Geochemistry of a Modern Anoxic Environment:
Buck Run, Mt. Morris, Livingston County, New York

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Abstract- A small pool approximately 10 m in diameter and 0.7 m deep in Buck Run, Mt. Morris, Livingston County, New York, becomes anoxic during periods of surface water low flow. The water in the pool is stratified, with the boundary between oxygenated water above and anoxic water below occurring at approximately 40 cm beneath the surface. Water samples were collected for the purpose of characterizing the general chemistry of the water. Measurements of pH, Eh, temperature, and dissolved oxygen were taken in October, 2000. The temperature of both waters was 18 oC. The anoxic water had a pH of 6.2 and Eh of -230 mV. The oxic water had a pH of 7.3, and Eh of 110 mV. Dominant ions in the anoxic water (Na^+, Ca^{2+}, Cl^-, and SO_4^{2-}) were measured using ion chromatography. Dominant ions in the oxic water were the same, but at lower concentrations. The chemistry of the anoxic water closely that of groundwater in shale, which underlies and surrounds the stream. Development of an anoxic environment in a shallow, clear flowing stream conducive to mixing is unusual. The anoxia appears to be due to the discharge of groundwater that has percolated through pyritic black and gray shales.

Key Words- Anoxia, Aqueous Chemistry, Geochemistry, Groundwater, Organically-controlled redox, Redox, Reducing, Shales

Introduction

Buck Run is a tributary of the Genesee River located 1.8 km south of the village of Mt. Morris in Livingston County (Fig. 1). The stream has an average gradient of approximately 19 m/km. Water in the stream flows primarily over bedrock and through gravel during typical low flow periods. In the areas where water is not flowing through gravel it collects into pools, with depths ranging from 0.5 - 1.5 m. Typical pool widths range from 2.0 - 15.0 m.

The subject of study is a pool in Buck Run (Fig. 2), located approximately 1.8 km south of Mt. Morris (Fig. 1). It is 10.0 m wide and reaches a maximum depth of 0.7 m (Fig. 3). A stratification horizon exists approximately 40 cm below the surface during low flow periods. There is a strong sulfur odor in the air surrounding the pool. Water flowing in the stream is typically clear, while water beneath the stratification boundary in this pool has a greenish color. A groundwater seep flows from the Rhinestreet Shale into the pool (Fig. 3). Other interesting features include what is presumed to be methane being released from underlying black and gray shales and bubbling up into the pool, and white bacteria is living in the vicinity of the groundwater seep. No other algae or other macrofauna is living below the stratification horizon. The goal of this study is to describe the stratified water chemically, and to determine the reason for stratification.

Background

Typically, rivers and other freshwater drainage systems are in equilibrium with the atmosphere and are oxidizing environments. Groundwater systems, by contrast, are isolated from the atmosphere and any oxygen consumed by hydrochemical or biochemical processes is not replenished. In isolated environments, organic matter forms a redox couple with the inorganic substances available. The organic matter becomes oxidized, and the inorganic matter is reduced. Microbes that survive by facilitating the process of electron transfer catalyze the redox reactions (Freeze and Cherry, 1979).

