



Project Summary

Dissolved Oxygen and Oxidation-Reduction Potentials in Ground Water

Thomas R. Holm, Gregory K. George, and Michael J. Barcelona

Water samples were collected from various depths in a pristine sand and gravel water table aquifer at monthly intervals over a period of one year. Dissolved oxygen concentrations were near saturation 9 feet below the water table and decreased to nearly zero at 78 feet below the water table. Changes in the Eh values were consistent with changes in the dissolved oxygen concentrations. Hydrogen peroxide was detected in nanomolar concentrations at all depths, but not on every sampling run. Of all oxidation-reduction potentials calculated from substituting analytical results into the Nernst equation, only the Fe^{3+}/Fe^{2+} couple in the deepest well agreed with the measured Eh within 50 millivolts. For the O_2/H_2O_2 and NO_3^-/NH_4^+ couples the range of potentials calculated from one year's data overlapped the range of measured Eh values, so there was some agreement on the average. However, for a given sampling run, the various calculated potentials spanned several hundred millivolts, which means that the activity ratios for the various couples differed by many orders of magnitude (i.e. the system was not in redox equilibrium). The concentration profiles of many solutes, including dissolved oxygen, suggest mixing of shallow and deep ground waters. The observed concentration profiles were relatively constant over the duration of the sampling.

This Project Summary was developed by EPA's Robert S. Kerr Environmental Research Laboratory, Ada, OK, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

If ground-water quality is defined in terms of the concentrations and properties of substances dissolved in the water, then the presence or absence of dissolved oxygen affects many aspects of ground-water quality. The mobilities, reactivities, and toxicities of many elements depend on their oxidation states. Microbial populations are distinctly different in oxic and anoxic waters and, therefore, the rates of microbial degradation of organic compounds are also quite different. Thus, dissolved oxygen affects both the geochemical and microbial processes which are likely to influence water quality. In this project we have begun the chemical characterization of a shallow aquifer with dissolved oxygen concentrations ranging from near-saturation to near-anoxic, conditions that are typical of many aquifers which are susceptible to contamination. The results of this study should, therefore, be useful to microbiologists, geochemists, and engineers studying ground-water quality and the fate of contaminants in ground waters.

Aquifer contamination may be partially mitigated by natural physical processes, but the time scale for flushing a conservative substance from an aquifer is proportional to the hydraulic residence time, which can be hundreds of years in some aquifers, and the time required for the flushing of a hydrophobic contaminant that is strongly sorbed by the aquifer solids may be much longer than the residence time. Clearly, physical processes for aquifer self-purification can be very slow. However, natural chemical and biological processes, many of which are redox-

sensitive, can also contribute to aquifer self-purification.

In view of the importance of the redox status of ground water and other natural waters it is desirable to have a convenient, reliable redox indicator. The potential of a platinum electrode, or Eh, is often used as a geochemical redox indicator because the Eh of a water sample can be readily measured and, in certain aquatic environments, the Eh can be quantitatively related to chemical speciation. However, using the Eh as a redox potential for an entire aquatic system is only meaningful in systems that are in chemical equilibrium and that contain electroactive solutes at approximately millimolar concentrations. Most ground waters are not in equilibrium, and the concentrations of electroactive species are often less than one micromolar.

Despite its limitations, the Eh can be a useful qualitative indicator of the redox status. Consistently measured or calculated Eh values can indicate relative redox levels in a single system, such as successive depths in sediment or zones in flow systems with similar concentrations of major electrolyte ions and electroactive minor ions. On the other hand, comparison of the Eh values of very different waters, e.g., of ground waters that are well-poised and anoxic with those that are poorly-poised and oxic, is probably not meaningful. A more reliable characterization of the redox level of a natural water involves a complete chemical analysis, including all redox-active species as well as Eh. This approach has been taken in this project.

Materials and Methods

Four monitoring wells were installed in the Sand Ridge State Forest near Havana, Illinois, in the Havana Lowlands water table aquifer. Three wells were completed at depths of 35, 50, and 65 feet in October, 1984, and the fourth well was completed at 104 feet in September, 1985. A detergent- and acid-cleaned Teflon positive-displacement bladder pump and Teflon tubing were installed in each well.

