

Incorporating dissolved oxygen contamination into redox assessment frameworks

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ABSTRACT

Characterizing redox conditions in groundwater is a difficult challenge because of potential errors associated with electrode measurement or accurately determining the concentrations of the redox couples present in a water sample to calculate an Eh value using a Nernst equation approach. Redox classification frameworks have been developed to avoid using Eh alone to determine redox conditions in groundwater. These frameworks typically identify redox-related parameters in a sample or identify the terminal electron accepting process such as iron reduction or methanogenesis. These frameworks have improved redox characterization but low-oxygen conditions continue to be a challenge for redox classification frameworks and for redox characterization, which causes uncertainty because dissolved oxygen remains critical in driving biodegradation reactions. A protocol for sampling for dissolved oxygen in groundwater and accepting or rejecting the dissolved oxygen results is developed. The protocol recommends commonly accepted practices to determine dissolved oxygen concentrations in the field. Iron and sulphide should also be measured in the field and if dissolved oxygen and iron or sulphide are present together then leaks in the sampling apparatus should be considered. If re-sampling continues to show the presence of dissolved oxygen together with iron or sulphide then the dissolved oxygen concentrations should be discarded, unless there is reason to believe there is mixing of groundwater in the well or borehole or the samples are collected from an uncommon environment (e.g. a microbial mat or tidal flat).

PRÉCIS

La caractérisation des conditions rédox (oxydoréduction) dans les eaux souterraines est un défi de taille en raison des erreurs potentielles associées aux mesures faites à partir d'électrode ou à l'identification précise des concentrations des couples rédox présents dans un échantillon d'eau étant utilisé pour calculer la valeur Eh en utilisant l'équation de Nernst. Les cadres de classification rédox ont été développés pour éviter l'utilisation seul du Eh pour déterminer les conditions rédox dans les eaux souterraines. Ces cadres identifient généralement les paramètres liés à la réduction d'un échantillon ou par l'identification du processus d'acceptation d'électron terminaux tel que la réduction du fer ou la méthanogénèse. Ces cadres ont amélioré la classification rédox, cependant les conditions ayant une faible concentration en oxygène continuent d'être un défi pour la classification et la caractérisation rédox, ce qui cause une incertitude puisque l'oxygène dissous reste un élément essentiel lors d'une réaction de biodégradation. Un protocole d'échantillonnage pour l'oxygène dissous dans les eaux souterraines et l'acceptation ou le rejet des résultats est développé. Le protocole utilise des pratiques couramment utilisées et acceptées pour déterminer les concentrations d'oxygène dissous sur le terrain. Le fer et le sulfure doivent également être mesurés sur le terrain. Si l'oxygène dissous, le fer et/ou des sulfures sont présents, il faut envisager qu'il y a une fuite possible dans l'équipement d'échantillonnage. Si après le rééchantillonnage les résultats continus de montrer des concentrations d'oxygène dissous ainsi que du fer ou du sulfure, nous nous devons d'éliminer les concentrations d'oxygène, à moins qu'il n'y ait lieu de croire qu'il y a un mélange d'eau souterraine dans le puits ou le forage ou que les échantillons sont prélevés d'un environnement peu commun telle qu'un tapis microbien ou d'une terrasse de marée.

1 INTRODUCTION

Redox conditions in a groundwater system are controlled by the reduction-oxidation potential, which is a measure of the tendency for a chemical species to gain or lose an electron. Redox reactions involve the transfer of electrons from the reducing agent to the oxidizing agent. The redox conditions of a groundwater environment can have an effect on the aesthetic quality of water as well as the behaviour and fate of contaminants including nitrate, metals and organic compounds. Characterizing the redox conditions at a site can provide site managers with the information required for remediation strategies or water treatment processes.

Characterizing redox potential in groundwater environments is typically carried out by electrode

measurement (Nordstrom and Wilde 2005), but the redox potential can also be calculated using the activities of chemical species that are part of a redox reaction (e.g. reduced ferrous iron and oxidized ferric iron) through the Nernst equation (pg. 240 in Appelo and Postma, 1996). The measured or calculated redox potential is then compared to published ranges (e.g. Figure 7.11 in Stumm and Morgan 1981) of redox processes to determine which redox processes may be occurring (e.g. nitrate reduction, iron reduction or methanogenesis).

