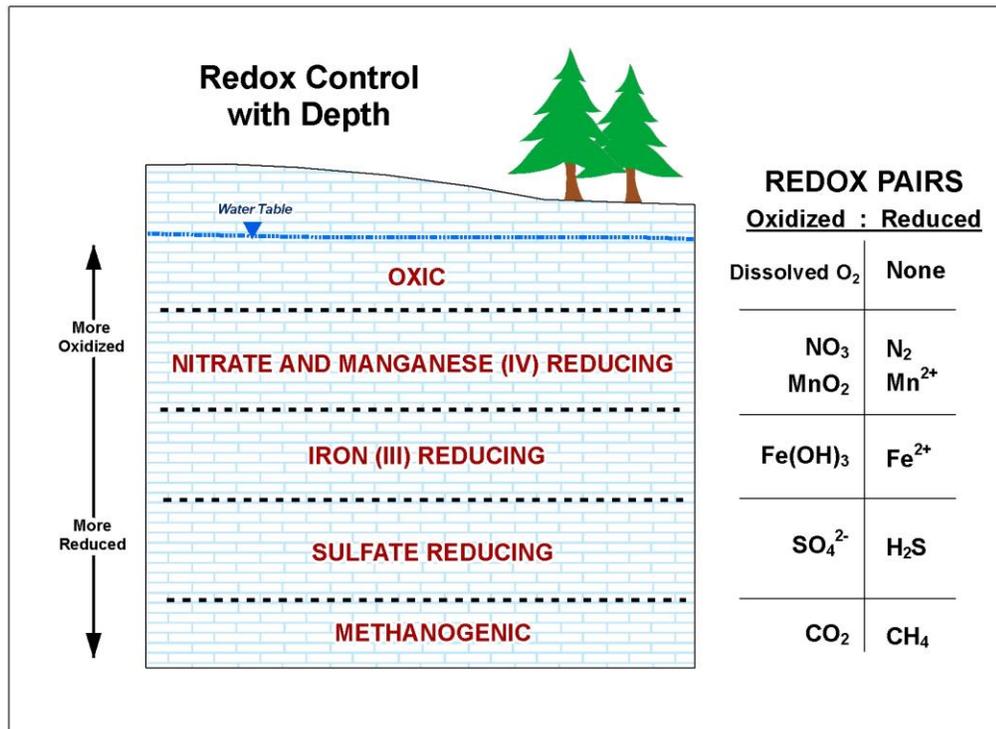


Reduction-Oxidation (Redox) Control in Ohio's Ground Water Quality



The Technical Series on Ground Water Quality:

This series of reports provides information to the professional/technical community about ground water quality in Ohio's aquifers. These reports use data from:

- the ambient ground water quality monitoring program; and
- the public water system compliance programs.

These data, representative of raw water, are used to characterize the distribution of selected parameters in ground water across Ohio. The goal is to provide water quality information from the major aquifers, exhibit areas with elevated concentrations, and identify geologic and geochemical controls. This information is useful for assessing local ground water quality, water resource planning, and evaluating areas where specific water treatment may be necessary.

A series of parallel fact sheets, targeted for the general public, provide basic information on the distribution of the selected parameters in ground water. The information in the fact sheets is presented in a less technical format, addresses health effects, outlines treatment options and provides links to additional information.

Disclaimer

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Reduction-Oxidation in Ohio's Ground Water

Abstract

The redox condition of water is a conceptual framework for understanding the behavior of some of the most common water quality parameters. For example, the iron staining of plumbing fixtures, ground water with a rotten egg smell, and the presence of arsenic all relate directly to the reduction-oxidation (redox) state of the water. All bodies of water, from aquifers to streams to glasses of water, have redox states that are mediated by microbes and electron transfer reactions. While complicated geochemically, redox condition is not difficult to grasp conceptually. Oxidation describes the loss of electrons by an electron donor, while reduction is the simultaneous gain of an electron by an electron acceptor.

This technical report focuses on a general understanding of redox as it relates to ground water quality, using Ohio raw water data to illustrate these themes. Also included are several examples that show how redox concepts can be applied to understand the behavior and persistence of some common ground water contaminants, both natural and anthropogenic.

Introduction

The redox (**RED**uction-**OX**idation) state of water exerts significant control on its chemistry. Redox conditions influence both the solubility and stability of many common parameters. Consequently, understanding the processes that control the redox conditions of ground water helps to understand its geochemistry. Redox, however, is not a dissolved component itself, but rather a geochemical control on a set of common ground water constituents.

The purpose of this report is to define reduction-oxidation in ground water, and illustrate the controls that redox conditions exert on Ohio water quality using Ohio EPA's Ambient Ground Water Quality Monitoring Program (AGWQMP) water quality data. Redox conditions vary widely across the state, even within the same aquifer at a single location. Once the controlling processes are understood, water quality of selected parameters can be used to indicate redox state.

The predictive power of the ground water redox framework allows us to understand and even anticipate certain changes in water quality for constituents that are sensitive to redox conditions. These include dissolved oxygen, nitrate, manganese, iron, arsenic, hydrogen sulfide gas, methane and uranium, as well as some pesticides and certain chlorinated Volatile Organic Compounds (VOCs) such as trichloroethene (TCE), tetrachloroethene (PCE), trichloroethane (TCA) and vinyl chloride (VC).

Redox Principles

The redox state of ground water controls a number of important processes, including: 1) the mobilization (or sequestration) of naturally occurring metals and radionuclides, 2) the preservation (or degradation) of human-influenced contaminants, such as nitrates or VOCs; 3) the generation of undesirable by-products, such as dissolved iron or iron bacteria, hydrogen sulfide gas (with its characteristic rotten egg smell) and methane.

