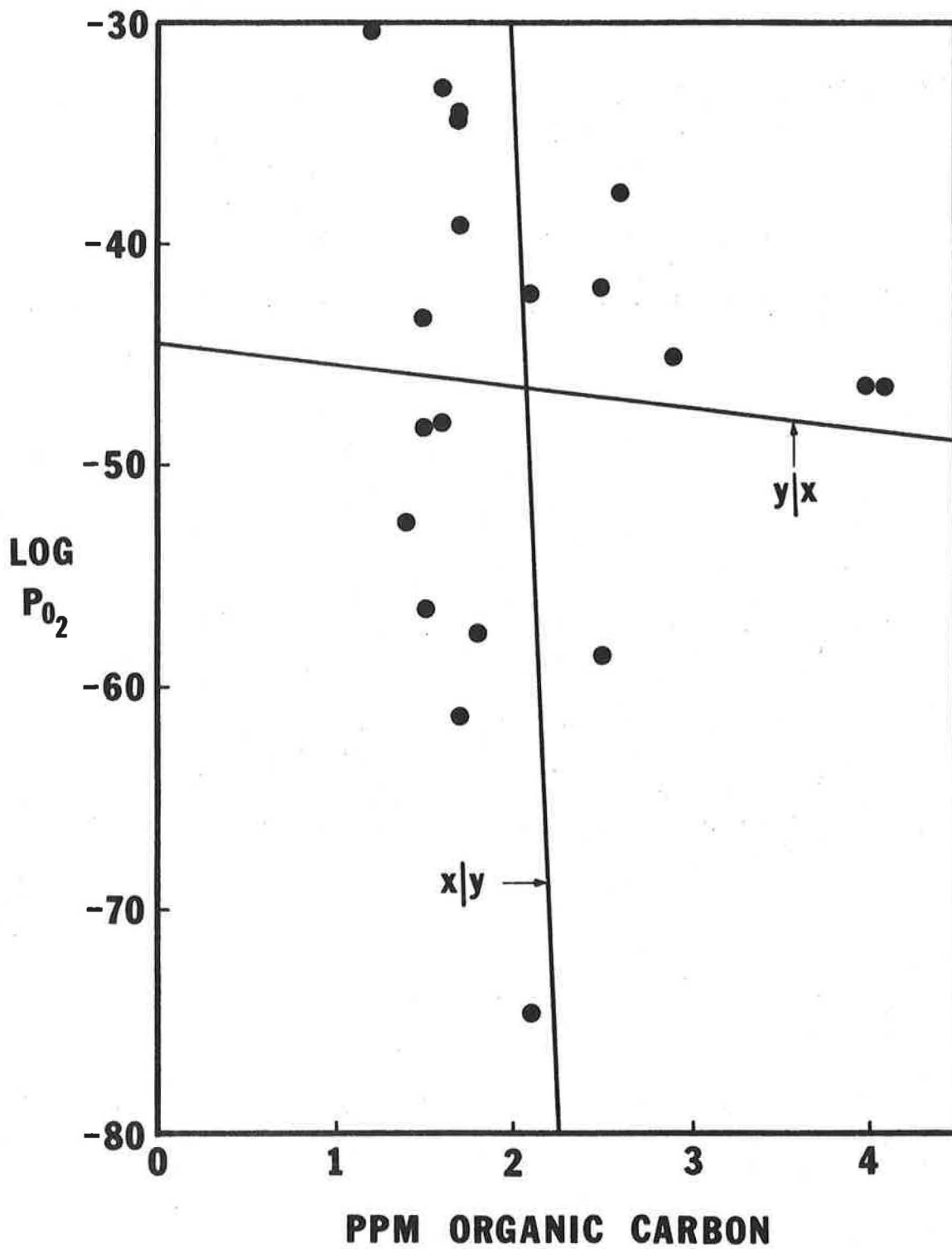


Figure 11. Relationship between $\log P_{0_2}$ and ppm organic carbon together with the regression lines y on x ($y|x, P_{0_2}|\text{organic carbon}$) and x on y ($x|y, \text{organic carbon}|P_{0_2}$).

(Figures 12 and 13), with r_s values of $-.148$ and $.360$ respectively. The probability of these r_s values being achieved by chance is greater than ten percent.

Bacteria

The data in Table 6 indicate that bacteria are indeed present in the ground water of northern Missouri. Although there was no evidence of coliform or streptococcus organisms (with three exceptions), none of the water samples were sterile. In each well, one to four genera of nonpathogenic bacteria were present, the vast majority being nitrate reducers. Sulfate-reducing bacteria were found in three of the waters sampled.

If a given genus is not reported as present in a certain sample, that does not necessarily mean that it is not present in the aquifer. Some bacteria are filtered out of the water as it passes through the pores in the aquifer and thus the population of the sample waters may not be as high as in the underground environment. Zobell (1946) has shown that some bacteria attach themselves to various types of substrate and are not detected when the water is sampled even though the bacteria are present in the system. Another consideration is that some bacteria probably do not survive the sampling and culturing process.

In spite of those difficulties, the bacteria data do show that bacteria are present in most ground waters at least to a depth of 1200 feet (the deepest well sampled). The mere presence of bacteria with their proven catalytic properties suggests that the water chemistry will be strongly influenced by the microorganisms. The results of the biochemical tests confirm that some of the bacteria are capable of reducing nitrate and sulfate.