Unfortunately, measured Eh values rarely correspond to Eh values calculated using the Nernst Equation (Walton-Day et al. 1990) or to aqueous concentrations of various redox couples (Lindberg and Runnels 1984) and these discrepancies can lead to errors when

characterizing redox conditions and determining the viability of monitored natural attenuation (MNA).

Redox classification frameworks have been developed to guide the interpretation of reduction-oxidation data to improve the understanding of depositional environments (Berner 1981), drinking water quality (McMahon and Chapelle 2008; Chapelle et al. 2009) or biological reactions that may be occurring (Canfield and Thamdrup 2009, Bradley 2012). These classification frameworks used field-based measurements and observations to identify the redox conditions and aid in the identification of potential redox reactions that may be important for determining the depositional environment, drinking water quality or biological reactions that may be occurring and that guide site-remediation projects relying on MNA.

The challenge with redox classification frameworks is that they do not consider potential errors associated with measuring redox potential or measuring the chemical species that are part of a redox reaction. Errors associated with the measurement techniques for redox potential or chemical species that are part of a redox reaction can be carried forward into the redox classification framework and results in an erroneous interpretation of the water quality or reactions occurring.

This paper examines the errors associated with characterizing redox potential and develops a protocol for identifying dissolved-oxygen contamination in redox measurements.

2 CHALLENGES ASSOCIATED WITH MEASURING REDOX POTENTIAL

2.1 Challenges with electrode measurement

The redox potential of a system provides information on the potential reactions that may be occurring, but there are challenges obtaining representative measurements of redox potential. Electrodes used to measure Eh have a platinum electrode (or measurement electrode) and a reference electrode. The platinum electrode acts as a catalyst for the reaction between the redox couple (e.g. H_2 and H^+ in a Standard Hydrogen Electrode or Fe^{2+} - Fe^{3+}) and the platinum develops a potential that is distinctive of the reaction if certain electrochemical conditions are met. The reference electrode maintains a constant potential with which the potential in the platinum electrode is compared.

Examples of reference electrodes are the AgCl/Ag and calomel (Hg_2Cl_2/Hg) electrodes. If we use the AgCl/Ag reference electrode as an example, a constant potential is maintained because the concentration of the dissolved Ag associated with the Ag electrode metal is kept constant by the solubility product of AgCl. The constant potential of the AgCl/Ag electrode makes it a non-polarizable electrode. It is important to note that these electrodes measure the redox potential and not a concentration of electrons, similar to how a pH electrode measures proton concentrations in water. Hydrated electrons essentially do not exist in solutions, with activities between 10^{-35} and 10^{-65} M in most natural waters (Thorstenson 1984).

Nordstrom and Wilde (2005) indicate that Eh measurements are generally not recommended because

of the difficulties inherent in its theoretical concept and its practical measurement. For the platinum electrode to respond to the redox potential of the water the following conditions must be met (Champ et al., 1979; Stumm and Morgan, 1970):

1. The couple must be electro-active, i.e., electron transfer reactions are rapid and reversible such that equilibrium is attained.

2. Both members of the couple must be present at concentrations greater than about 10^{-5} M.

3. There are no species (e.g., dissolved oxygen, sulphide, chloride, cyanide, elemental sulphur) adsorbed onto the electrode surface, thereby affecting the measured potential.

Whitfield (1974) also covered the impact of surface oxides and sulphide coatings on platinum electrodes. Platinum sulphide coating may push the measured Eh values to more negative potentials.

Nordstrom and Wilde (2005) added to the list of Champ et al. (1979) and identify the following potential interferences and limitations associated with the electrode method:

1. Organic matter and sulphide may contaminate surfaces on the electrode

2. Chromium, uranium, vanadium, titanium and other ions that are stronger reducing agents than hydrogen or platinum will yield unstable readings.

3. High iron concentrations in groundwater may react with any Zobell standard left on an electrode to cause erratic readings.