For pH, Eh, specific conductance, and temperature measurements, ground water was pumped from the well and through a flow-cell. When all parameters reached stable values (i.e., less than 0.05 pH units, 10 mV, or 10 $\mu\text{S cm}^{-1}$ change in successive casing volumes) the water that was being pumped from that point on was considered to be representative of the aquifer water. These stable values were recorded.

After well flushing, unfiltered water samples were collected for organic car-

bon, ammonia, hydrogen peroxide, hydrogen sulfide, and dissolved oxygen determinations. Mass transfer calculations indicated that oxygen diffusing through the sampling tubing probably did not appreciably contaminate any of the samples from the 35-, 50-, or 65-foot wells but may have contaminated the samples from the 104-foot well.

After collection of the unfiltered samples, filtered samples were collected for determination of alkalinity, metals, and anions. In-line filtration was used to prevent air contact. Standard preservatives and holding times were used to preserve and store the water samples. Field blanks were collected by filtering deionized water.

Determinations of the unstable solutes, dissolved oxygen (DO), alkalinity, and hydrogen peroxide were performed immediately after sample collection. In water samples from 35, 50, and 65 feet, DO was determined using the azide modification of the Winkler method. In samples from 104 feet a field colorimetric method (Chemetrics Inc., Calverton, VA) was used to determine DO.

Hydrogen peroxide concentrations were determined using the fluorimetric scopoletin/horseradish peroxidase method. Reagent blanks were run substituting distilled, deionized, and freshly distilled water for ground water. Hydrogen peroxide concentrations in the blanks were equal to or up to three times greater than those of the samples for many sampling runs. Varying the reagent concentrations had no effect on the blanks. The H_2O_2 signal in the blanks was eliminated by addition of the enzyme prior to the scopoletin. Storing distilled water did not increase the concentrations of H_2O_2 over those in freshly distilled water. The stoichiometry of the reaction in distilled water blanks was close to the accepted value of 1.0, which suggests that side reactions were not responsible for fluorescence quenching. Therefore, the measured quenching in the reagent blanks was due to H_2O_2 present in the distilled water and was not introduced with the reagents or produced by the analytical method.

Blanks have not been addressed in the literature on this method. However, a number of authors have suggested that H_2O_2 can be produced in deionized distilled water as a result of microbial activity, photochemical reactions, or by sparging with air. It is likely that hydrogen peroxide is a normal trace component of our distilled water, produced in the distillation process or carried over from the feed water and varying with inputs of radiation and

dissolved oxygen. Therefore, while a large fraction of our H_2O_2 determinations do not satisfy the conventional analytical criterion of low blanks, we feel that we have positively identified H_2O_2 in ground waters from the Sand Ridge site.

Manual colorimetric methods were used to determine ammonia in all samples and iron in samples from 35, 50, and 65 feet. Manganese determinations in the 35, 50, and 65-foot samples were performed using cathodic stripping and anodic stripping voltammetry. For the 9/19/85 and 10/17/85 samples, Fe and Mn were determined by atomic absorption spectrophotometry. Automated adaptations of standard colorimetric methods were used to determine orthophosphate, dissolved silica, sulfate, nitrite, and nitrate. Chloride was determined by automated potentiometric titration. Volatile and nonvolatile organic carbon fractions were determined by wet oxidation and infrared CO_2 detection.

Results and Discussion

The profiles of DO and Eh are shown in Figure 1. The shallowest ground waters were nearly saturated with DO and the deepest waters were nearly anoxic. The measured DO concentration of 0.2 mg L^{-1} in the 104-foot samples may have been an artifact of sampling (see below). The highest Eh values were measured in the shallow oxic ground waters and the lowest Eh values were measured in the nearly anoxic deep waters. Dissolved oxygen concentrations fluctuated up to 1.5 mg L^{-1} between some sampling runs at all depths (Figure 2), which is greater than the uncertainty in the Winkler titration; therefore the observed fluctuations were not an artifact of the analyses. Most of the Eh values in the three shallow wells varied between +330 and +430 mV (Figure 3) with a fairly constant difference of less than 50 mV between the Eh values at 35 and 65 feet.