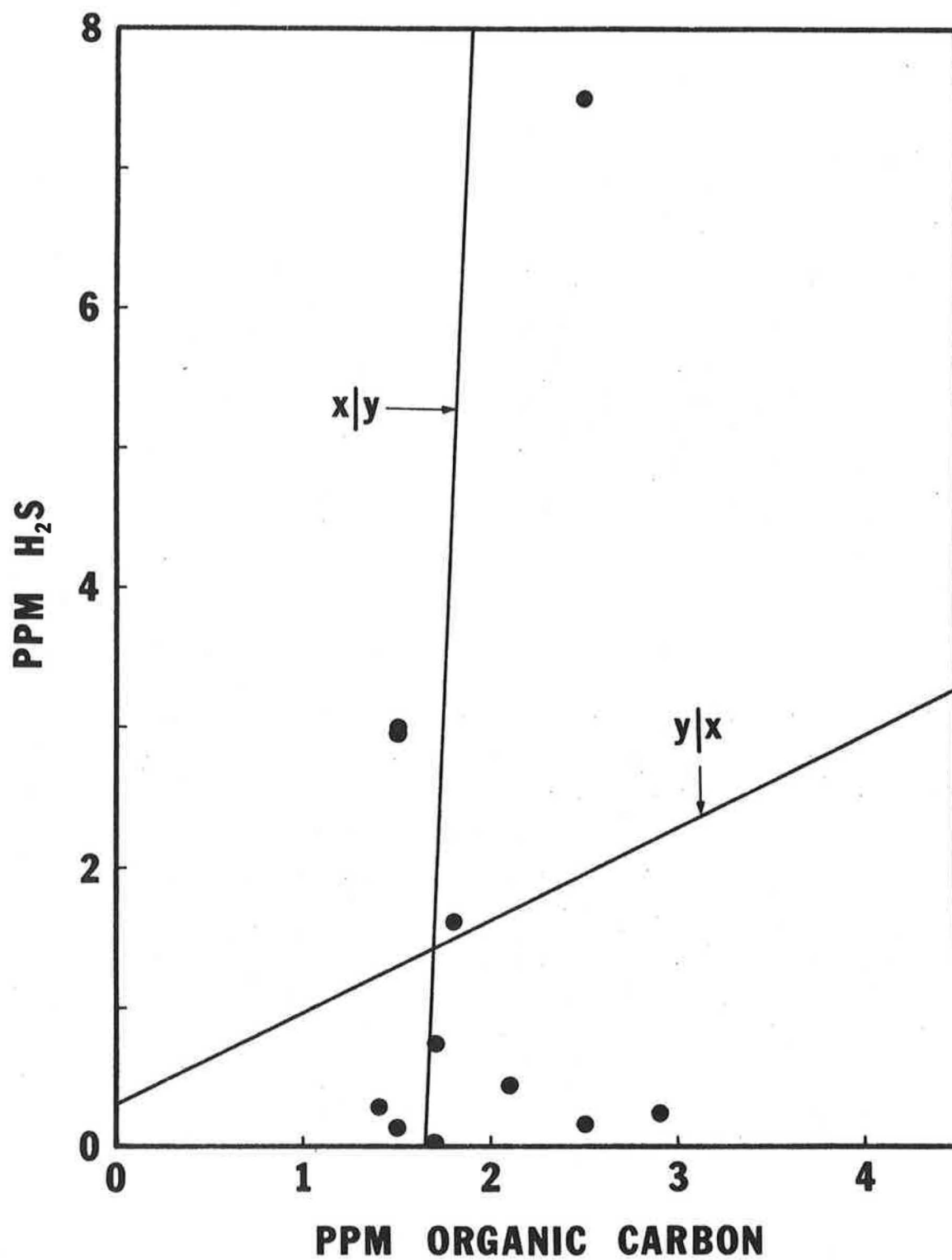


Figure 12. Relationship between ppm H₂S and ppm organic carbon together with the regression lines y on x ($y|x$, H₂S|organic carbon) and x on y ($x|y$, organic carbon|H₂S).

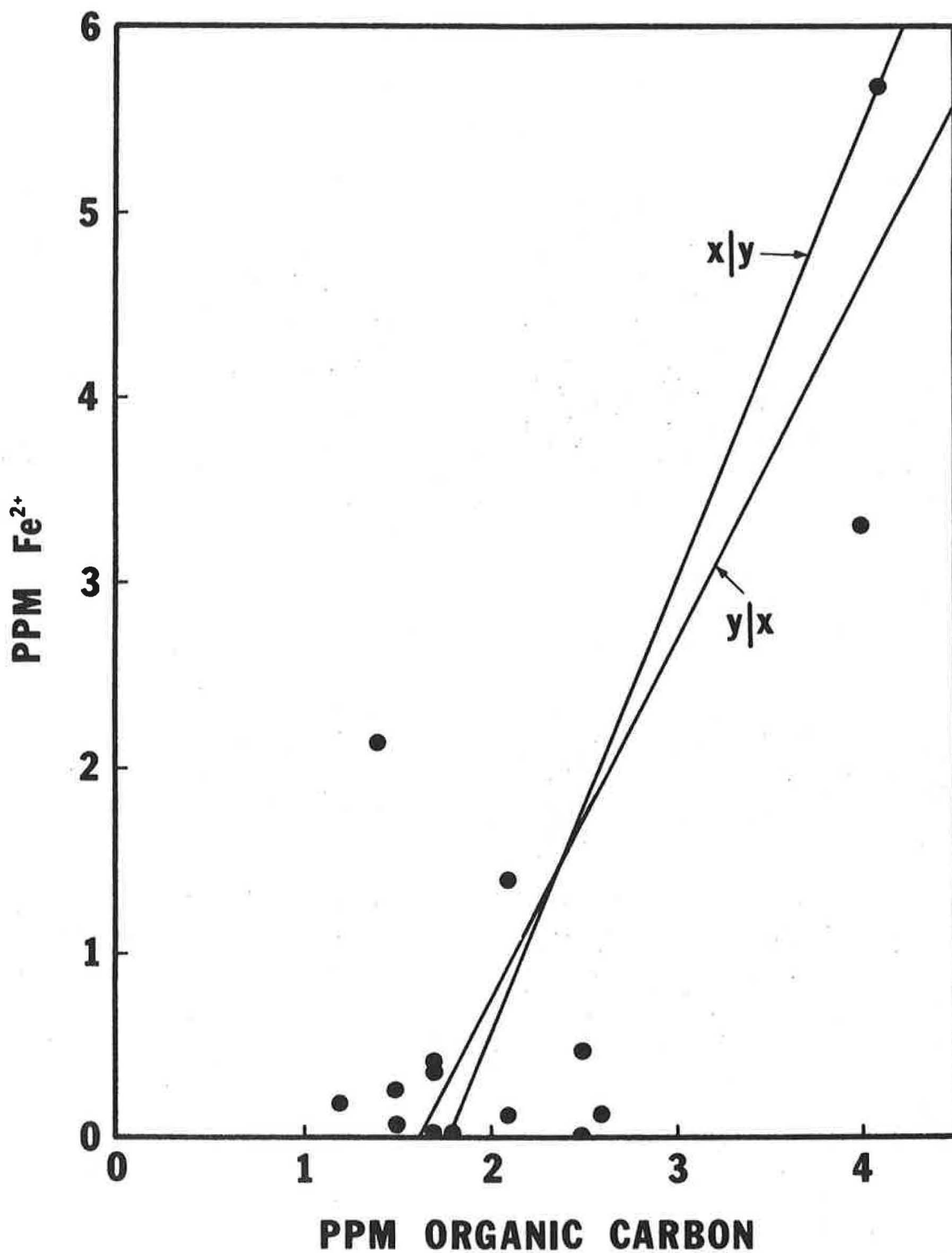


Figure 13. Relationship between ppm Fe²⁺ and ppm organic carbon together with the regression lines y on x ($y|x, \text{Fe}^{2+}|\text{organic carbon}$) and x on y ($x|y, \text{organic carbon}|\text{Fe}^{2+}$).

Chemistry

Forms of Iron in Ground Water: A comparison of the data for filterable iron ($<0.025 \mu$) and dissolved (bathophenanthroline) ferrous iron suggests that up to 89 percent of the iron in water passing through a 0.025μ filter is in the form of colloidal ferric oxyhydroxides or ferrous sulfides (Table 7). It is therefore absolutely necessary to use a complexing technique such as bathophenanthroline to measure the ferrous iron actually in solution. The assumption that the total iron in a filtered sample is equivalent to the iron in true solution is likely to be seriously in error and will lead to conclusions or inferences which may also be seriously in error.

In the samples containing measureable H_2S , it is suspected that the iron-bearing particles are predominantly iron sulfides. Because the dissolved ferrous iron is much lower than the filterable iron in the samples containing H_2S (Table 7), it appears that bathophenanthroline discriminates between dissolved ferrous iron and particulate ferrous sulfides. This observation suggests that the bathophenanthroline method is necessary in making measurements of ferrous iron in true solution.