4. Elements with more than one oxidation state do not exhibit a reversible behaviour at the platinum electrode surface may give mixed potentials depending on the redox couples.

5. Methane, bicarbonate, nitrogen gas, sulphate and dissolved oxygen generally are not in equilibrium with platinum electrodes.

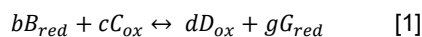
Electrodes with larger surface areas can be used to improve the reliability of measurements in dilute solutions but large electrode areas can magnify the effects of impurities on the electrode surface and mixed potentials (pg. 360 in Stumm and Morgan 1970). Mixed potentials arise when two or more redox processes may be occurring simultaneously and produce results that become difficult to interpret quantitatively.

It is also important to note that reversible electrode potentials are not established for NO_3^- - NO_2^- - NH_4^+ , SO_4^{2-} - H_2S or CO_2 - CH_4 systems (Stumm and Morgan 1970). This is important because the Nernst Equation assumes that reactions are reversible, but if the reactions are not reversible at the platinum electrode then the Eh measured is not representative of the redox potential.

One final challenge is that many reactions proceed only at significant rates when catalyzed by bacteria (pg. 239 Appelo and Postma 1996). If few bacteria are present then the concentrations of a redox couple such as SO_4^{2-} - H_2S may not be representative of the actual redox potential.

2.2 Calculating Redox Potential from Nernst Equation

The redox potential may be calculated using the activities of products through the Nernst equation (pg. 240 in Appelo and Postma 1996) that is expressed below specifically for the Standard Hydrogen Electrode (SHE):



$$Eh = E^0 + \frac{RT}{nF} \ln \frac{[D_{ox}]^d [G_{red}]^g}{[B_{red}]^b [C_{ox}]^c} \quad [2]$$

Where Eh is the electromotive force potential in volts and when the reference electrode is the SHE the electromotive force is termed Eh; E^0 is the standard potential in volts; R is the gas constant; T is the temperature; n is the number of electrons transferred in the reaction; and F is the Faraday constant. The standard potential, E^0 , for common reactions are published in standard references (e.g. Appelo and Postma 1996).

Calculations using the Nernst Equation have been particularly useful when studying iron chemistry in groundwater (Doyle 1968). Applying the Nernst equation to ferrous and ferric iron results in the following equation:

$$Eh = E^0 + \frac{RT}{nF} \ln \frac{[Fe^{3+}]}{[Fe^{2+}]} \quad [3]$$

Theoretically, if the activities of ferric and ferrous iron in a sample are determined and both members of the couple are present at concentrations $\geq 10^{-5}$ M, the equation above allows a meaningful Eh to be calculated. One advantage of the Nernst approach is that the transfer of electrons does not need to be measured, which may be difficult to do as discussed above. The Nernst Equation does assume that the environment is in equilibrium and calculates an Eh for one redox pair (Fe^{2+} and Fe^{3+} above).

One challenge using this technique is to determine the contribution of each redox couple to the overall Eh of the environment. For example, an environment with Fe^{2+} , Fe^{3+} and SO_4^{2-} - H_2S may have an Eh that is more controlled by one redox couple but that may not be possible to determine. Also, the concentrations of each redox pair may not be in equilibrium, particularly if the kinetics of a redox reaction are catalyzed by microorganisms where one reaction occurs more rapidly than the other (Stumm and Morgan, 1970). These challenges of redox disequilibrium are significant and have been examined by others as reviewed in the following section.

2.3 Redox Disequilibrium

Several authors have concluded that geochemical environments may not be differentiated based on their pH and Eh characteristics (e.g. Lindberg and Runnells 1984; Champ et al. 1979) in part because the environments are not in redox equilibrium.

Stumm and Morgan (1970) and Thorstenson (1984) discussed the possibility of partial equilibrium, where some redox reactions are occurring sufficiently rapidly that equilibrium is achieved. Other redox reactions may be occurring too slowly to achieve equilibrium. Reactions catalyzed by microorganisms may add error to the measurement because the reaction cannot be measured

directly at the electrode's surface since the reaction is catalyzed within a microorganism.