Iron and Mn concentrations were below the detection limits of approximately 1 $\mu\text{g L}^{-1}$ in all samples from the 35-, 50-, and 65-foot wells. In the samples from the 104-foot well, Fe and Mn concentrations were approximately 0.5 and 0.2 mg L^{-1} , respectively. Assuming that most of the dissolved Fe is in the ferrous form and using the published rate law for ferrous iron oxidation by dissolved oxygen, the half-life of ferrous iron in the aquifer should be less than two hours, which is much shorter than the hydraulic residence time. Therefore, the DO measured in the 104-foot samples was probably the result of oxygen contamination during sampling.

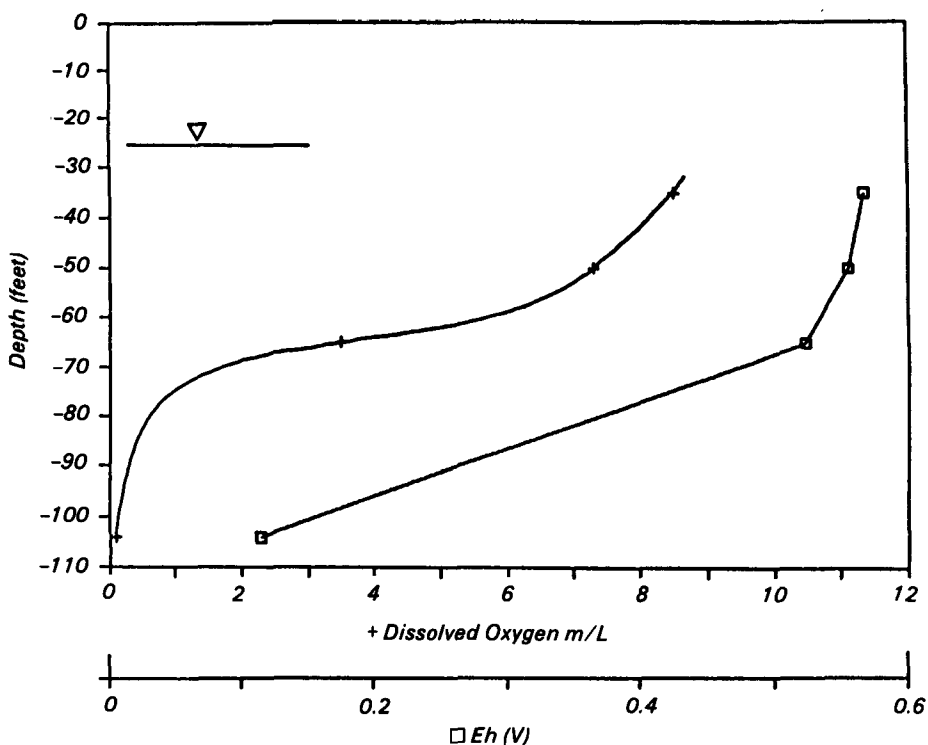


Figure 1. Concentrations of dissolved oxygen and Eh values in ground waters of Havana lowlands aquifer, 9/19/85.