A sequence of redox reactions takes place, the extent of which depends on the abundance of organic matter and the amount of reducing bacteria present (Table 1). Dissolved oxygen is the first compound to become exhausted, by means of aerobic respiration
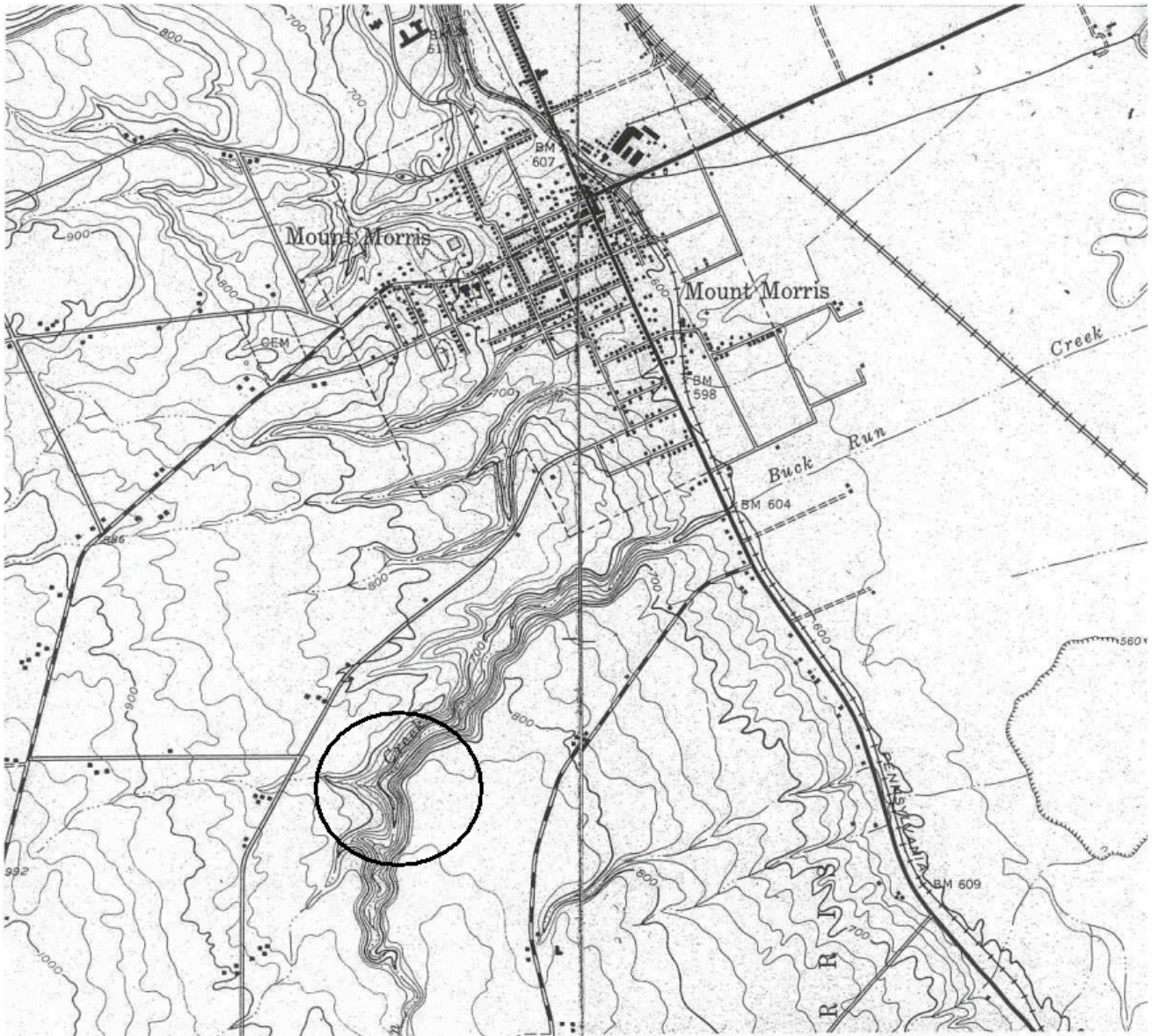
Figure 1- A location map of Mt. Morris and Buck Run. The location of the stratified pool is circled.

(Stumm and Morgan, 1996). The succession of these reactions follows the decreasing pe (pe = - log electron activity).

The reduction of NO3- and MnO2 occur at the same pe level, occurring only if nitrogen or manganese is present in the system. If pe is low enough, the reduction of iron occurs. Fermentation and the reduction of sulfate and carbon dioxide take place simultaneously (Stumm and Morgan, 1996). Organic compounds are unstable over the entire pe range, but anaerobic conditions tend to be more favorable to the preservation of organic matter than aerobic conditions. Equilibrium is often not attained within these reactions, as with most natural reactions, even over geological time spans (Drever, 1988). Microorganisms do not always drive the environment to a stable state. Equilibrium models can be used to characterize the conditions but quantitative inferences must be made with caution, as in any natural water system (Stumm and Morgan, 1996).