Both Thorstenson (1984) and Stumm and Morgan (1970) concluded that most natural waters are at disequilibrium or in partial equilibrium with respect to redox reactions, which means that unique redox potentials in most natural waters do not exist and the disequilibrium or partial equilibrium phenomenon is likely responsible for the difficulty of measuring Eh in natural waters.

Jackson and Patterson (1982) demonstrated that shallow groundwaters at Chalk River Nuclear Laboratories exhibited very different redox results for measurements using the Pt electrode (i.e., Eh) of the sulphate-sulphides (where sulphides includes H_2S , HS^- , and S^{2-}) system.

Lindberg and Runnells (1984) completed calculations for 611 groundwater samples and showed that aqueous redox systems are generally not at equilibrium and cannot be represented by a "master" value measured in the field such as Eh. Both Lindberg and Runnells (1984) and Thorstenson (1984) concluded that an equilibrium redox potential does not exist and attempting to measure it with electrodes or calculated potentials will fail and lead to misleading results for normal groundwaters.

Slow reaction rates will impact both electrode measurement of Eh as well as Eh calculation by a Nernst equation approach since the concentrations of the reactants and products may not be in equilibrium with the redox conditions if the reaction rate is too slow. Redox disequilibrium, particularly where reaction kinetics are a significant factor with the disequilibrium, may produce erroneous electrode measurements of Eh by shifting the measured or calculated Eh closer to the potential of the reaction with the faster kinetics.

3 REDOX CLASSIFICATION FRAMEWORKS

Redox classification frameworks have been developed to address the difficulties with characterizing redox conditions using Eh by electrode measurement or calculated using the Nernst equation. The classification frameworks focus on the presence and concentration of key redox parameters. Key redox parameters can differ depending on the environment being characterized but Stumm and Morgan (1970) identified carbon, nitrogen, sulphur, iron and manganese as the predominant participants in aquatic redox processes.

Berner (1981) classified sediments based on their depositional environment and diagenetic reactions. The classification framework begins with two readily measurable molecules, dissolved oxygen and sulphides. Depositional environments were classified into oxic, post-oxic, sulfidic and methanic as shown in Table 1, which was modified from Berner (1981).

Berner (1981) indicates that dissolved oxygen and sulphides cannot coexist in solution. It is not thermodynamically favourable for the two to coexist at measureable concentrations ($>10^{-6}$ M) in water and they rapidly react in a matter of minutes to hours at pH 6-8 to form oxidized sulphur species and water. Due to this reactivity and mutual exclusivity, Berner (1981) selected

oxygen and sulphides as ideal candidates for primary variables in the classification framework (Table 1).

The classification framework was based on analytical limitations of 1 µmol/L for all of the dissolved analytes and the minerals listed in the table were selected to be common minerals encountered in modern sediments which are thermodynamically stable in their respective environments. This classification framework is based on the oxidation-reduction properties of sediments and does not include pH or dissolved redox sensitive species such as nitrate, arsenic, or methane, as shown in Table 1.

Table 1. Redox classification framework based on Berner (1981)

Environment	Examples of Characteristic Phases
I Oxic (Concentration O ₂ ≥ 10 ⁻⁶)	Hematite, MnO ₂ minerals, no organic matter
II Anoxic (Concentration O ₂ < 10 ⁻⁶)	
A. Sulfidic (Concentration H ₂ S ≥ 10 ⁻⁶)	Pyrite, rhodochrosite, organic matter
B. Nonsulfidic (Concentration H ₂ S < 10 ⁻⁶)	
1. Post-oxic	Glauconite, other Fe ²⁺ -Fe ³⁺ silicates and carbonates, rhodochrosite; no sulphide minerals
2. Methanic	Siderite, rhodochrosite; sulphide minerals; organic matter

An interesting aspect of using sedimentary rocks to define redox conditions is that they may represent an intermediate redox condition, depending on the diagenetic condition. For example, the presence of secondary pyrite indicates the redox conditions were iron reducing and sulphate reducing at one point. However, methanogenesis could have occurred and oxic conditions may have occurred. A similar approach is commonly used to determine the boundary of a wetland, based on the distribution gleys where predominantly saturated conditions allow ferric iron to be reduced to ferrous iron and produce the characteristic gleyic colour pattern.