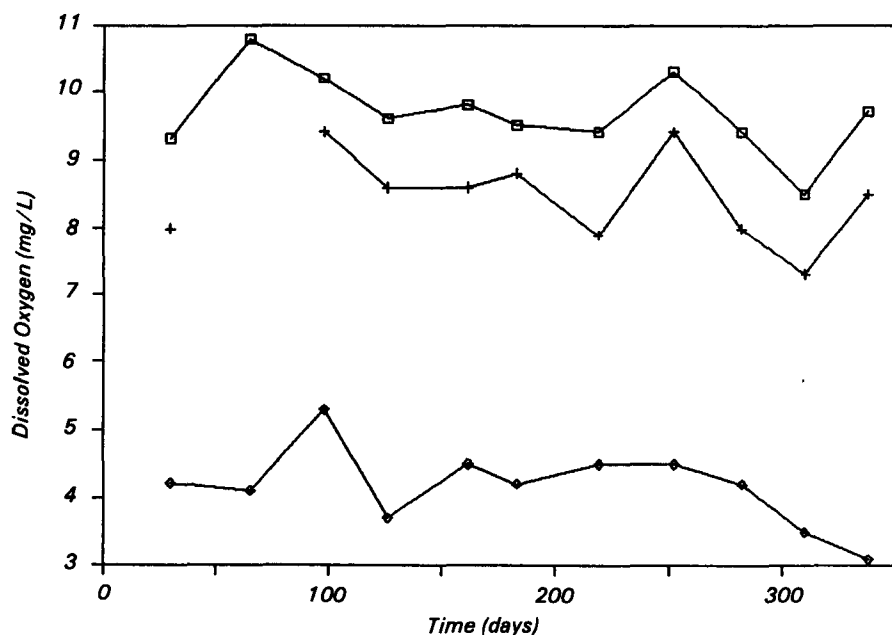


Figure 2. Time series graph of dissolved oxygen concentrations in ground waters of Havana lowlands. □ 35, + 50, ◇ 65 feet.

The time series graph of hydrogen peroxide is shown in Figure 4. The highest concentrations were measured on 1/17/85. The 2/19/85 concentrations were somewhat lower than those observed on 1/17. There was no consistent profile for H_2O_2 .

The O_2/H_2O_2 couple may be a significant participant in the redox chemistry of certain natural waters, but its influence has not been studied. In the Sand Ridge ground waters, H_2O_2 concentrations may be comparable to those of other electroactive solutes. For example, dissolved Fe concentrations were below the detection limit of approximately $2 \mu g L^{-1}$, or 36 nM, which is similar to H_2O_2 concentrations measured on some sampling runs. In principle, the oxidizing power of dissolved oxygen can be controlled by the kinetics of its reduction. If the rate of reduction of H_2O_2 is slower than the rate of its formation, then the potential is effectively that of O_2/H_2O_2 , and O_2 becomes a weaker oxidant than if it were directly reduced to H_2O .

There is now evidence that H_2O_2 is formed and accumulates, in the photooxidation of organic compounds in surface and ground waters. However, the presence of H_2O_2 in untreated ground water has not previously been reported. Since H_2O_2 concentrations in precipitation are frequently orders of magnitude greater than in ground water due to atmospheric photoproduction, rain water may also be a source of peroxide in ground water (i.e. relict H_2O_2 from recharge). Despite the wide-ranging sampling and detailed analysis of H_2O_2 photoaccumulation rates, no measurements of H_2O_2 in ground waters prior to irradiation have been reported. The few reported ground water H_2O_2 measurements were below detection limits.

The concentration profiles of nitrate and orthophosphate (Figure 5) were representative of most sampling runs. Nitrate concentrations decreased with depth, while phosphate concentrations increased. The decrease to a nearly undetectable nitrate concentration in the 104-foot well is consistent with the sharp decrease in DO and Eh between 65 and 104 feet. However, reduced nitrogen species, nitrite or ammonia, were not detected. Nitrate concentrations tended to decrease with time (Figure 6), while phosphate concentrations showed no temporal trend.

The concentration profiles of DO, NO_3^- , and, possibly, $o-PO_4^{3-}$ had two inflection points. Such profiles can be produced by diffusion/dispersion. The conceptual model is that upgradient from the