Sulfate reducers and methane fermenters (methanogenic bacteria) compete when both are present in a system. Sulfate reducers obtain more energy per unit of substrate oxidized than methane fermenters. It is typically assumed that sulfate reducers outcompete methane fermenters as long as sulfide is available to the system.

Morel (1983) presents a model of a lake becoming "titrated" by organic compounds, and determined the chemical condition of the lake. Thermodynamics demonstrate that oxygen is quickly depleted by aerobic respiration (Table 1, Eq. 1). Also the reduction of sulfate proceeds until the organic substrate is eliminated. The lake water was calculated to have a pH = 6.23, pe = -2.66, and no dissolved oxygen (Morel, 1983). This example makes solid predictions, but does not account for the possibility of an inexhaustable supply of organic compounds.

Methods

Water samples were collected from the upper and lower zones within the pool in Buck Run determine the chemical characteristics of this environment. Temperature, pH, Eh, and dissolved oxygen were measured in situ using a Corning portable probe. Water samples were collected from the anoxic and surface water using a Masterflex portable peristaltic pump and stored in Nalgene bottles. Concentrations of Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, and SO_4^{2-} in the water were determined by an ion chromatography. Alkalinity of the water was measured by titration. Samples of the Rhinestreet Shale were collected from the stream-bed surrounding the groundwater seepage, and analyzed for major element concentration on a Scanning Electron Microscope with Energy Dispersive System.

Results

The temperature of the pool water ranged from 18 to 22 $^\circ$C. The pH of the upper and lower zones were 7.3 and 6.2, respectively (Table 2). Dissolved oxygen was measured in the anoxic zone at $PO_2 <$ 0.1%, while the surface water proved to be typical fresh water, with $PO_2 = 13.0\%$. The Eh values of the upper and lower zones were measured at +110 mV and -230 mV, respectively. The alkalinity of the oxic and anoxic waters were 162.9 mg $CaCO_3$/l and 219.3 mg $CaCO_3$/l, respectively. The surface water consisted of Ca^{2+} - SO_4^{2-} dominated water, and the anoxic water consisted of Na^+ - SO_4^{2-} water (Table 3).

Anoxia in the pool is ephemeral. A rain event measuring 3.4 cm (1.34 inches) occurred on September 23, 2000. The resulting run-off increased stream discharge sufficiently to completely flush the anoxic environment at Buck Run. The creek returned to base flow over the next few days. Seven days after the rain event, the anoxic environment was completely re-established. The Rhinestreet is an organic rich black shale that is approximately 2-3% pyrite (FeS_2) by volume. Secondary gypsum ($CaSO_4 \cdot 2H_2O$) occurs in fractures and bedding planes of weathered Rhinestreet Shale, but was not found in the unweathered strata.

Discussion

Measurements of pH = 6.2 and Eh = -230 mV (table 2) are characteristic of reducing environments and are consistent with groundwater that is isolated from the atmosphere (Fig. 4). Such water is typical in organic-rich black shales with low permeability where the groundwater has a long residence time. Also diagnostic of a reducing environment is the electron activity (pe), also called redox potential. The electron activity can be calculated from the Eh by