The redox state of a ground water is the end result of a set of electron transfer reactions that *naturally* occur in any body of water (from aquifers to swimming pools to glasses of water). These reactions, facilitated by a variety of microorganisms, control the transfer of electrons between electron donors (such as an aquifer's carbon content, certain VOCs, pyrite, etc.) and electron acceptors (such as dissolved O₂, nitrate, iron, etc.). The naturally occurring

microorganisms compete aggressively for the available electron donors and acceptors to extract energy to sustain their growth within the aquifer.

Many microorganisms have evolved to exploit particular electron acceptors or donors, and will out-compete others to facilitate their preferred reactions. Dissolved oxygen (DO) will accept electrons quite readily and oxygen-reducing microorganisms will out-compete all others to utilize this easily accessible electron sink. Oxygen-reducing reactions will continue until all available DO is depleted, at which time the next most easily exploited electron acceptor (nitrate) becomes available, and the water becomes more 'reducing.' This well-established pattern of reaction preferences for common inorganic constituents is as follows:



The orderly depletion of these electron acceptors is the basis on which we establish a ground water's redox condition, which is named for the water sample's predominant electron acceptor (redox process) within the above sequence. Figure 1 illustrates this sequence applied vertically through an aquifer. Infiltrating precipitation carries with it dissolved oxygen as it enters the ground water system at the water table. As this water flows downward through the aquifer, it is no longer in contact with the atmosphere. If electron donors, microbes and a carbon food source are present, the dissolved oxygen is consumed and the water becomes more reducing as it flows down gradient.

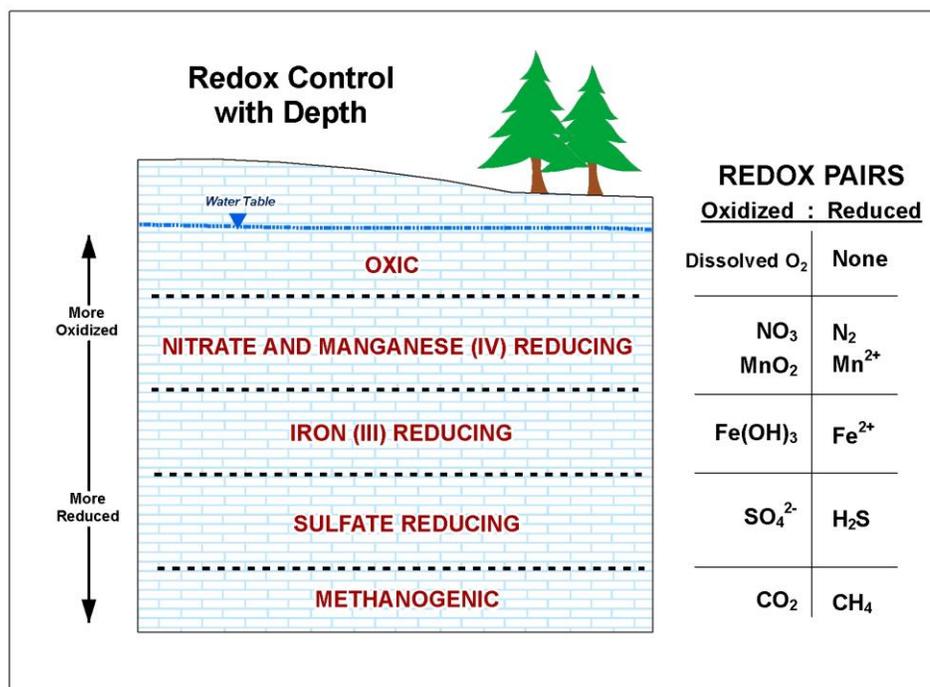


Figure 1. Sequence of redox-sensitive parameter changes with depth.

The electron acceptors are various inorganic constituents that are reduced during reactions. The redox pair (Figure 1) thus refers to the different forms of the same element; one oxidized and one reduced. These pairs will most often not exist together, but rather either one or the other will dominate depending on where the water lies along the redox spectrum. As ground

water is reduced, the redox pairs will move from oxidized to reduced, in an orderly progression as indicated in Figure 1. Using this pathway of successive reduction, general redox conditions can be inferred by the presence and absence of these reactants and products. Generally, a water sample's redox state is termed "oxic" (oxidized, aerobic or oxygen-bearing) if its dissolved oxygen exceeds 0.5 mg/L, and "anoxic" (reducing, anaerobic or oxygen depleted) if it falls below 0.5 mg/L. Anoxic conditions can be further divided into sub-categories named for the inorganic compound acting as the predominant electron acceptor within the process (nitrate-reducing, manganese-reducing, iron-reducing or sulfate-reducing) or for the reduced form of the redox pair (methanogenic).

Knowing a sample's redox state allows certain predictions to be made regarding its water quality at the time of sampling, as well as anticipate how contamination might change water quality. For example, if detectable DO (> 0.5 mg/L) is found in a ground water sample, oxygen-reducing microorganisms have not completed their reactions to deplete the available O₂. In this case, the water's redox condition is at least mildly oxidizing, leading to stable nitrate and the persistence of the chlorinated VOCs TCA, TCE and PCE and the chlorination byproduct chloroform, as well as conditions conducive to the natural attenuation of gasoline-related hydrocarbons such as benzene and toluene. Similarly, the presence of detectable nitrate in a water sample implies that the water is oxic or nitrate-reducing. The presence of nitrate buffers the redox condition until nitrate-reducing bacteria have completed degrading all the available nitrate. This means that even if reduction is underway, it has not moved forward to Mn (IV) or even Fe (III) reducing conditions.

Because ground water redox conditions can be influenced by factors such as recharge, introduction of contaminants, local ground water flow and pumping conditions, and especially by the available electron acceptors, it follows that redox zones are established in response to these factors. This zonation is an expression of the spatial variability of the determining factors that make up the redox condition. Consequently, wells that extract water exclusively from a single redox zone will generally be stable with respect to redox, and those that draw water from multiple redox zones will display a more mixed redox character. The latter scenario is common to public water supply wells, which often derive their water from multiple formations through more deeply set and longer screens, or long, open bore holes. Wells that extract water from multiple formations often include an aerobic water from a near-surface aquifer influenced by recharge, mixed with deeper, more reducing waters.