Thorstenson (1984) adapted the naming system presented by Berner (1981) for groundwater environments to oxygenated (oxic), iron-rich (post-oxic), sulphide-rich (sulfidic) and methane-rich (methanic), which changes the focus from sedimentary rock classification to dissolved parameter classification.

McMahon and Chapelle (2008) developed a redox classification framework to assess redox conditions in groundwater from major aquifers across the United States. The classification framework was updated by Chapelle et al. (2009) and is summarized in Table 2. It is important to note that the Chapelle et al. (2009) framework is applied to water chemistry, where the Berner (1981) framework was based on sediments.

The Chapelle et al. (2009) framework applies threshold concentrations to electron acceptors to categorize redox environments. The concentration thresholds were selected to be broadly applicable to ambient regional aquifer system and were based on considerations of microbial physiology, field studies and analytical reporting limits. The selected concentration thresholds should be considered approximate because of the wide range of processes that can affect these concentrations and mixing multiple flow paths may impact some thresholds such as the oxygen threshold for nitrate reduction to occur. McMahon and Chapelle (2008) and Chapelle et al. (2009) point out that the concentration thresholds presented in their framework were project-specific, and should be updated for each individual project.

The Chapelle et al. (2009) classification framework includes a suboxic and mixed category and differentiates between manganese and iron reduction, but does not differentiate between iron and sulphate reduction because iron and sulphides are reactive together. The suboxic designation indicates low O₂ conditions, but further definition of redox processes is not possible without additional redox data. The anoxic category includes nitrate reduction, manganese reduction and iron reduction. The classification of methanogenesis is related to iron and sulphate concentrations and not the presence of methane as the authors indicate that methane is not commonly sampled in regional-scale sampling programs.

The oxygen concentration thresholds for the suboxic category in Table 2 are specific for the microorganisms present and for the context the geochemical results are being interpreted (Canfield and Thamdrup 2009). Bradley (2012) shows that low concentrations of dissolved oxygen (<0.5 mg/L) may be important for biodegradation of electron-acceptor contaminants such as chloroethenes and that it is important to characterize low concentrations of dissolved oxygen and not categorize the low concentrations as anoxic. This highlights the importance of characterizing low dissolved oxygen concentrations with high certainty. There may be significant measurement error associated with low dissolved oxygen concentrations, which is discussed in more detail in the following section.

Canfield and Thamdrup (2009) suggest abandoning non-specific terms including suboxic and instead use terms to describe the specific process, such as iron-reducing, that may be occurring. However, it is possible for multiple redox processes to be occurring together and may produce a naturally mixed redox environment as described by the classification framework developed by Chapelle et al. (2009). For example, Canfield et al. (1993a,b) showed iron reduction and sulphate reduction were occurring in the same sediments. But it may be important, especially where monitored natural attenuation is a proposed remedial option, to identify that each of these processes are occurring together rather than simply lumping the results into a mixed category.

Table 2. Threshold Concentrations for Identifying Redox Processes in Regional Aquifer Systems from Chapelle et al. (2009)

Redox Process	O ₂	NO ₃ ⁻	Water Quality Criteria (mg/L)			Fe ²⁺ /H ₂ S Ratio	Comments
			Mn ²⁺	Fe ²⁺	SO ₄ ²⁻		
Oxic							
O ₂ Reduction	≥0.5	–	<0.05	<0.1	–		
Suboxic	<0.5	<0.5	<0.05	<0.1	–		Further definition of redox processes not possible
Anoxic							
NO ₃ ⁻ Reduction	<0.5	≥0.5	<0.05	<0.1	–		
Mn(IV) Reduction	<0.5	<0.5	≥0.05	<0.1	–		
Fe(III)/SO ₄ ²⁻ Reduction	<0.5	<0.5	–	≥0.1	≥0.5		
Fe(III) Reduction	<0.5	<0.5	–	≥0.1	≥0.5	>10	
Mix Fe(III)/SO ₄ ²⁻ Reduction	<0.5	<0.5	–	≥0.1	≥0.5	≥3≤10	
SO ₄ ²⁻ Reduction	<0.5	<0.5	–	≥0.1	≥0.5	>10	
Methanogenesis	<0.5	<0.5	–	≥0.1	<0.5		
Mixed	–	–	–	–	–		Criteria for more than one redox process are met