$p^Q Fe(OH)_3$ in Ground Water: The $p^Q Fe(OH)_3$ values for the water samples are listed in Table 8. It appears that the p^Q values do not cluster around a particular number but are quite variable, in agreement with the results obtained by Langmuir (1969) and Langmuir and Whittemore (1971).

Langmuir and Whittemore (1971) published pH, pe, and $p^Q Fe(OH)_3$ data for several groundwater samples in the same pH range as that covered in this investigation (Figure 14). On the basis of these data, Langmuir and Whittemore (1971) suggested that as the pH of a ground water is

TABLE 7.

Iron in Ground Water (mg/l)

Sample	Total Sulfide as H_2S	Filterable Fe^1 ($<0.025 \mu$)	Bathophenanthroline Iron	Percent Dissolved Iron
6b	<0.05	0.71	0.13	18
7	7.5	2.00	0.48	24
9	<0.03	51.3	5.68	11
10	<0.03	12.7	3.56	28
11	0.30	13.0	2.14	16
13a	0.15	0.24	0.08	33
13b	0.75	1.23	0.36	29
14	0.45	7.96	1.40	17
17	<0.03	0.48	0.11	23
18	0.05	1.96	0.43	22

¹Concentration of iron in sample that passes through a 0.025μ filter.

TABLE 8.
 $p^0\text{Fe(OH)}_3$ of Water Samples

Sample	$p\text{Fe}^{2+}$	peE	$p\text{Fe}^{3+}$	pOH	$p^0\text{Fe(OH)}_3$
6a	6.60	5.87	14.0	6.93	34.7
6b	5.79	3.00	16.0	7.06	37.2
7	5.34	-1.52	20.1	6.68	40.1
8	6.01	2.44	16.5	6.78	36.8
9	4.12	3.17	14.2	8.29	39.0
10	4.25	2.84	14.7	7.96	38.6
11	4.85	0.09	18.0	6.73	38.2
12	6.73	3.31	16.6	7.31	38.6
13a	6.08	1.54	17.8	7.10	39.1
13b	5.43	3.65	15.0	6.94	35.8
14	5.08	-5.00	23.3	7.16	44.8
15	6.34	-1.49	21.1	6.39	40.2
16	6.46	4.53	15.2	6.59	34.9
17	5.96	4.51	14.7	7.44	37.0
18	5.37	-1.29	19.9	7.56	42.6

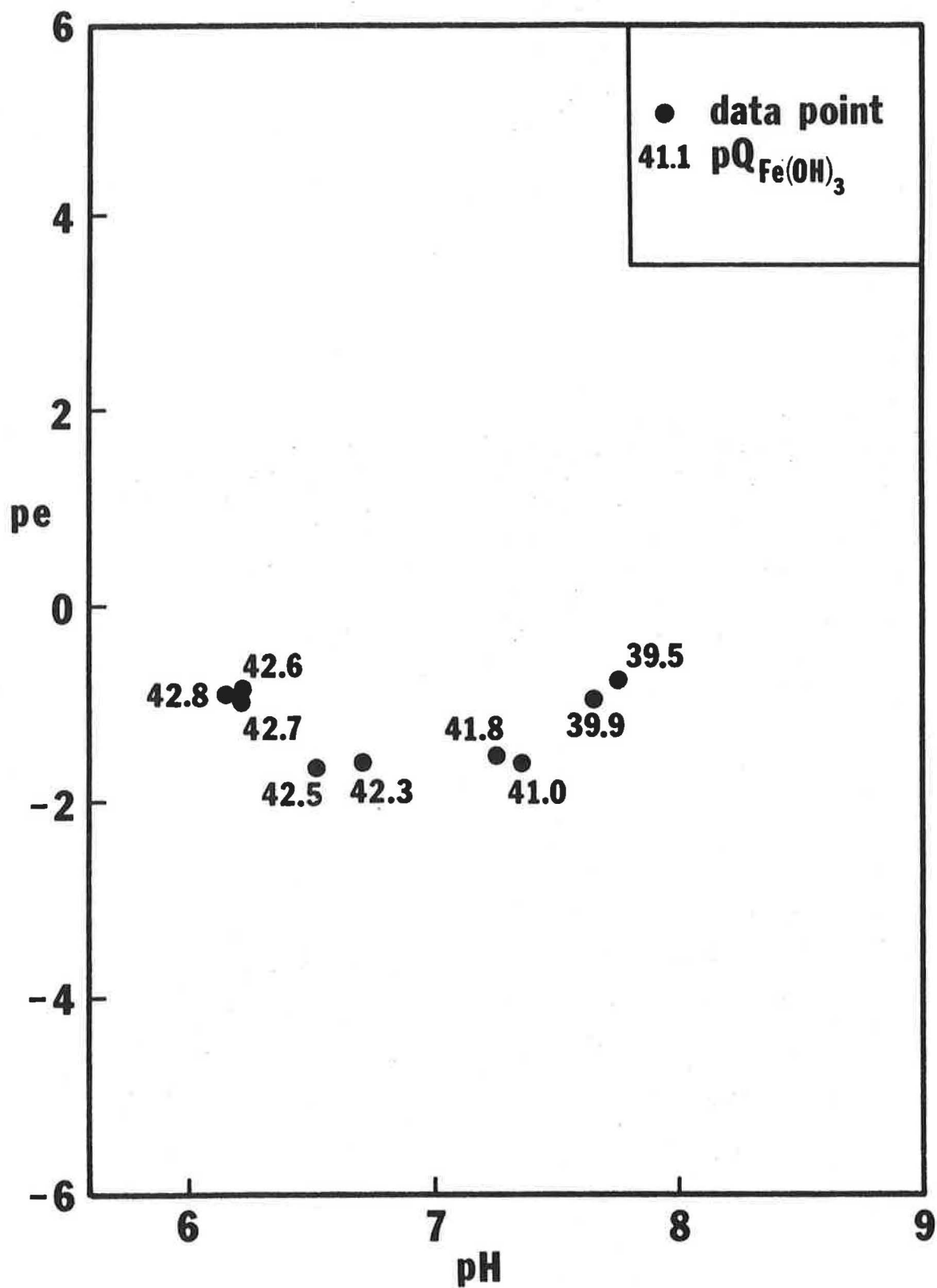


Figure 14. Relationship between pe , pH , and $p^0Fe(OH)_3$. Data from Langmuir and Whittemore (1971).

lowered, the more soluble ferric oxyhydroxides are leached away, leaving the more stable forms behind. The present investigation has obtained data on a larger number of samples over a wider range of redox potentials. These data are shown in Figure 15 with the two least squares regression lines (x against y and y against x). The r_s for this relationship is $-.218$, which is not significant at the 10 percent confidence level. This indicates that these data show no statistically significant relationship between pH and $p^0\text{Fe}(\text{OH})_3$.