How Redox is Measured

The method used to measure redox condition varies with accuracy requirements. The easiest method is to deduce the redox condition based on the concentrations of a few standard inorganic constituents: nitrate, iron, sulfate and dissolved oxygen. This provides a general sense of where the water is relative to the list of constituents consumed with progressive reduction. These inorganic parameters are available for testing at most environmental laboratories.

Another method of estimating a water's redox condition is to measure the "*oxidation-reduction potential*" (ORP, measured in millivolts), which is the tendency of the entire solution to gain or lose electrons. ORP is not a concentration but rather an activity level. It is measured using a standard probe, and is often paired with other probes such as for pH and temperature. Although ORP has practical limitations, it is useful for monitoring basic redox changes. Ground water with lower ORP is more reduced. ORP is best collected in the field under controlled conditions, as exposure to the atmosphere can quickly invalidate the measured value. More technical estimates of redox condition include measurements of E_o, the standard reduction potential, as

well as monitoring the hydrogen gas output of redox reactions. These methods are not discussed here, but interested readers are directed to Stumm and Morgan (1981).

Inorganic Parameters as Redox Indicators

The framework for understanding the influence that redox reactions have on ground water has three broad levels:

- 1) the consumption of reactants;
- 2) the intermediate product (hydrogen gas); and
- 3) the generation of products.

This report focuses on examining patterns of reactants and products common to basic ground water chemistry in Ohio. The intermediate product, hydrogen gas, is an effective tool for studying redox reactions, but its analysis is more complicated and expensive.

For example, if ground water exhibits detectable nitrate, it indicates that the water is at least slightly oxidized or nitrate-reducing; however, if water includes dissolved iron (Fe^{2+}), it suggests that the ground water is more reduced and that iron oxide (Fe^{3+}) has been mobilized. Figure 2 plots dissolved iron against dissolved nitrate for AGWQMP data illustrating the mutually exclusive relationship between nitrate and iron imposed by the microbial-mediated redox reactions. Oxidized or nitrate-reducing ground water, as indicated by the presence of dissolved nitrate (NO_3), carries no dissolved iron and suggests some recent connection with the atmosphere.

Average Total Iron vs Nitrate in AGWQMP wells

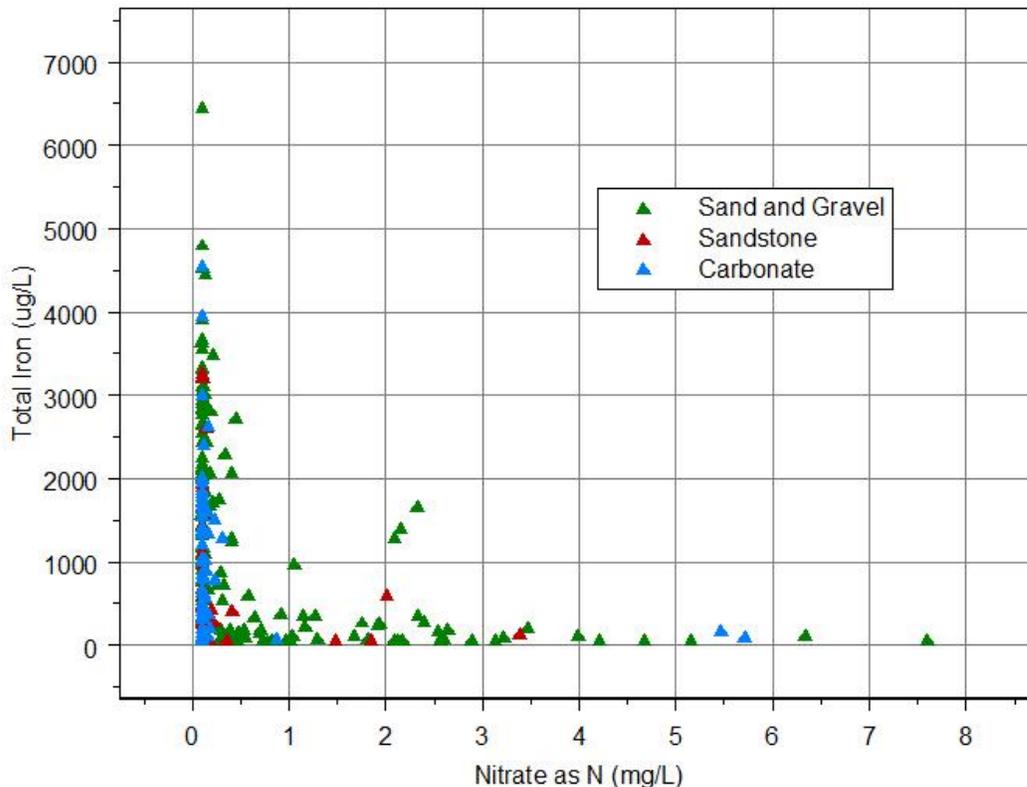


Figure 2. Average total iron as a function of nitrate in AGWQMP wells.

If the ground water is reduced, as indicated by the presence of elevated dissolved iron, it suggests that the ground water is isolated from the atmosphere and is not actively receiving oxygenated surface recharge. Figure 2 also shows a few data points that suggest a mixture between reducing and oxidizing conditions (those with elevated nitrate *and* iron). These data points probably indicate mixing between water sources with unlike redox conditions, which can occur when water from more than one formation flows into a well with a long screen or along an open bore hole.

Figure 3A illustrates the association between ORP and nitrate, which delineates the oxidized or nitrate-reducing systems with elevated nitrate (nitrate values > 2 with ORP > 0). Systems with the highest ORP values are considered to be in contact with the atmosphere and are likely to contain shallow, young ground water. ORP is plotted against concentrations of manganese and iron in Figure 3B. As expected from the microbial-mediated sequence (Figure 1), both manganese and iron are low in oxidized ground water, but as ground water becomes more reduced, manganese and iron concentrations increase - the mirror image of nitrate.