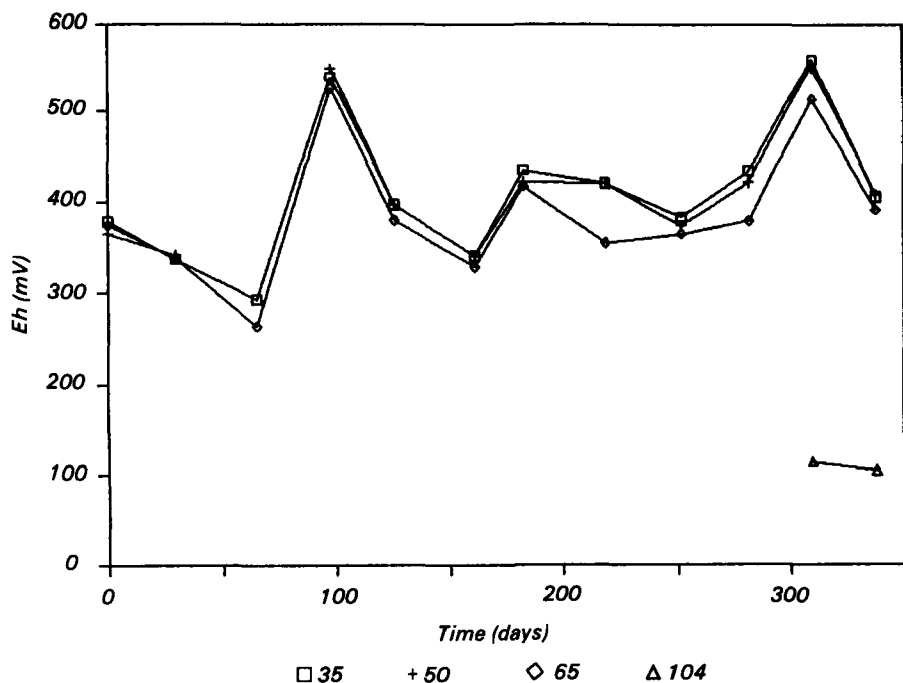


Figure 3. Time series graph of Eh values of ground waters of Havana lowlands. □ 35, + 50, 65, Δ 104 feet.

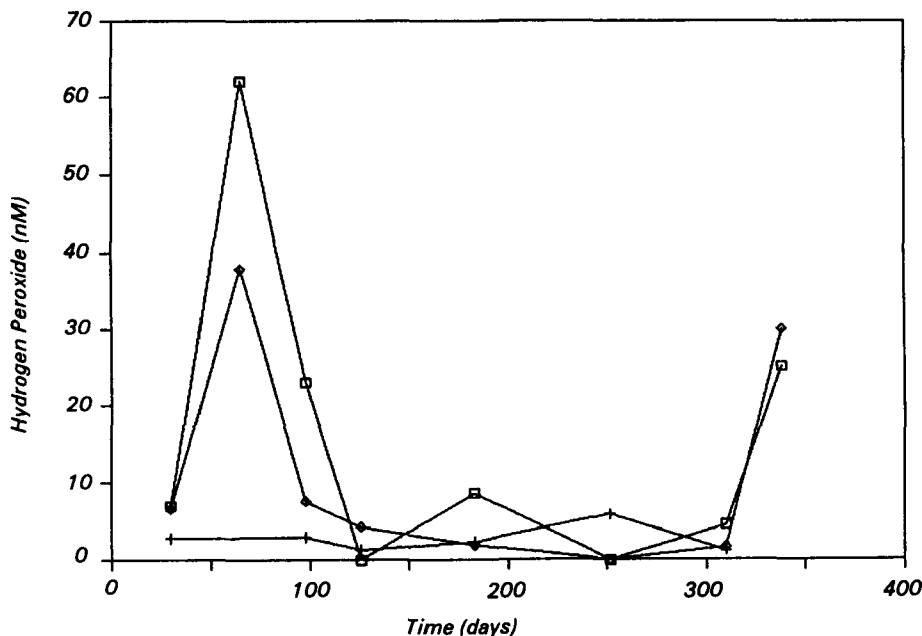


Figure 4. Time series graph of hydrogen peroxide concentrations in ground waters of Havana lowlands. □ 35, + 50, 65 feet.

monitoring wells' two layers of ground water, i.e. oxic recharge waters that leach nitrate from fertilized fields and deep anoxic ground waters that are low in

nitrate, are separated by a thin transitional region. Diffusion and dispersion causes the transitional layer to broaden and produces the observed profile. It may be

possible to estimate the average vertical dispersion coefficient in the aquifer by modeling the concentration profiles of DO, nitrate, and other solutes.

Calculating Redox Potentials

The redox couples considered were O_2/H_2O_2 , $Fe(III)/Fe(II)$, NO_3^-/NH_4^+ , $Mn(III)/Mn(II)$ and SO_4^{2-}/HS^- . For each couple a range of potentials was calculated by substituting analytical values of the various solutes into the Nernst equation. These calculated potentials were then compared to the observed range of Eh values. As an example, the maximum calculated O_2/H_2O_2 potential was for water samples collected from the 35-foot well with a DO of 9 mg L^{-1} and pH of 7.5. The minimum potential was for 65-foot samples with DO of 3 mg L^{-1} and pH of 8. The DO concentrations measured in the 104-foot well were not considered because the values were questionable. A range of H_2O_2 concentrations of 0.1-10.0 nM was assumed. The calculated DO/ H_2O_2 potentials ranged from +430 to +535 mV, which overlaps the observed range of most of the Eh measurements for the 35- to 65-foot ground waters.