Figure 2- The stratified pool in Buck Run, Mt. Morris, NY. View is to the South.
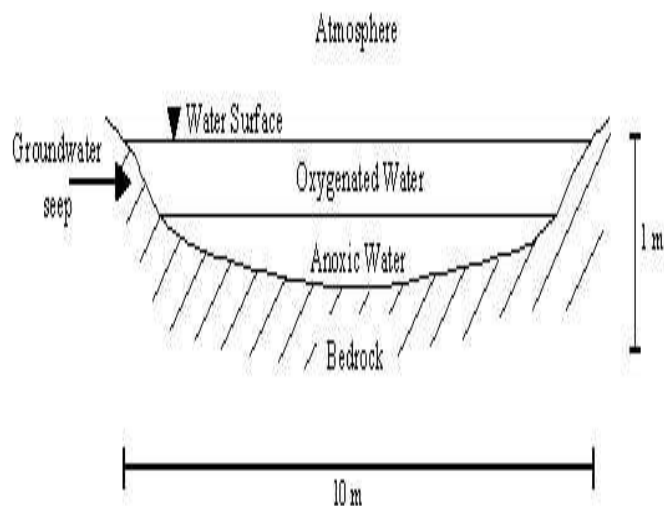

Figure 3- A conceptual model of the stratified pool in Buck Run. It is approximately 10 m wide and 0.7 m deep. The horizontal boundary between oxygenated and anoxic water is approximately 40 cm below the water surface. Groundwater seeps out of the black shale, shown on the left. The substrate and surrounding bedrock are black and gray shales.

Table 1- The sequence of progressive reduction by organic matter. The species (CH2O) represents a simple carbohydrate, but polysaccharides, saccharides, fatty acids, amino acids, and phenols may be the actual compounds involved in these redox reactions (Modified after Stumm and Morgan, 1996).
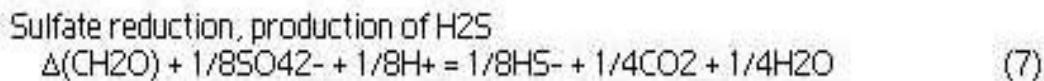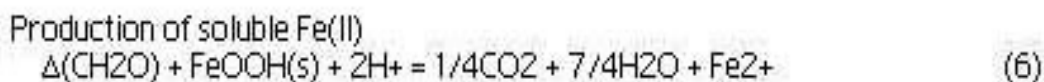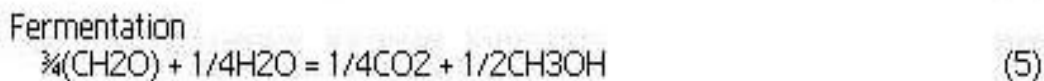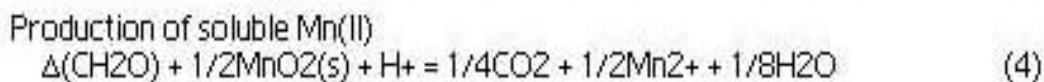
Aerobic Respiration
$$\Delta(CH_2O) + \Delta O_2 \quad \Delta CO_2 + \Delta H_2O \tag{1}$$

Denitrification
$$\Delta(CH_2O) + 1/5 NO_3^- + 1/5 H^+ = 1/4 CO_2 + 1/10 N_2 + 1/2 H_2O \tag{2}$$

Nitrate reduction
$$1/4(CH_2O) + 1/8 NO_3^- + 1/4 H^+ = 1/4 CO_2 + 1/8 NH_4^+ + 1/8 H_2O \tag{3}$$

Production of soluble Mn(II)
$$\Delta(CH_2O) + 1/2 MnO_2(s) + H^+ = 1/4 CO_2 + 1/2 Mn^{2+} + 1/8 H_2O \tag{4}$$

Fermentation
$$\tfrac{3}{4}(CH_2O) + 1/4 H_2O = 1/4 CO_2 + 1/2 CH_3OH \tag{5}$$

Production of soluble Fe(II)
$$\Delta(CH_2O) + FeOOH(s) + 2H^+ = 1/4 CO_2 + 7/4 H_2O + Fe^{2+} \tag{6}$$

Sulfate reduction, production of H2S
$$\Delta(CH_2O) + 1/8 SO_4^{2-} + 1/8 H^+ = 1/8 HS^- + 1/4 CO_2 + 1/4 H_2O \tag{7}$$

Methane fermentation
$$\Delta(CH_2O) = 1/8 CH_4 + 1/8 CO_2 \tag{8}$$

Table 2- The summary of water measurements taken in situ.