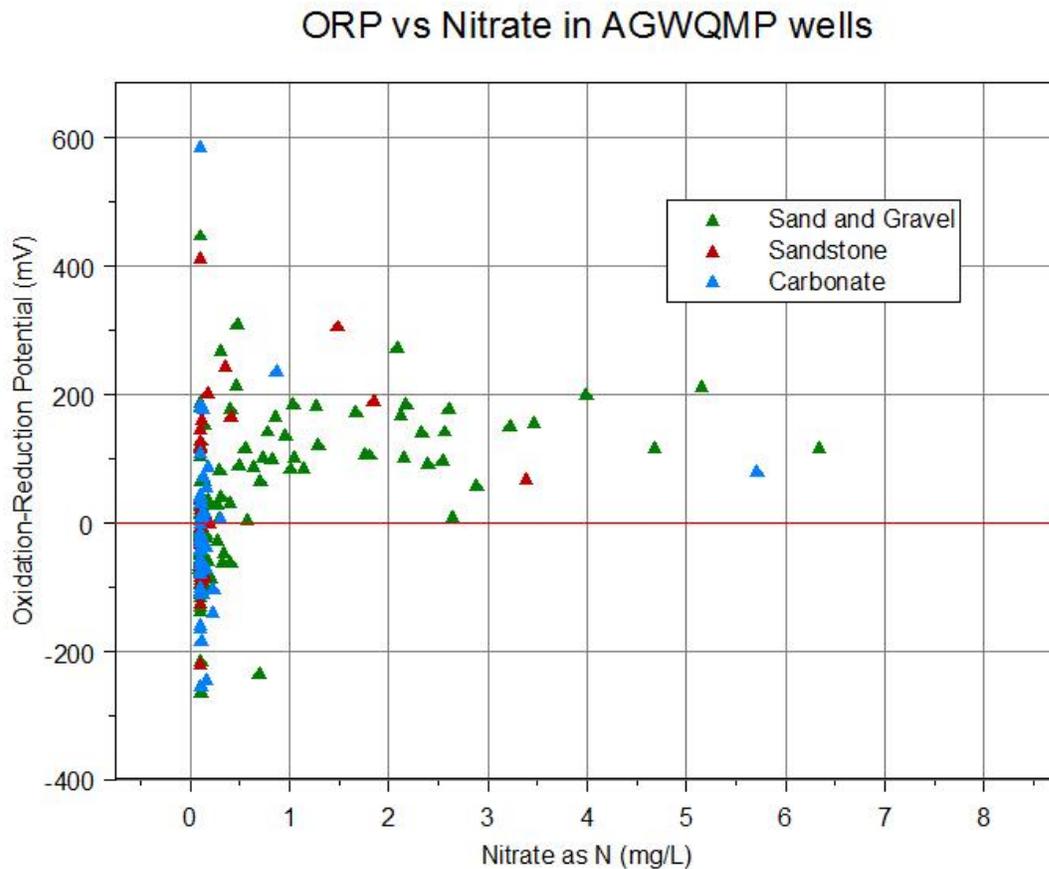


Figure 3A. ORP as a function of nitrate in AGWQMP wells.

Manganese and Iron concentrations vs ORP

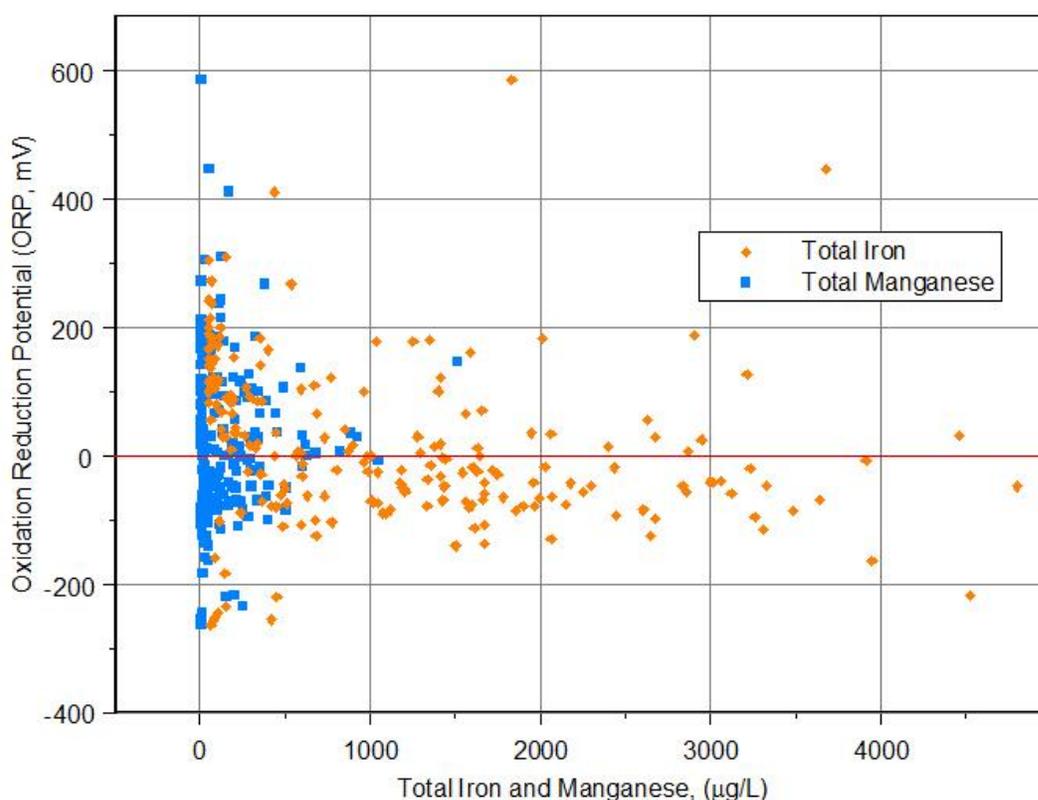


Figure 3B. ORP as a function of Total Iron and Manganese.