For the NO_3^-/NH_4^+ couple only nitrate was detected. As a result, the Nernst equation becomes an inequality (equation 1)

$$E(\text{mV}) > 884 + 7.08 (\log (NO_3^-) - 10 \text{ pH} - \log \text{DC}) \quad (1)$$

where the standard potential at 12°C is 884 mV, braces indicate ionic activities and DL is the detection limit for ammonia nitrogen (0.05 mg L^{-1}). The calculated lower bound for NO_3^-/NH_4^+ potentials was +324 mV, which is consistent with the observed range of Eh values. The calculated potentials would fall in the observed Eh range if the NH_4^+ concentration were less than 7 ng L^{-1} . In order for NO_3^-/NH_4^+ potential to be consistent with the observed Eh, NO_3^- must be below detection and NH_4^+ must be detected. However, NH_4^+ was not detected. Thus, the NO_3^-/NH_4^+ couple was apparently not in equilibrium in the deep waters.

Iron and manganese were below detection in all samples collected from the 35-, 50-, and 65-foot wells. However, hydrous oxides of Fe and Mn were extracted from aquifer and sand samples. Thus, lower bounds for calculated potentials of couples involving these metals were calculated assuming equilibrium with the oxides. For the couple $Fe(OH)_3/Fe^{2+}$ the

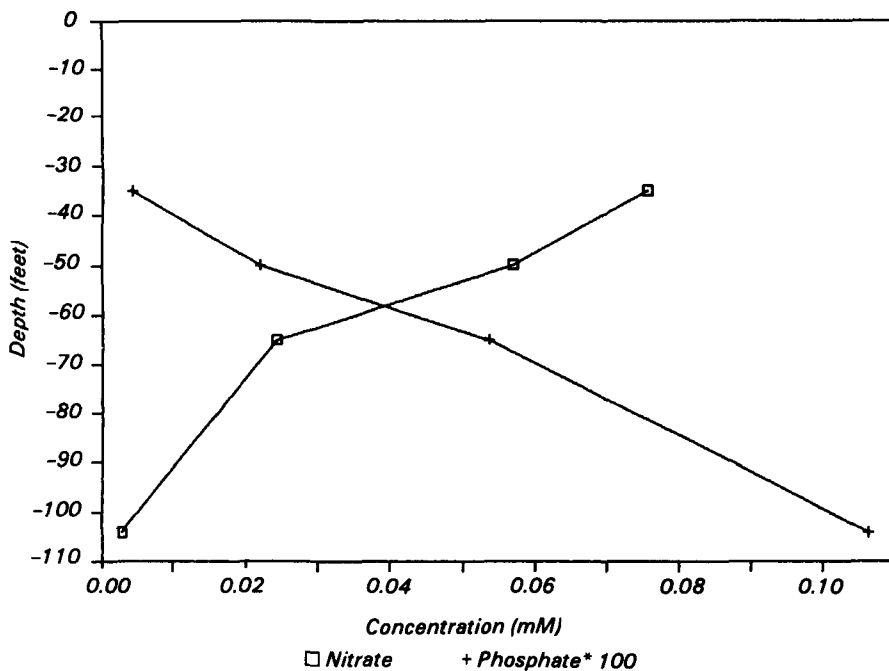


Figure 5. Profile of nitrate and orthophosphate concentrations in ground waters of Havana lowlands. 9/19/85. □ nitrate, + orthophosphate.