	Surface water	Anoxic water
pH	7.3	6.2
Eh	+110 mV	-230 mV
Dissolved Oxygen	13.0 %	< 0.1%

$$pe = -\log[e^-] = \frac{F}{2.303\ RT}\ Eh$$

where F is the Faradays constant (F = 96.42 kJ/V g eq), and R is the gas constant (R = 8.314 x 10-3 kJ/deg mol). The temperature was measured at T = 293.15 K. The pe was calculated to be -3.69, characteristic of a reducing environment. Any inorganic compound introduced into an environment with high electron activity will quickly be reduced.

The measured partial pressure of oxygen was PO2 < 0.1 %, indicating that all the oxygen is being consumed by aerobic respiration (Eq. 1). Mixing takes place between the stream and the atmosphere so it would be unlikely to have oxygen consumption taking place at a rate high enough to create anoxia. Anoxia is common in groundwater, especially in water flowing through organic-rich media. Groundwater feeding into Buck Run is flowing through the organic-rich Rhinestreet Shale.

The Eh and pH measurements are also indicative of an environment isolated from the atmosphere (Fig. 4). An Eh of -230 mV is consistent with groundwater having a long residence time flowing through a reducing medium.

The measurements of SO42- and the strong sulfur odor indicate the presence of the SO42-/HS- redox couple. The systematics of organic compound redox are such that sulfate reduction (Eq. 7) and fermentation (Eq. 5) take place simultaneously. All three redox reactions are probably taking place in the groundwater adjacent to Buck Run.

The water in Buck Run has a Na+/Ca2+ ratio of 1.63. Meteoric precipitation in the area has a considerably lower Na+/Ca2+ ratio of 0.49 (Faure, 1998). Since calcium is much more abundant in meteoric water than sodium, calcium in the fresh water must be exchanging with sodium in the shale along the groundwater flowpath.

Groundwater flowing through the organic-rich black shales eventually seeps into Buck Run, causing

Table 3- Ion concentrations of major species measured in the stratified pool of Buck Run. All values are reported in mg/l.