Figure 4 plots manganese against ORP to explore the suggestion of low manganese in strongly reduced ground water. There is some variability, but it is clear that manganese decreases with lower ORP, after peak manganese around an ORP range of about +50 to -50 mV. Thus, elevated iron without dissolved manganese suggests more reduced ground water than elevated iron and manganese together, which is consistent with the electron acceptor sequence presented in the redox principles section.

One concern with using inorganic parameters as proxies for ground water redox conditions is the mixed nature of the water samples from some wells. A well with a long screen or extensive open hole section is collecting water over a significant vertical section of the saturated zone and, consequently, the water collected and pumped may represent a mixture of redox conditions. In cases where multiple saturated thicknesses are intercepted by a well screen, the resulting water sample will represent multiple redox zones, and an ORP measurement of such a sample will reflect mixed potentials. The consistency in the previous graphs, presented to illustrate the rationale for using inorganic parameter proxies of redox conditions, indicates that this is not a major problem, but it is a concern that needs to be evaluated.

ORP vs Manganese

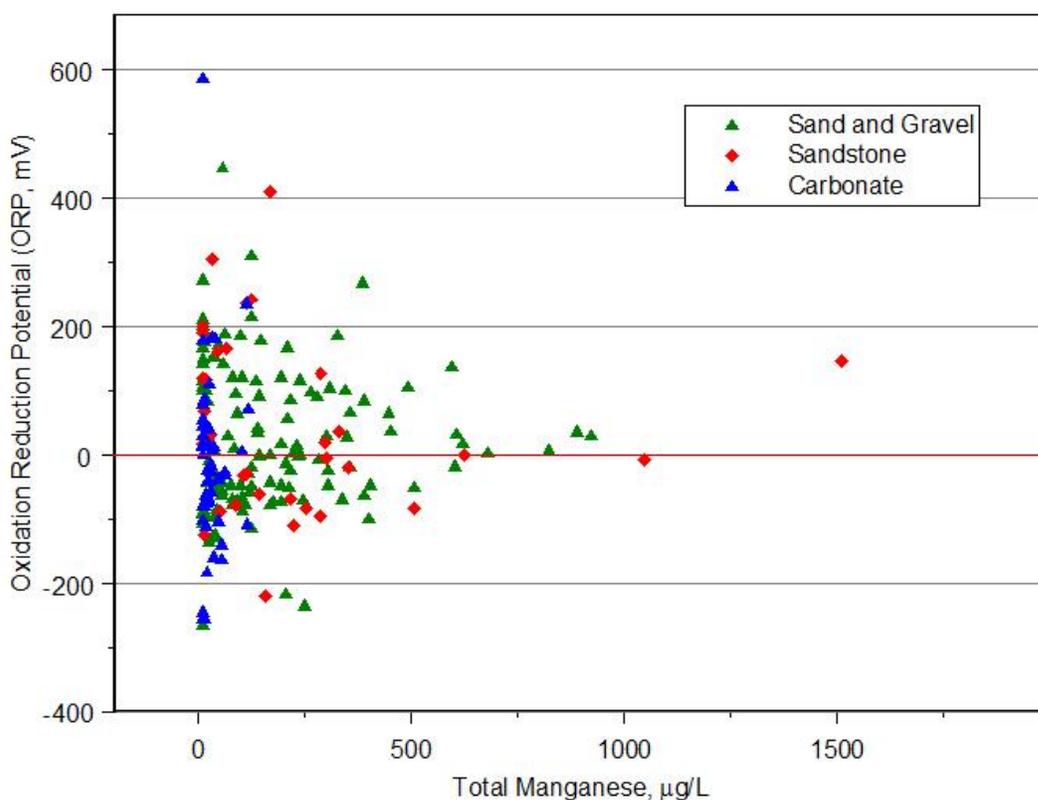


Figure 4. ORP as a function of Total Manganese.

The USGS has documented that public water system production wells frequently produce water of a mixture of waters with varying age. Large production wells collect water from multiple stratigraphic levels and, consequently, produce water with a mix of travel times and redox conditions (Eberts and others, 2013). Thus, wells that produce water from multiple stratigraphic levels require careful interpretation of redox conditions.

Examples

The following examples illustrate the utility of using inorganic parameter data to identify redox conditions. Local-scale geochemical conditions are better understood when redox parameters are used as proxies to interpret redox conditions. Understanding the behavior of redox pairs provides insight into ground water processes because redox, as a process, ultimately controls a considerable part of local hydrogeologic conditions. Brief descriptions of each example are provided to help the reader apply the example to situations they may be evaluating.

Example 1

The first example illustrates how manganese concentrations in ground water can be used to infer redox conditions. Figure 5 shows the distribution of manganese in Ohio ground waters. The distribution indicates an association of elevated Mn concentrations (> 600 µg/L) and the buried valley sand and gravel aquifers. Box plots in Figure 6 confirm that most sites with elevated Mn occur in sand and gravel or sandstone, rather than in carbonate aquifers.