Plotting the $p^0\text{Fe}(\text{OH})_3$ data on a pe-pH diagram provided some indication that the lines of equal $p^0\text{Fe}(\text{OH})_3$ parallel lines of equal P_{O_2} (Figure 16). A scatter diagram of the $p^0\text{Fe}(\text{OH})_3$ and $\log P_{\text{O}_2}$ (Figure 17) shows that there is a strong negative correlation between these two parameters. The r_s is $-.919$ which is statistically significant at less than the 0.1 percent level. In other words, the probability of achieving this r_s by chance alone is much less than 0.1 percent.

When similar data from Barnes and Back (1964) are used to calculate the correlation between $p^0\text{Fe}(\text{OH})_3$ and $\log P_{\text{O}_2}$ for their 30 samples, the r_s is $-.575$ which is also significant at the 0.1 percent confidence level. The correlation for the Barnes and Back data is probably lower because the measurements were made before the advent of high impedance electrometers which greatly increase the precision of redox potential measurements.

The apparently high correlation between $\log P_{\text{O}_2}$ and $p^0\text{Fe}(\text{OH})_3$ may well be related to the fact that both of these parameters are calculated from the same peE value measured with a platinum electrode (see equations (15), (27), and (30)). The determination of whether or not there is a real correlation between these parameters may have to

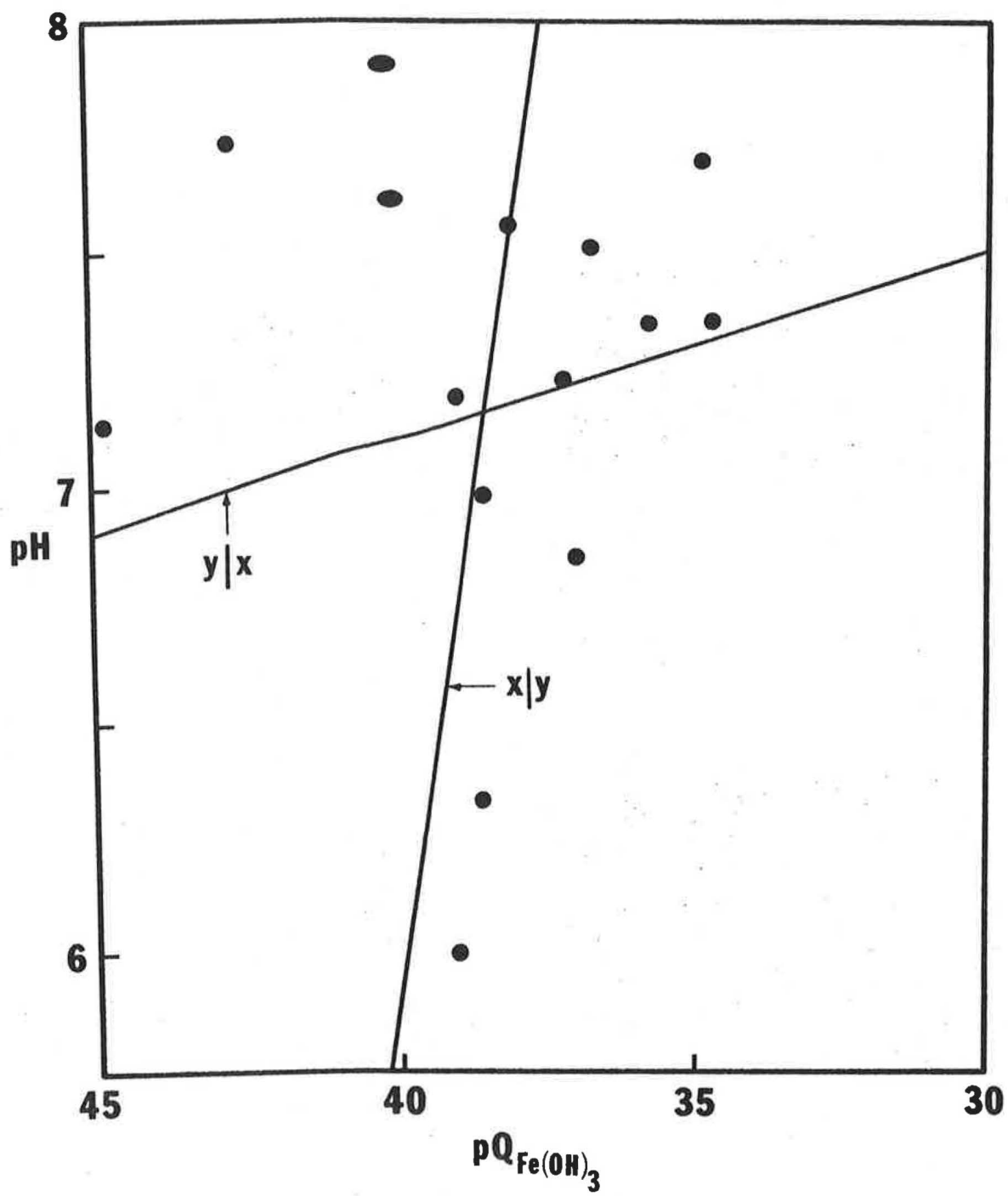


Figure 15. Relationship between pH and $pQ_{Fe(OH)_3}$ for the waters sampled together with the regression lines y on x ($y|x$, $pH|pQ_{Fe(OH)_3}$) and x on y ($x|y$, $pQ_{Fe(OH)_3}|pH$).