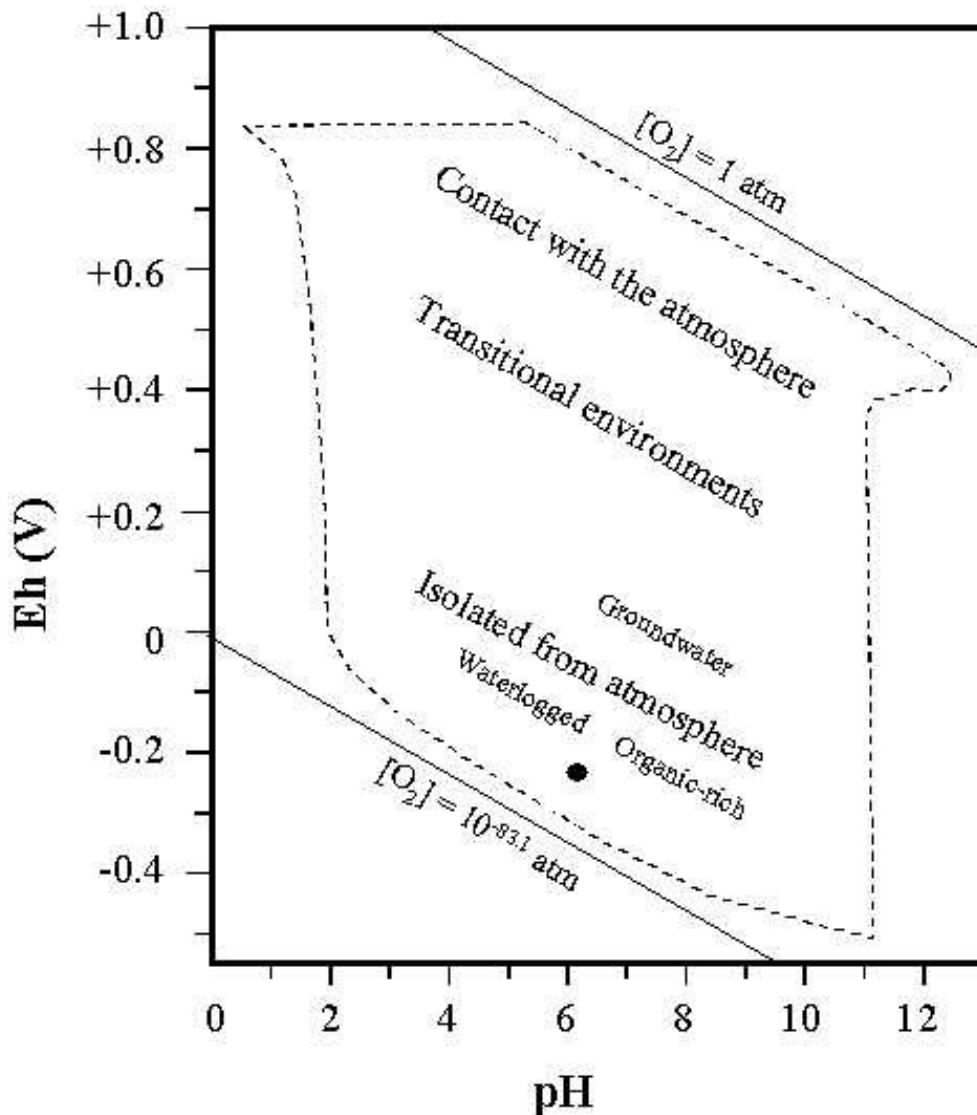| Ion	Surface water	Anoxic water
Na^+	32.5	96.7
Ca^{2+}	71.0	59.2
Mg^{2+}	21.9	17.5
SO_4^{2-}	55.9	99.0
Cl^-	20.0	68.2

Figure 4- An Eh/pH plot showing typical environments for given conditions (Modified after Garrels and Christ, 1965). The anoxic water of Buck Run plots at Eh = -230 mV, pH = 6.2, shown by a solid black circle.

an anoxic environment. Evolution of the groundwater can be traced to explain its character upon release into Buck Run (Fig 5).

Precipitation percolates into the Rhinestreet Shale, while surface weathering causes the oxidation of the sulfur in pyrite to sulfate (S_2- à SO_4^{2-}), which in turn bonds with calcium to form gypsum ($CaSO_4*2H_2O$). Hydrogen sulfide and sulfate ions enter the groundwater system as water percolates downward. Some iron from dissolved pyrite remains at the surface giving weathered shale surfaces a red stain (Hematite Fe_2O_3), while the rest travels in solution with the groundwater.

Groundwater in the black shale begins redox reactions, oxidizing organic compounds while reducing inorganic compounds. Oxygen is quickly exhausted by the aerobic respiration of microbes that catalyze the entire sequence of redox reactions taking place. SO_4^{2-} becomes reduced to HS- and H_2S, the Eh becomes negative, and the pH drops to < 6.0.