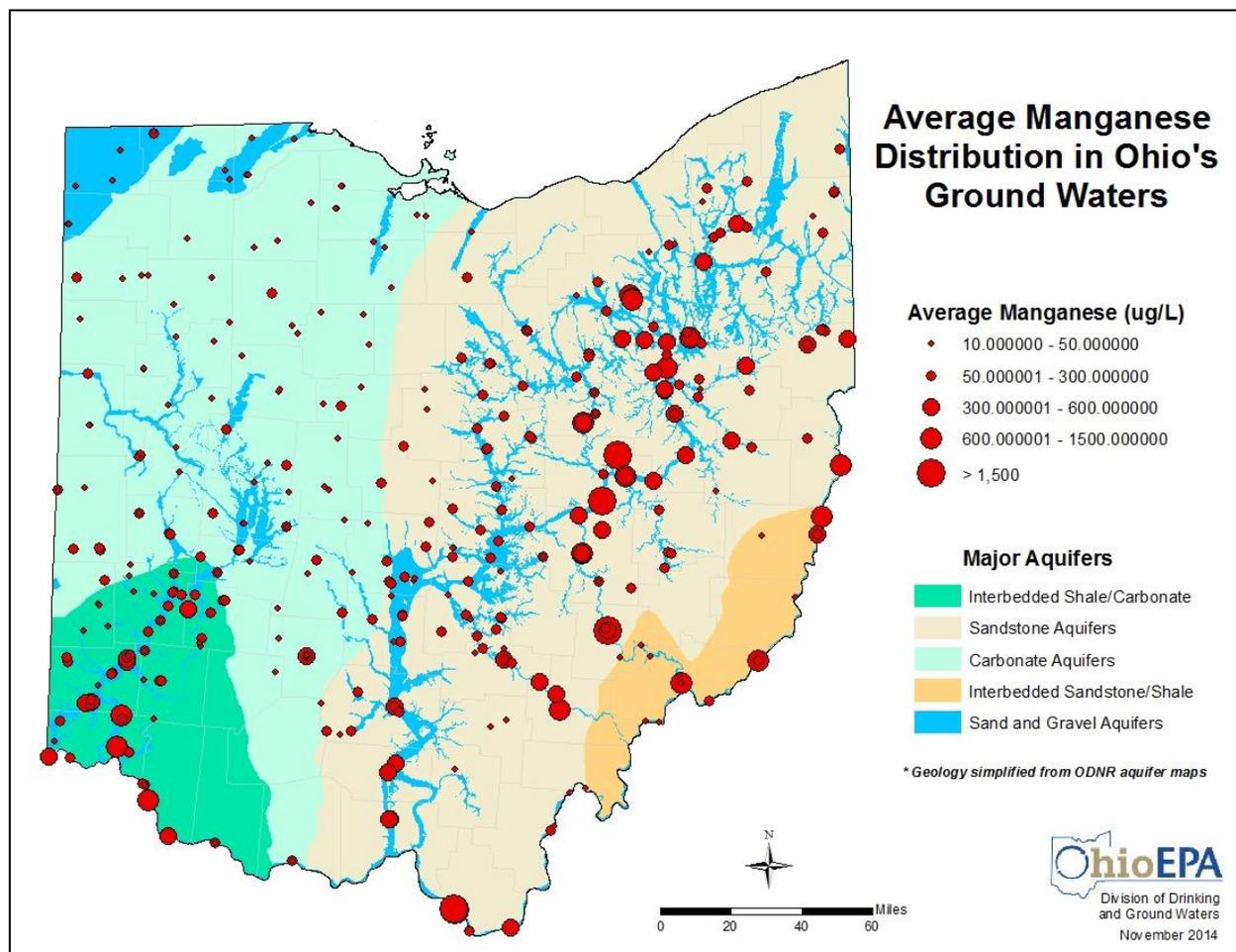


Figure 5. Manganese distribution in ground water sampled from Ambient Ground Water Monitoring Wells.

Because the “window” for manganese to mobilize to ground water is rather small, it might be reasonable to assume that only a limited number of public water systems would be affected with manganese, but that is not the case (see Figure 5). In oxic conditions, manganese attaches naturally to the iron oxide coatings of the sand and gravel grains that make up the bulk of the aquifer material in buried valleys. In mildly-reducing conditions, the manganese dissolves and is released to ground water. Detections of high Mn (> 600 µg/L) can be inferred to represent a relatively specific position on the redox spectrum indicating the buried valleys are mildly reducing at production depths in many wells. Of course, the distribution of manganese also influences the presence of manganese in ground water.

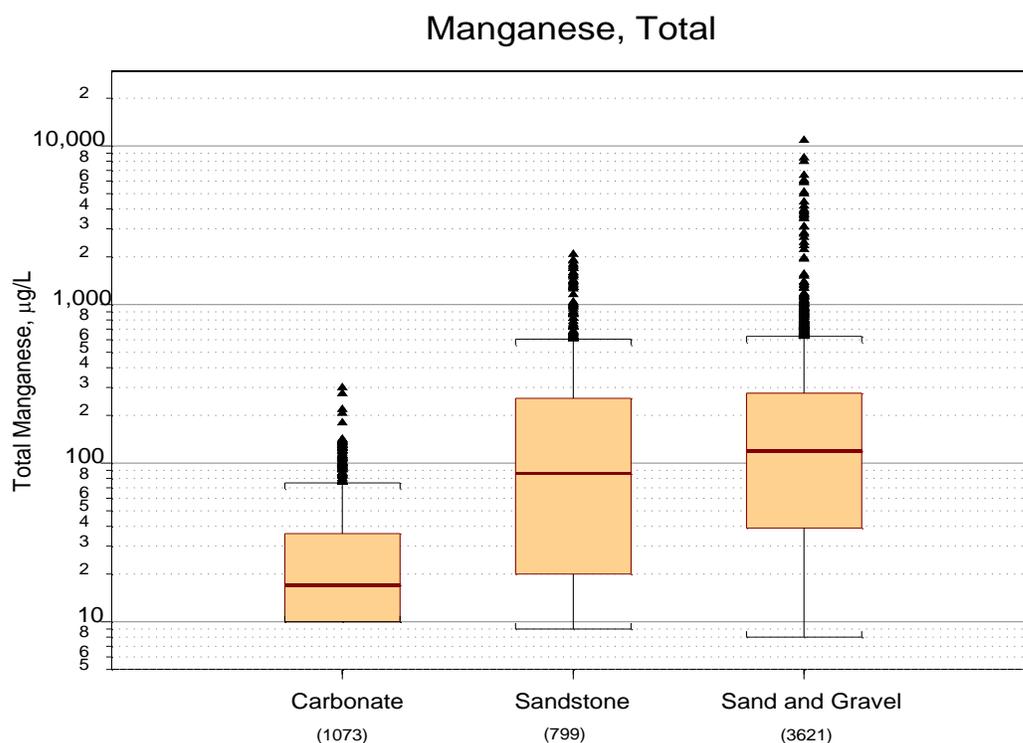


Figure 6. Box plot of manganese concentrations in major aquifers.