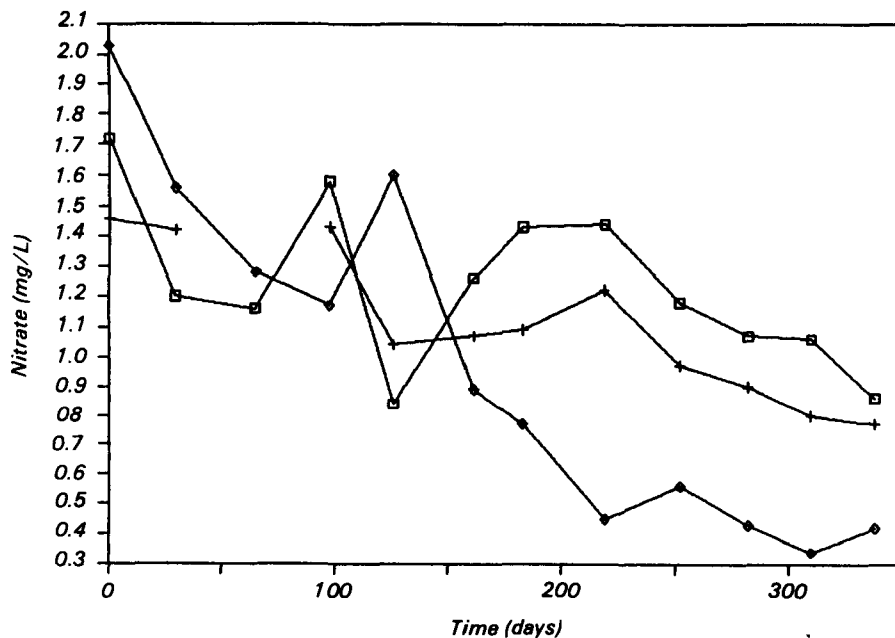


Figure 6. Time series graph of nitrate concentrations in ground waters of Havana lowlands. □ 35, + 50, 65 feet.

Nernst equation becomes the inequality given by equation 2

$$E(\text{mV}) > 756 + 56.6(4.88 - 3 \text{ pH} - \log \text{DL}) \quad (2)$$

where a detection limit of $1 \mu\text{g L}^{-1}$ is assumed for Fe determination by the ferrozine method, all soluble Fe is assumed to be Fe^{2+} , and 4.88 is the log of the

solubility product of $\text{Fe}(\text{OH})_3$. (Note that the only variable in equation 9 is pH.) The lower bound for the $\text{Fe}(\text{OH})_3/\text{Fe}^{2+}$ potential was estimated to be +155 mV, which is not close to but is consistent with the observed Eh values. The calculated $\text{Fe}(\text{OH})_3-\text{Fe}^{3+}$ potential would fall in the observed Eh range if the Fe^{2+} concentrations were less than 20 ng L^{-1} , and Fe^{3+} levels were in equilibrium with $\text{Fe}(\text{OH})_3$ as assumed. The calculated $\text{Fe}(\text{OH})_3/\text{Fe}^{2+}$ potential in the 104-foot ground waters was +38 mV. An uncertainty in the value of the solubility product of $\text{Fe}(\text{OH})_3$ of one logarithmic unit, a pH reading that was high by 0.33 pH units, or a combination of smaller uncertainties in these parameters could account for the disagreement between the calculated and measured potentials. The solubility product determined at 25°C was used for the potential calculation because the enthalpy change of the reaction was not listed, which precluded a temperature correction. Thus, the calculated $\text{Fe}(\text{OH})_3/\text{Fe}^{2+}$ potential agrees reasonably well with Eh.

The lower bound for calculated MnOOH (Manganite)/ Mn^{2+} potentials in the 35- to 65-foot ground waters was calculated as for $\text{Fe}(\text{OH})_3/\text{Fe}^{2+}$. The resulting value of +570 mV is greater than all but two extreme Eh measurements. In order for the calculated Mn potential to fall in the measured Eh range the Mn^{2+} concentration would have to be greater than 40 mg L^{-1} , which would have been easily detectable. Assuming the presence of MnOOH at 104 feet, the calculated $\text{MnOOH}/\text{Mn}^{2+}$ potential is +474 mV, which is much higher than the observed value of +100 mV. Apparently the $\text{MnOOH}-\text{Mn}^{2+}$ couple is not at equilibrium in the aquifer.