The Berner (1981), Thorstenson (1984) and Chapelle et al. (2009) frameworks each identify the Terminal Electron Accepting Processes (TEAPs) in rock or water as a means of categorizing the redox potential of the environment. By identifying the TEAPs, a measured or calculated Eh or redox potential is not required. This avoids the uncertainty of electrode error, and accepts the concept of redox disequilibrium by allowing the potential for multiple TEAPs to be occurring concurrently. The redox potential can be categorized based on what TEAPs can be identified by examination of the mineralogy or the water chemistry.

4 OXYGEN AS A CONTAMINANT

One of the challenges with redox classification frameworks for water is how the framework addresses oxygen. The concentration of oxygen in the atmosphere is 286 mg/L as O₂ based on a 21% oxygen concentration by volume and at 25°C (Langmuir 1997). Atmospheric oxygen diffuses into water where it becomes dissolved oxygen or dissolved oxygen. If water has sufficient contact time with the atmosphere to reach saturation, dissolved oxygen saturation is controlled by temperature, atmospheric pressure and the total dissolved solids concentration of the water. This can lead to reporting an erroneously high oxygen concentration (Rose and Long 1988).

Atmospheric oxygen also has the potential to oxidize iron, manganese or other species dissolved in water thereby lowering their apparent concentration (Pohlmann and Alduino 1992). Oxidation of reduced ferrous iron to oxidized ferric iron has important implications to the speciation and concentrations of many constituents in ground water samples and to the interpretation of the redox conditions based on the sampling results. This oxidation may also impact the accuracy of Eh using the Nernst equation approach.

Atmospheric oxygen may be added to samples by direct contact between the sample and the atmosphere during measurement of unstable field parameters (e.g. temperature, dissolved oxygen, specific electrical conductance), but atmospheric oxygen may also diffuse through sampling equipment and enter the sample. Holm et al. (1988) developed a model to calculate the diffusion of gases, including dissolved oxygen, through sampling tubing. The model predicts the amount of gas that may enter the water inside the tubing and shows the gas contamination is proportional to the length of the tubing and inversely proportional to the pumping rate. Experimental results for the same study showed an increase in dissolved oxygen of 0.6 mg/L for sample tubing 3 m long and a flow rate of 0.5 mL/s. These results also do not consider oxygen ingress to the sample water that may occur at tubing junctions. The type of tubing material is an important factor to determine how much oxygen can diffuse into the sample water.

There is no clear or simple test to assess the validity of a sampling method but that practitioners should consider their sampling protocols and examine the data to determine the level of contamination (Rose and Long 1988).

4.1 Challenges Measuring Dissolved Oxygen

The USGS identifies colourimetric, electrode (amperometric or optical) or titrimetric methods for determining dissolved oxygen concentrations and provides a rationale for selecting the most appropriate method for a field study as well as sources of error and uncertainty for the three methods (Rounds et al. 2013).

Colourimetric field methods, such as rhodazine D or indigo carmine, reduce dissolved oxygen and cause a predictable change in colour that can be compared to a colour chart to determine the dissolved oxygen concentration. Easily reduced species such as ferric iron (Fe³⁺) or nitrate (Gilbert et al. 1991) will also react with

rhodazine D or indigo carmine and will cause the same change in colour that dissolved oxygen does, leading to erroneously high dissolved oxygen values (White et al. 1990). Due to the low solubility of ferric iron, the source of ferric iron may be fine-grained ferric hydroxide colloids. Interferences from salinity, major dissolved inorganic species, dissolved gases, or temperature are typically negligible with rhodazine D or indigo carmine. Rounds et al. (2013) recommend using colourimetric methods for dissolved oxygen concentrations less than 2 mg/L.