Example 2

The second example shows how changing redox conditions with depth can affect nitrate and manganese concentrations in ground water. In this example, the distribution of redox-sensitive parameters, including nitrate, iron and manganese, are recorded in a vertical sequence at several depths in a sand and gravel aquifer to investigate the behavior of nitrate at different depths.

This particular boring was drilled to investigate the possible sources of nitrate contamination in ground water. Water that contains septic, fertilizer or manure input carries with it both a significant nitrate load as well as high concentrations of carbon, which serves as a food source

for reducing bacteria. Thus, we would expect nitrate concentrations in the deepest screened interval to be lower than initial input concentrations at the land surface due to nitrates being reduced at depth by microbial activity.

The water quality results are presented in Figure 7. The depth below the ground surface is shown on the y-axis. Samples were taken from three discrete depth intervals, indicated by the blue rectangles (54-58 feet, 66-70 feet and 82-86 feet).

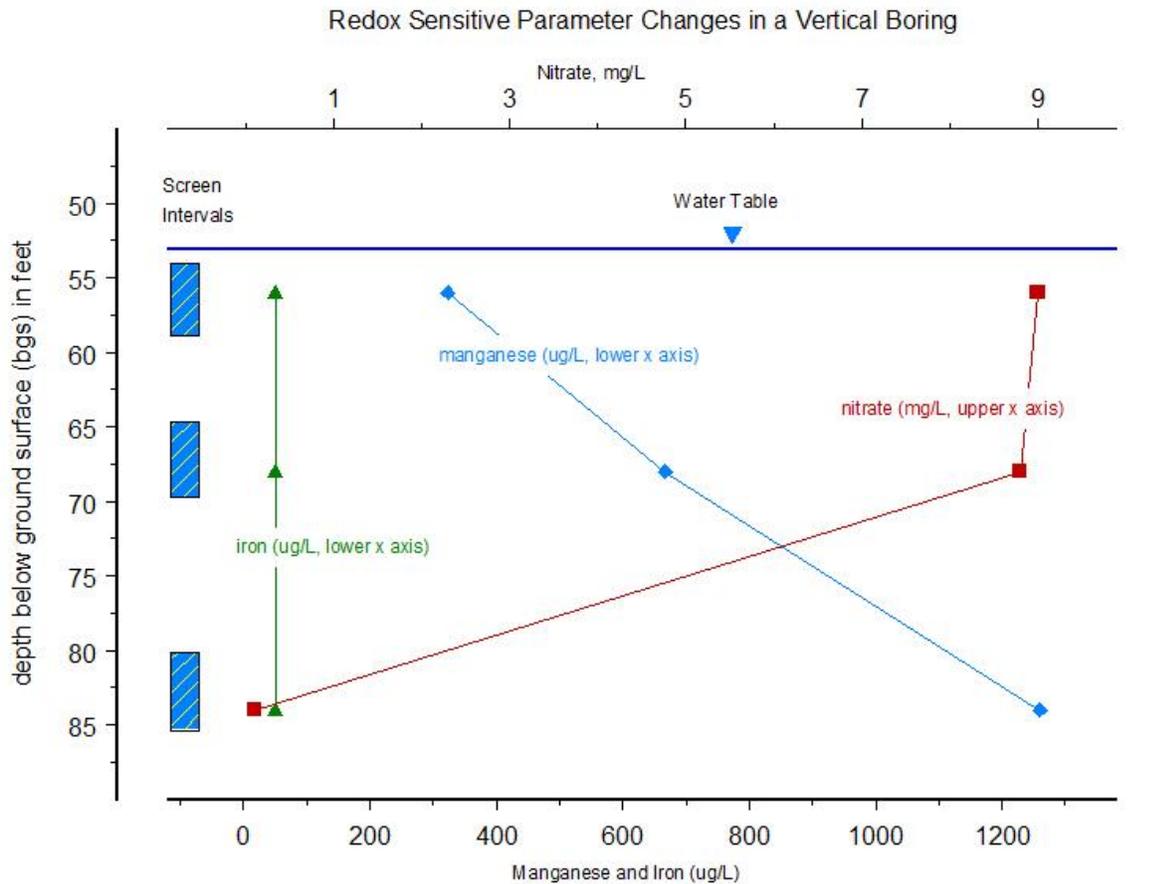


Figure 7. Redox-sensitive parameters showing concentration changes due to redox zonation.

Figure 7 illustrates a reversal of redox zones, from fully oxidized or nitrate-reducing in the upper sampling screened interval (nitrate ~ 9.0 mg/L, and manganese is present, but moderately low) to an intermediate redox value at the middle interval, where nitrate is still high but changing, and manganese is beginning to be mobilized at greater concentrations. At the deepest sampling point, manganese has more than tripled from the upper interval to more than 1,200 ug/L, while nitrate has been reduced to less than the level of detection. The dissolved iron across all three sampling intervals remains low (non-detect), suggesting that the source of the manganese is either not primarily related to the dissociation of iron oxides within the aquifer, or it is being selectively mobilized from mainly manganese oxides. Alternatively, the water may be manganese-reducing but not yet iron-reducing.