Measured and calculated potentials are compared in Figure 7. The best agreement between calculated and measured potentials was for Fe in the nearly anoxic 104-foot well. The potentials of the other couples differed from the Eh by amounts that were not possible to explain by experimental uncertainty. In the shallower, oxic wells, the range of potentials calculated for the $\text{O}_2-\text{H}_2\text{O}_2$ couple overlapped the range of Eh values measured over one year. However, for individual samples, the differences between calculated and measured potentials correspond to differences in the ratio of O_2 to H_2O_2 concentrations of many orders of magnitude. Similar lack of agreement between measured potentials and potentials calculated from analytical data has been noted in an examination of published ground water data

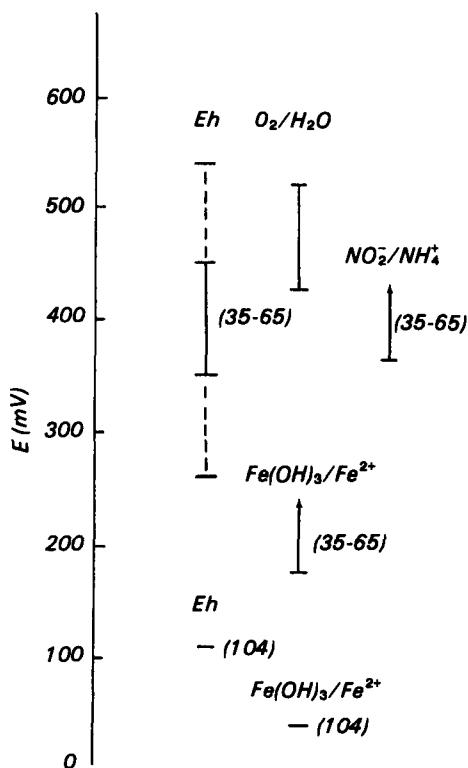


Figure 7. Comparison of Eh values and calculated redox potentials of ground waters of Havana lowlands ground waters.

(Linberg, R.D. and D.D. Runnels. 1984. Science 225:925-927). In certain special situations, e.g. anoxic waters at low pH values, measured Eh values have been found to correspond to speciation of one or more elements. However, in oxic waters at near neutral pH, the measured Eh is usually far from that calculated from elemental speciation. The probable reason for the lack of agreement between measured and calculated Eh is that the system is not in redox equilibrium.

Conclusions

The relative redox status of ground water at the Sand Ridge site is related to the dissolved oxygen concentration as shown by Eh measurements and chemical speciation calculations. The Eh qualitatively indicates the relative redox status of the ground waters, i.e. the lower the DO the lower the Eh. In the deepest waters sampled, the Eh is quantitatively related to Fe speciation. However, for other redox couples and at other depths, there is no quantitative relationship between redox speciation and Eh. The aquifer-ground

water system is not in redox equilibrium at any depth sampled because calculated redox potentials for several couples differ by up to hundreds of millivolts, corresponding to differences in activity quotients of orders of magnitude. The concentration profile of DO is fairly constant and is consistent with mixing of layers of oxic and anoxic water. Modeling the DO profile may help understand mixing in the aquifer.

Recommendations

The field studies should be expanded to include very anoxic ground waters in a similar hydrologic environment, preferably in the same aquifer. Solid oxidants and reductants in the aquifer should be studied to determine their role in redox processes. Geochemical extractions can give an estimate of the aquifer oxidizing or reducing capacity. Redox titrations of aquifer sediments can estimate the redox buffer capacity of the aquifer system. Respirometry experiments may estimate kinetics of aquifer redox processes. Characterization of the organic matter in ground water is essential to understanding aquifer redox processes in both oxic and anoxic waters. This characterization should include complexation of electroactive metals, which may influence measured Eh values, and molecular weight and functional group determinations, which can indicate potential substrates for microbial respiration.

Thomas R. Holm, Gregory K. George, and Michael J. Barcelona are with Illinois State Water Survey, Champaign, IL 61820-7407.

Bert E. Bledsoe is the EPA Project Officer (see below).

The complete report, entitled "Dissolved Oxygen and Oxidation-Reduction Potentials in Ground Water," (Order No. PB 86-179 678/AS; Cost: \$11.95, subject to change) will be available only from:

National Technical Information Service

5285 Port Royal Road

Springfield, VA 22161

Telephone: 703-487-4650

The EPA Project Officer can be contacted at:

Robert S. Kerr Environmental Research Laboratory

U.S. Environmental Protection Agency

P.O. Box 1198

Ada, OK 74820

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