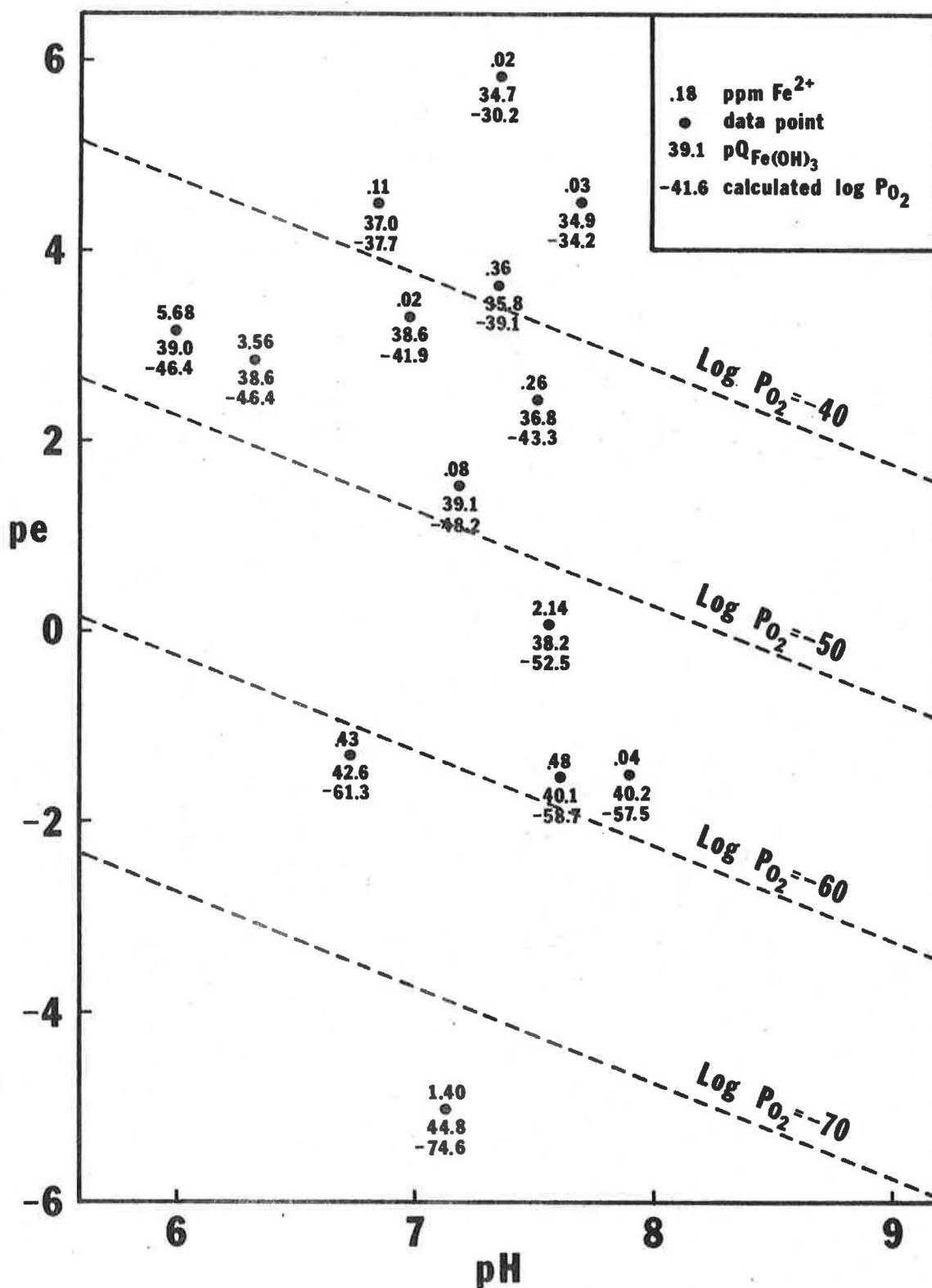


Figure 16. Calculated values of $pQ_{\text{Fe}(\text{OH})_3}$ and $\log P_{\text{O}_2}$ in fourteen ground water samples.

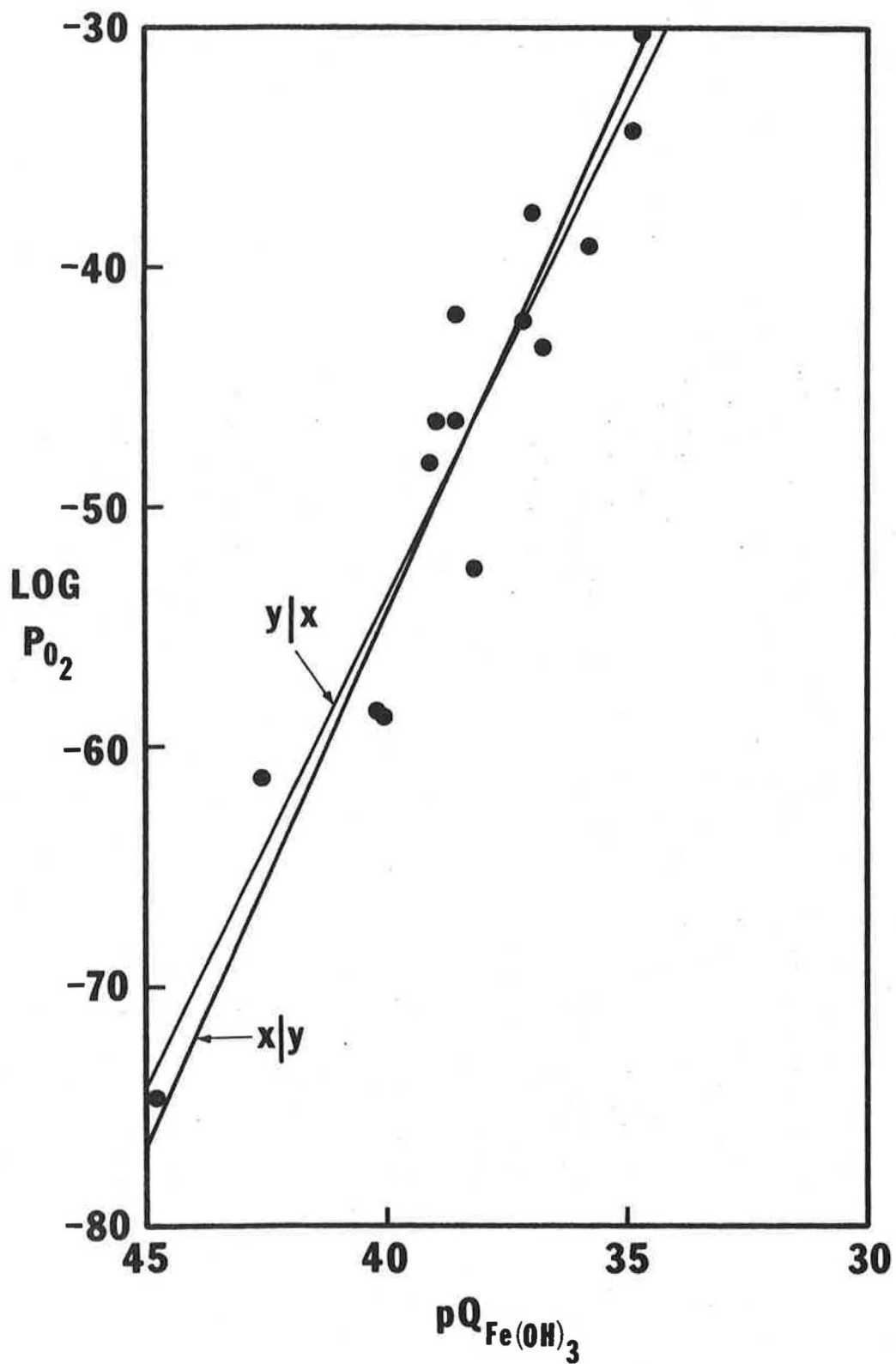


Figure 17. Relationship between $\log P_{0_2}$ and $p^Q \text{Fe(OH)}_3$ together with the regression lines y on x ($y|x, P_{0_2}|p^Q \text{Fe(OH)}_3$) and x on y ($x|y, p^Q \text{Fe(OH)}_3|P_{0_2}$).

wait until they can be determined independently of each other over a significant range of pH and redox potential. It may be as Doyle (1968) has suggested, that the observed peE is controlled by the character of the ferric oxide coating which forms on the surface of the platinum electrode. Whether the character of this coating is related only to the "redox potential" of the water or is affected by variations in the concentration of hydrogen sulfide, the activity of carbonate ion, or other factors remains to be studied.

Oxidation-Reduction Reactions: Whenever both nitrate and ammonia or hydrogen sulfide and sulfate were present in a sample, a redox potential was calculated from the analytic data by the methods described above.