The sharp redox reversal shown in Figure 7 is due to redox zonation that occurs naturally with increasing depth in an aquifer. Previous studies of AGWQMP data indicate that nitrate will normally be changed to more reduced forms of nitrogen (nitrite, ammonia, etc.) at distances greater than about 70-75 feet, even without additional carbon source input. In the illustrated case, the carbon source within the organic waste further supports a new reducing environment below the oxidizing zone, and the opportunity for a completely different microbial species to gain energy, and thus promote the reducing environment.

Example 3

This example shows how redox conditions within a landfill can result in leachate that causes mobilization of arsenic and iron when it reaches local ground water. The material at a modern municipal landfill contains a significant amount of organic material such as food debris, paper products and other waste organics. These materials are “capped” with clay, usually on a daily basis, to isolate them from the surface and to minimize recharge moving through the landfill cell. As these materials degrade, they decompose by the action of communities of microbes. The resulting organic and inorganic fill becomes highly reducing, and when mixed with infiltrating water, will generally produce a leachate (water that has passed through a landfill cell) containing organic acids that is itself highly reducing in nature.

Most modern landfills are designed to either 1) capture the leachate in a piping system and route it away from infiltration to ground water, or 2) isolate the leachate by way of a liner (plasticized or geotextile). Many landfills utilize both isolation methods. Older landfills may have neither a liner nor a leachate capture system. In older landfills without liners, over time some volume of leachate may reach the ground water. It is common for leachate to have a starkly different (most often more reduced) condition than the local ground water. In this sense, the leachate represents a contaminant plume, even though it may not hold any water quality contaminants itself (such as nitrates, arsenic, lead, etc.). However, because of its reducing nature, the leachate may have leached contaminants from the landfill materials. For simplicity, we will consider that a leachate plume contains no contaminants. Its main characteristic is that it is highly reducing as it passes the boundaries of the landfill cell and enters the water table. This scenario is depicted in Figure 8.

The most common negative effect on local ground water in this case is the mobilization of arsenic and free iron to downgradient ground water. This is especially noticeable where the local water table is itself in an oxidized state, which would preclude the presence of detectable arsenic for most typical ground water systems in Ohio. As the reducing plume mixes and moves downgradient with the local ground water, it strips the iron oxide coatings off mineral and sand grains within the aquifer. These oxide coatings may contain arsenic in a form that is highly insoluble under oxic conditions. But as the leachate flows and mixes into the surrounding ground water, it slowly changes the redox state of the ground water, and creates the conditions necessary for the reduction and mobilization of iron and arsenic. The iron and arsenic are thus changed from their mineralized to a dissolved form, and can then flow freely with the ground water as long as water’s redox state is kept reduced enough to retain them in their dissolved form.

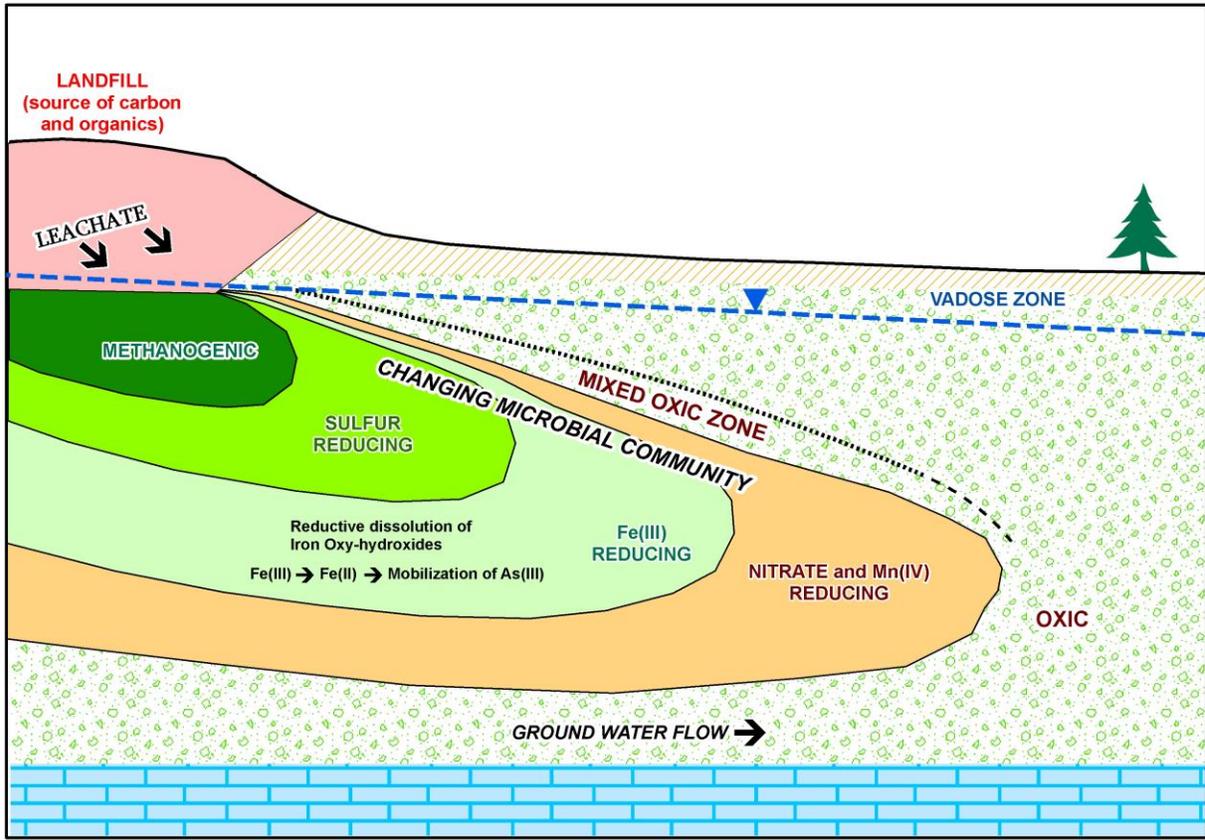


Figure 8. Redox zonation resulting from leachate input to local ground water from an unlined landfill cell.

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