Ultimately, strongly reducing groundwater is released into Buck Run containing significant amounts of dissolved sulfur, an acidic pH, and a negative Eh. It is possible that the groundwater is more dense than the surface water of Buck Run, and stratifies. The shallow nature of Buck Run causes some mixing to take place between the surface water and the anoxic water, and causes the more reducing
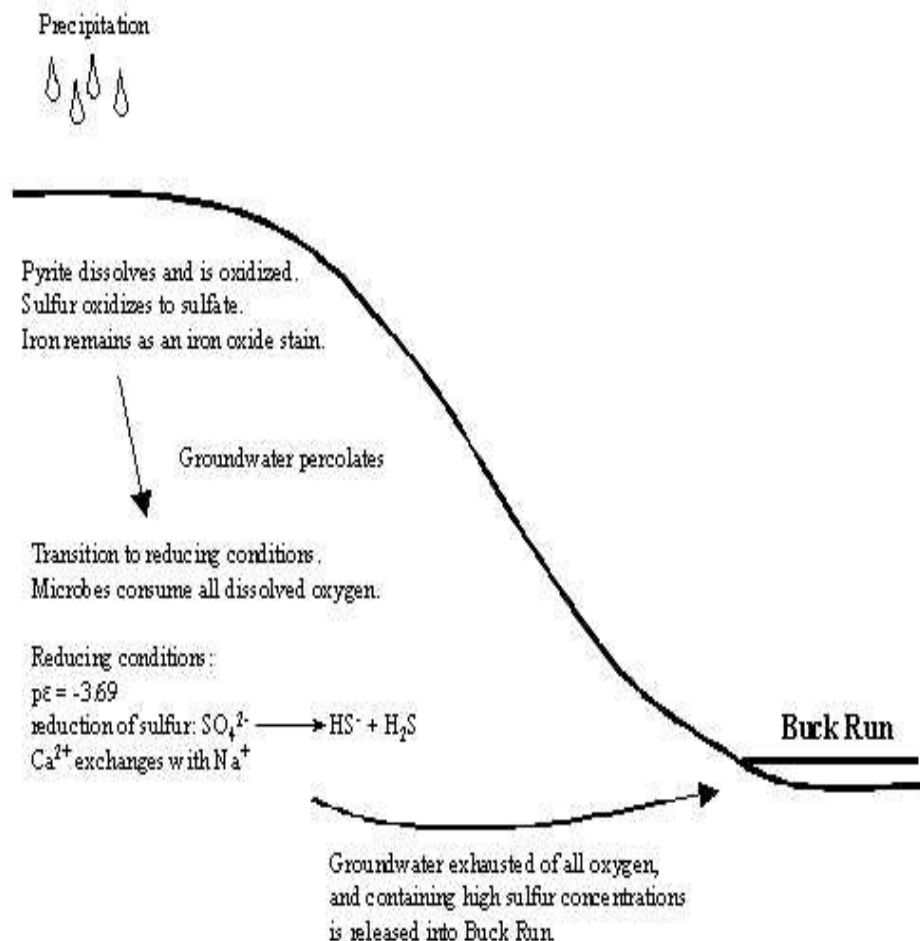
Precipitation

Pyrite dissolves and is oxidized.
Sulfur oxidizes to sulfate.
Iron remains as an iron oxide stain.

Groundwater percolates

Transition to reducing conditions.
Microbes consume all dissolved oxygen.

Reducing conditions:
$p\varepsilon = -3.69$
reduction of sulfur: $SO_4^{2-} \longrightarrow HS^- + H_2S$
Ca^{2+} exchanges with Na^+

Buck Run

Groundwater exhausted of all oxygen,
and containing high sulfur concentrations
is released into Buck Run.

Figure 5- A conceptual model of the chemical evolution and flowpath of groundwater that feeds the anoxic environment of Buck Run.

groundwater to be slightly buffered in the stream.

Conclusions

The Rhinestreet Shale is the source of sulfur and organics that result in redox conditions. The bottom water in the stratified pool of Buck Run is a reducing environment in which the reduction of sulfur is taking place. The source of the bottom anoxic water is groundwater seeping out of the Rhinestreet Shale. Dissolved oxygen is consumed by aerobic respiration of microbes along the groundwater flowpath within the Rhinestreet Shale. The Eh/pH measurements suggest that the groundwater that feeds the pool is isolated from the environment, and therefore probably has a long residence time in the Rhinestreet Shale. The chemistry of the Rhinestreet Shale is adequate to create redox conditions and anoxia. It is conclusive that the mechanism for anoxia in the stratified pool of Buck Run is a seepage of groundwater coming from the Rhinestreet Shale.

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