Electrode determinations are the simplest methods available for determining dissolved oxygen in ground water, but they lack consistent accuracy at low dissolved oxygen levels, below 1 ppm (Wilkin et al. 2001). Optical dissolved oxygen sensors are preferred because these sensors do not consume oxygen, there are no known sources of interference, and because they do not have an anode or a cathode and do not require an electrolyte, the cleaning and maintenance is simplified (Rounds et al. 2013). The optical sensor must be replaced at least annually.

Amperometric sensors require electrolytes and a membrane, and because this method consumes oxygen, the sensor requires flowing water. Sulphides and other reactive compounds may interfere with the electrode surfaces (Rounds et al. 2013).

Membrane-covered electrodes are a type of amperometric sensor that provide rapid method for measuring dissolved oxygen concentrations, however the reproducibility of the results may be questioned and low dissolved oxygen concentrations (Wilkin et al. 2001). The membranes are permeable to dissolved oxygen and allow dissolved oxygen to pass from the sampled water, through the membrane, to the electrode chamber, where the dissolved oxygen is reduced. The reduction of the dissolved oxygen produces electrons and the electrical current the electrons produces is measured and converted to a dissolved oxygen concentration. Ideally, the membrane is permeable to oxygen but not to other dissolved gases or other impurities in the water, preventing erroneous measurement of dissolved oxygen or electrode poisoning.

Dissolved oxygen measurements through membranes are limited by the rate of diffusion of the oxygen across the membrane. Also, the reduction of dissolved oxygen is a consumptive reaction, therefore, it is important not to deplete the dissolved oxygen in the sample which would result in an erroneously low measurement. Dissolved oxygen measurements from flowing water are ideal to prevent the depletion of dissolved oxygen in a sample.

Membrane fouling can decrease the permeability of the membrane to dissolved oxygen, resulting in inaccurate results without any indication that poor results are being obtained. In practice, sulphides, thioorganic, and other organic compounds are the most problematic to continued reliable electrode performance (Wilkin et al. 2001).

The Winkler method is an accurate method for determining but it generally no longer used as a standard field method for measurement of dissolved oxygen because (Rounds et al. 2013):

- 1) the accuracy and reproducibility of the results are dependent on the experience and expertise of the data collector;
- 2) the potential environmental interferences from common species such as nitrite, ferrous iron, and organic matter; and
- 3) the time required to complete the analysis combined with field conditions can make preventing exposure of the sample to atmospheric oxygen difficult.

5 PROTOCOL TO ASSESS DISSOLVED OXYGEN CONTAMINATION

Recognizing that oxygen is an important contributor for biodegradation reactions it is important to minimize errors associated with measuring dissolved oxygen. Figure 1 shows a protocol for dissolved oxygen measurements that is discussed here. Dissolved oxygen must be measured in the field and should be measured using two techniques to limit the possibility of measurement interference. Two methods could be by electrode and colourimetric.

The results of the two dissolved oxygen measurements should be compared to each other to identify the potential for interference. If the measurements are similar then compare the dissolved oxygen results to the dissolved oxygen saturation concentrations in water to determine if the result is possible. Dissolved oxygen saturation tables are available from the USGS (Rounds et al. 2013). If the results are above saturation, then inspect the sampling apparatus for areas of ingress and review the sampling an analytical techniques to ensure atmospheric oxygen is not contaminating the analyses.

We have confirmed that, if Eh measurements with Pt electrodes are obtained, it is possible to use Whitfield's (1974) Pt-O relationship to confirm DO contamination of groundwater samples. This involves a simple Eh-pH plot of data with the equation of the formation of an oxide surface coating (Pt-O):

$$Eh = E_0(\text{Pt} - \text{O}) - 0.06 \text{ pH} \quad [4]$$

Where E_0 between platinum and oxygen is 880 mV. Eh-pH data that plot below the Pt-O line from Equation 4 confirm that the measured dissolved oxygen is not in equilibrium with the Eh of the water sample and that the dissolved oxygen is likely due to air seepage into sample tubing or fixtures around the flow cell. This test serves as a simple verification of suspect air contamination.

The next step is to analyze for iron and sulphides in the field. This should also be completed in the field to allow for immediate comparison to the dissolved oxygen results. Colourimetric methods are available for iron and sulphides and depending on the accuracy required, these analyses may be done in place of laboratory analyses or done to support laboratory analyses.