The large difference in pe between the predominance fields of nitrate and hydrogen sulfide (Figures 3 and 4) is such that these two species should never both be detectable in a sample in thermodynamic equilibrium. Nine samples, however, contained measureable amounts of both nitrate and H₂S. For these samples, the numerical values for pe were obtained by three independent methods; peN and peS from the analytical data and the peE obtained from measurements with the platinum electrode. These results are summarized in Figure 18 and in Table 9. It is obvious that the calculated pe of the sulfate-sulfide couple differs considerably from that of the nitrogen couple in each case. In addition, the platinum electrode pe (peE), presumably controlled by the ferrous ion-ferric oxide couple, differs from both of the other two. If the waters were in internal equilibrium, the redox potential calculated from all pairs of species would have the same value. These data substantiate Carpenter's suggestion that many ground

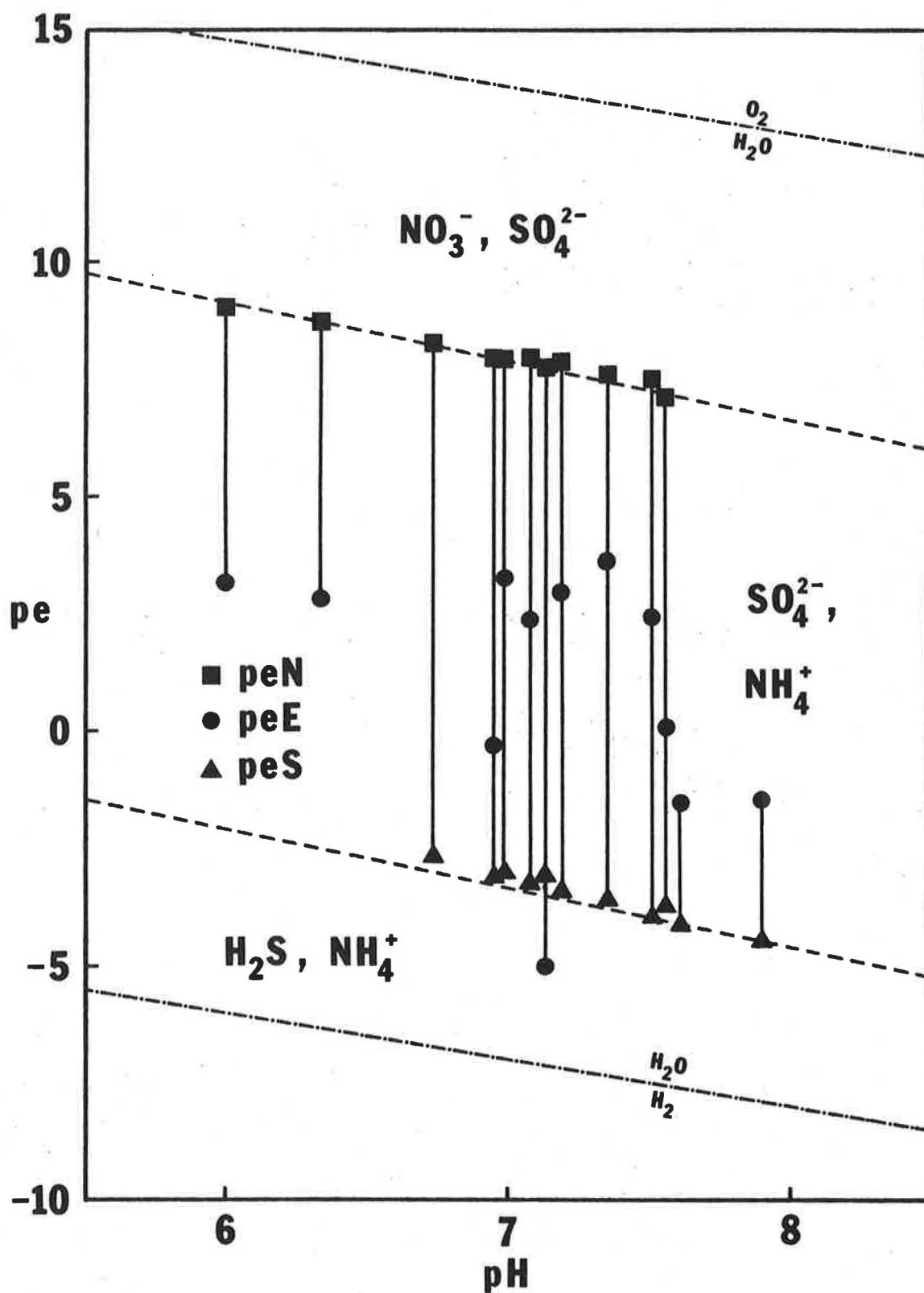


Figure 18. peN, peS, and peE of 13 groundwater samples. Data points on the vertical lines were calculated or measured in the same water sample.

TABLE 9.
 Comparison of Measured and Calculated Oxidation-Reduction
 Potentials in Groundwater Samples

<u>Sample</u>	<u>peE</u>	<u>peS</u>	<u>peN</u>
1	2.41	-3.21	7.97
2	1.80		
3	5.04		7.41
4	5.21		8.04
5	-0.26	-3.09	7.96
6a	5.87		7.67
6b	3.00		7.86
7	-1.52	-4.08	
8	2.44	-3.88	7.46
9	3.17		9.01
10	2.84		8.73
11	0.09	-3.72	7.12
12	3.31	-2.99	7.93
13a	1.54	-3.27	7.78
13b	3.65	-3.56	7.58
14	-5.00	-3.21	7.71
15	-1.49	-4.40	
16	4.53		
17	4.51		
18	-1.29	-2.61	8.27

waters are sufficiently out of redox equilibrium that they cannot be said to have a unique redox potential.

Carbonate Equilibria: As calcite and dolomite are the predominant minerals in the aquifers in northern Missouri, an attempt was made to determine if the water samples are in equilibrium with respect to these minerals. The ion activity product (I.A.P.) was calculated for both calcite and dolomite for each sample taking into account the changes in equilibrium constants with temperature. A measure of the degree of saturation can be calculated using the equation:

$$\% \text{saturation} = \frac{\text{I.A.P.}}{K_{spT}} \times 100 \quad (34)$$

where K_{spT} is the thermodynamic solubility product of calcite or dolomite at the temperature of the sample water. The I.A.P.'s, the percentages of saturation with respect to calcite and dolomite, and the log of the calcium to magnesium ratio are summarized in Table 10.

The ion activity product and the corresponding percent saturation are very sensitive to variations in the pH and in the activities of calcium and bicarbonate. Any errors in measuring these parameters will affect the calculated percent saturation. The calculated degree of saturation with respect to calcite or dolomite is most sensitive to the pH. It is likely that the uncertainty in measuring pH is approximately 0.1 pH unit. If the pH of sample 1 is raised by 0.1 units, the calculated calcite saturation changes from 60 percent to 75 percent and the dolomite saturation changes from 44 percent to 69 percent. If the pH is lowered by .1, the calcite and dolomite saturations change from 61 to 48 percent and from 44 to 28 percent, respectively.

TABLE 10.

Measures of Saturation with Respect to Calcite and Dolomite

<u>Sample</u>	<u>Log I.A.P. Calcite</u>	<u>% Calcite Saturation</u>	<u>Log I.A.P. Dolomite</u>	<u>% Dolomite Saturation</u>	<u>Log (Ca/Mg)</u>
1	-8.47	60	-17.0	44	0.10
2	-8.49	58	-17.1	40	0.10
3	-8.36	75	-16.6	106	-0.09
4	-8.48	59	-17.0	43	0.09
5	-8.49	54	-17.0	46	-0.02
6a	-8.44	65	-17.0	46	0.15
6b	-8.52	60	-17.1	46	0.07
7	-8.35	76	-16.6	98	-0.04
8	-8.35	75	-16.6	110	-0.12
9	-10.3	1	-20.9	.0	0.36
10	-9.46	5	-19.2	.2	0.30
11	-7.97	179	-15.9	480	0.01
12	-8.56	46	-17.2	29	0.05
13a	-8.42	68	-16.9	60	0.07
13b	-8.32	83	-16.6	120	-0.04
14	-8.31	86	-16.6	120	-0.01
15	-8.08	140	-16.2	300	0.03
16	-8.17	110	-16.4	170	0.05
17	-8.50	51	-17.2	25	0.20
18	-8.64	36	-17.4	15	0.12

Although the range of uncertainty in the calculations is great, it appears that most of the water samples are slightly undersaturated with respect to calcite and dolomite. It is unlikely that the slight undersaturation can be accounted for by the outgassing of carbon dioxide due to pressure release as the water moves up several hundred feet in the well. The release of CO_2 raises the pH and should increase the calculated percent saturation.

The logarithm of the calcium to magnesium ratio, as calculated by the equation:

$$\log \left(\frac{\text{Ca}}{\text{Mg}} \right) = \log \left(\frac{K_{\text{cal}}^2}{K_{\text{dol}}} \right) \quad (35)$$

should theoretically be .18 for the waters sampled if they are in equilibrium with calcite and dolomite. Many of the samples have ratios approaching this value. In summary, therefore, it appears that the samples from deep wells have been in equilibrium with calcite and dolomite and have suffered a slight subsequent dilution with carbonate-undersaturated water.

Geologic and Hydrogeologic Setting

When the geologic settings of the samples are compared, it appears that the low redox potentials are present where Pennsylvanian rocks overlie the producing aquifer. Noticeably higher redox potentials exist in the Clark (#4), Novinger (#9), Brashear (#10), Coon (#12), and Otterville (#6a) ground water which are the only locations where the producing zone is not covered by Pennsylvanian rocks. The abundant shale beds in the Pennsylvanian section of northern Missouri act to

greatly retard or even virtually eliminate the rate of recharge of oxygenated water to the aquifers and thus promote reducing conditions.

In addition, the Ordovician carbonates have been found to contain between 300 and 1300 parts per million organic carbon (Frank, 1975). This is more than two orders of magnitude greater than the concentration of organic carbon in the pore water. Many such solid organic compounds are readily digestible by bacteria in the presence of a suitable electron acceptor. Therefore, the organic content of the aquifers appears to be a more important factor than the concentration of dissolved organic carbon in controlling the redox potential of the water.

CONCLUSIONS

This study has shown that dissolved organic carbon occurs in quite low concentrations in northern Missouri. The concentration of organic carbon does not correlate with the $\log P_{O_2}$ or with the concentrations of iron and hydrogen sulfide in the ground water. This indicates that the dissolved organic carbon is not controlling the redox potential of the water.

Although organic carbon is present in low levels, it appears to be sufficient to support the growth of bacteria. This was confirmed by identifying at least one genus of bacteria in each sample, including one from a depth of 1200 feet. Many nitrate-reducing and some sulfate-reducing bacteria were identified indicating that these organisms may be important in influencing groundwater chemistry.

It was found that approximately three fourths of the iron that will pass through a 0.025 μ filter is in the form of ferric oxyhydroxides and is thus not in true solution. Predicting the concentration of iron that will be in solution at a given pH and pe is made difficult because this study confirmed that the ferric oxyhydroxides have variable solubilities as expressed by the index $p^0Fe(OH)_3$. It was found that the $p^0Fe(OH)_3$ does not correlate with pH as previously suggested. However, the $p^0Fe(OH)_3$ does show a strong negative correlation with $\log P_{O_2}$. This correlation may be due to the fact that both $\log P_{O_2}$ and $p^0Fe(OH)_3$ are calculated from the same measured redox potential.

The fact that widely differing redox potentials are calculated for the $\text{H}_2\text{S}-\text{SO}_4^{2-}$ and NH_3-NO_3 couples indicates that many ground waters are not in internal equilibrium with respect to the sulfur and nitrogen redox species. The waters sampled do appear to have been in equilibrium with calcite and dolomite in the aquifers at some time in the past.

The Pennsylvanian rocks of northern Missouri promote reducing conditions in the subsurface by eliminating any vertical recharge of oxygenated water to the aquifers. The abundance of organic matter in the Ordovician carbonate rocks suggests that the solid organic carbon in the aquifers may be a more important factor in controlling the redox potential than is the dissolved organic carbon.

This investigation has provided a set of background data on organic carbon and on bacteria present in ground water over an extensive part of Missouri. These data can be used as a baseline with which to compare future levels which may arise as a result of present and future waste disposal practices. Because ground water contains bacteria, the potential exists for water quality to degrade seriously if additional biodegradable organic carbon compounds are introduced during waste disposal.

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APPENDIX A

WELL LOG INFORMATION FOR SOME OF
THE WELLS SAMPLED IN THIS STUDY

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Owner: City of Harrisburg

County: Boone

Location: SW $\frac{1}{4}$ NE $\frac{1}{4}$ Sec 11 T50N R14W

Date of Drilling:

Elevation: 840 ft.

Production: 140 g.p.m. with 36 ft. of drawdown.

Casing: 585 ft. of 8" I.D. casing

Static Water Level: 250 ft.

Rock Units (ft. from surface)

0-140	not logged
140-182	Pennsylvanian
182-203	Warsaw Fm.
203-255	Keokuk Fm.
255-375	Burlington Fm.
375-490	Chouteau Group
490-495	Sulfur Springs Fm.
495-555	Devonian
555-565	St. Peter Fm.
565-830	Cotter Fm.
830-980	Jefferson City Fm.
980-1072	Roubidoux Fm.
1072-1100	Upper Gasconade Fm.

Owner: City of Sturgeon

County: Boone

Location: NE $\frac{1}{4}$ SE $\frac{1}{4}$ Sec 5 T51N R12W

Date of Drilling: 7-8-55

Elevation: 841 ft.

Production: 130 g.p.m. with 42 ft. of drawdown

Casing: 460 ft. of 8" casing, 75 ft. of 16" casing

Static Water Level: 198 ft.

Rock Units (ft. from surface)

0-30	glacial drift
30-145	Pennsylvanian shale, sandstone, and limestone
145-315	Burlington-Keokuk Fm.
315-325	Sedalia Fm.
325-425	Chouteau Fm.
425-430	Sky Creek Fm.
430-500	Devonian limestone, dolomite
500-555	St. Peter Fm.
555-570	Everton Fm.
570-865	Cotter Fm.
865-995	Jefferson City Fm.
995-1051	Roubidoux Fm.

Owner: City of Madison

County: Monroe

Location: NE $\frac{1}{4}$ NE $\frac{1}{4}$ Sec 14 T54N R12W

Date of Drilling: 10-60

Elevation: 797 ft.

Production: 48 g.p.m., drawdown to 520 ft.

Casing: 175 ft. of 8" I.D. casing, liner at 418-463 ft.

Static Water Level: 132 ft.

Rock Units (ft. from surface)

0-90	Warrensburg-Moberly Fm.
90-125	Cherokee Fm.
125-130	residium
130-310	Burlington Fm.
310-320	Sedalia Fm.
320-420	Chouteau Fm.
420-450	Grassy Creek Fm.
450-515	Devonian
515-565	Kimmswick Fm.
565-585	Decorah Fm.
585-620	Plattin Fm.
620-680	St. Peter Fm.

Owner: City of Clark

County: Randolph

Location: NE $\frac{1}{4}$ SW $\frac{1}{4}$ Sec 23 T52N R13W

Date of Drilling: 10-10-61

Elevation: 867 ft.

Production: 150 g.p.m. with 161 ft. of drawdown

Casing: 350 ft. of 8", 180 ft. of 12", and 82 ft. of 16" casing

Static Water Level: 240 ft.

Rock Units (ft. from surface)

0-170	glacial drift
170-310	Burlington-Keokuk Fm.
310-330	Sedalia Fm.
330-445	Chouteau Fm.
445-525	Devonian
525-585	St. Peter Fm.
585-750	Cotter Fm.

Owner: City of Otterville

County: Cooper

Well No. 2

Location: NW $\frac{1}{4}$ NW $\frac{1}{4}$ Sec 3 T45N R19W

Date of Drilling: 4-55

Elevation: 839 ft.

Production: 75 g.p.m. with 44 ft. of drawdown

Casing: 210 ft. of 8" casing, liner set at 705-751 ft.

Static Water Level: 116 ft.

Rock Units (ft. from surface)

0-15	detrital
15-40	Chouteau Fm.
40-80	Devonian limestone
80-235	Cotter Fm.
235-395	Jefferson City Fm.
395-500	Roubidoux Fm.
500-530	Upper Gasconade Fm.
530-750	Van Buren-Lower Gasconade Fm.
750-800	Gunter Fm.
800-815	Eminence Fm.

Owner: Rufus Arni

County: Saline

Location: NE $\frac{1}{4}$ SW $\frac{1}{4}$ Sec 3 T49N R23W

Date of Drilling: 1956

Elevation: 775 ft.

Production:

Casing: 238 ft. of 6 $\frac{1}{2}$ " casing

Static Water Level:

Rock Units (ft. from surface)

0-185	not logged
185-285	Burlington-Keokuk Fm.
285-295	Sedalia Fm.
295-355	Chouteau Fm.
355-440	Burlington Fm.
440-470	Chouteau Fm.
470-530	Devonian limestone
530-560	St. Peter Fm.

Owner: City of Brashear

County: Adair

Location: NW $\frac{1}{4}$ SW $\frac{1}{4}$ T62N R13W

Date of Drilling: 3-4-59

Elevation: 809 ft.

Production: 35 g.p.m. with 19 ft. of drawdown

Casing: 37 ft. of 8" and 30 ft. of 12" casing, the 8" casing extends
1 ft. 6 in. above the ground, 50 in. of 8" shutter screen gravel
packed

Static Water Level:

Rock Units (ft. from surface)

0-32 glacial drift

32-64 Pennsylvanian

Owner: Van Buckman

County: Shelby

Location: NW $\frac{1}{4}$ NW $\frac{1}{4}$ Sec 10 T56N R10W

Date of Drilling:

Elevation: 763 ft.

Production:

Casing:

Static Water Level:

Rock Units (ft. from surface)

0-10	not logged
10-76	glacial drift
76-115	Pennsylvanian
115-125	Mississippian residuum
125-220	Burlington-Keokuk Fm.
220-300	Chouteau Fm.
300-325	Hannibal Fm.
335-385	Grassy Creek Fm.
385-500	Devonian
500-550	Kimmswick Fm.
550-570	Decorah Fm.
570-600	Plattin Fm.
600-618	Glenwood-Joachim Fm.
618-675	St. Peter Fm.

Owner: City of Farber

County: Audrain

Well no. 2

Location: NE $\frac{1}{4}$ NE $\frac{1}{4}$ Sec 21 T52N R6W

Date of Drilling:

Elevation: 764 ft.

Production: 13 g.p.m. with 153 ft. of drawdown

Casing: 255 ft. of 8" casing, liner set 275 ft. to 400 ft.
and 450 ft. to 632 ft.

Static Water Level: 217 ft.

Rock Units (ft. from surface)

0-50	glacial drift
50-120	Pennsylvanian clay and shale
120-140	residual Mississippian
140-235	Burlington Fm.
235-245	Sedalia Fm.
245-307	Chouteau Fm.
307-325	Hannibal Fm.
325-340	Sulfur Springs Fm.
340-365	unnamed limestone and sandstone
365-465	Kimmswick Fm.
465-500	Decorah Fm.
500-535	Plattin Fm.
535-580	Joachim Fm.
580-625	St. Peter Fm.
625-632	Everton Fm.

Owner: Prairie Hill School

County: Chariton

Location: SW $\frac{1}{4}$ SW $\frac{1}{4}$ Sec 32 T55N R16W

Date of Drilling: 4-14-50

Elevation: 737

Production: 20 g.p.m.

Casing: 220 ft. of 6 $\frac{1}{2}$ " casing

Static Water Level: 65 $\frac{1}{2}$ ft.

Rock Units (ft. from surface)

0-90	glacial drift
90-205	Pennsylvanian shale
205-265	Warsaw-Spergen Fm.
265-410	Burlington-Keokuk Fm.

Owner: Ervin Bullington

County: Johnson

Location: SE $\frac{1}{4}$ SW $\frac{1}{4}$ Sec 16 T46 R26

Date of Drilling: 11-9-64

Elevation: 760 ft.

Production:

Casing: 257 $\frac{1}{2}$ ft. of 6 $\frac{1}{4}$ " casing

Static Water Level:

Rock Units (ft. from surface)

0-15	not logged
15-255	Cherokee Fm.
255-297	Burlington Fm.
297-310	Sedalia Fm.
310-400	Chouteau Fm.
400-465	Devonian
465-520	Cotter
520-663	Jefferson City Fm.

Owner: Tom Davis

County: Saline

Location: NE $\frac{1}{4}$ NE $\frac{1}{4}$ Sec 18 T49N R20W

Date of Drilling: 12-14-39

Elevation: 767 ft.

Production: 25 g.p.m., no drawdown

Casing: 148 ft. of 6 $\frac{1}{4}$ " casing

Static Water Level: 105 ft.

Rock Units (ft. from surface)

0-30	not logged
30-95	Burlington Fm.
95-130	Sedalia Fm.
130-225	Chouteau Fm.
225-270	Devonian Fm.
270-280	Kimmswick Fm.
280-395	Cotter Fm.
395-565	Jefferson City Fm.

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