Dissolved oxygen should not be detected together with either iron or sulfide since dissolved oxygen and sulphide cannot coexist in solution (Berner 1981). If dissolved oxygen is present with iron or sulphides, then

the sampling setup should be inspected and potentially corrected to prevent oxygen ingress into joints or the flow through cell. Also note that the length of tubing should be as short as possible to limit oxygen diffusion into the sample through the tubing (Holm et al. 1988).

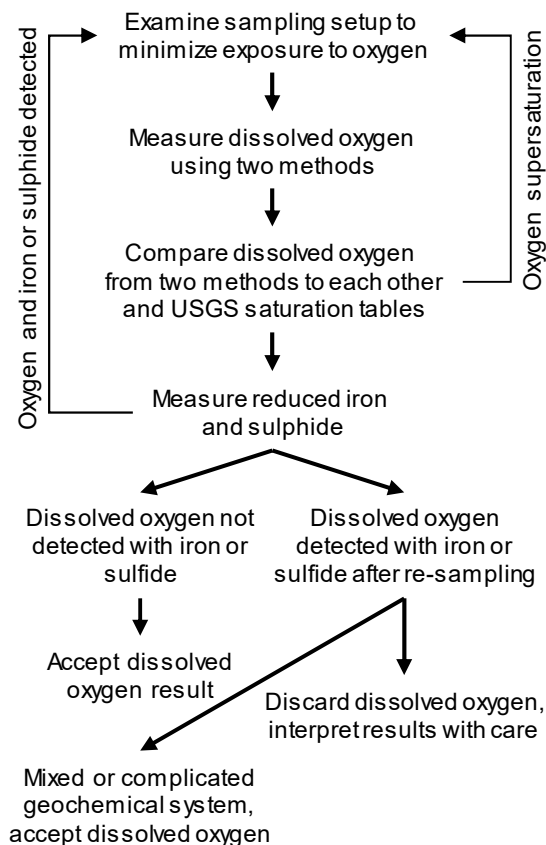


Figure 1. Flow chart representation of the dissolved oxygen protocol.

If dissolved oxygen and iron or sulphides continue to be detected despite improvements to the sampling setup then the results should be highlighted in the field notes and the dissolved oxygen result should be questioned and potentially discarded.

It may be possible that there is mixing of shallow (dissolved oxygen rich) and deep (dissolved oxygen poor) groundwater from a long sampling interval such as a 10 m screen or an uncased borehole. It may also be possible that the water sample is collected from a heterogeneous geochemical environment. For example, Canfield and Des Marais (1991) showed sulphate reduction occurring in an oxygenated bacterial mat in a saline system. If there is a logical reason for the dissolved oxygen to be present then the results may be accepted, otherwise the dissolved oxygen is likely a contaminant and the dissolved oxygen results should be discarded.

The presence of dissolved oxygen in the sample has the potential to oxidize reduced species (e.g. Mn^{2+} , Fe^{2+} , HS^-), which may impact the concentrations of these

species as well as cause precipitation of insoluble minerals (e.g. ferric hydroxides) and cause errors with the pH measurement and alkalinity concentrations. Each of these sources of error should be considered when interpreting geochemical results with suspected oxygen contamination.

6 SUMMARY

Adequately determining redox conditions is a challenge for characterizing groundwater geochemistry for numerous reasons including potable water supplies and understanding biodegradation conditions that affect contaminant remediation. Using electrodes or concentrations of redox couples to determine the Eh can be difficult to determine the accuracy of the results and thus the appropriate choice among remedial options.

Numerous redox classification frameworks have been created to overcome the challenges associated with measuring Eh and to more broadly categorize redox conditions by the overall redox processes that are occurring, such as dissolved oxygen reduction, sulfate reduction or methanogenesis. These redox classification frameworks have identified challenges associated with categorizing the low-oxygen environments due to the practical and technological challenges associated with measuring low dissolved oxygen concentrations, but the classification frameworks do not identify a protocol for accepting or rejecting the dissolved oxygen results.

We have outlined a general protocol based on commonly accepted field-practices to collect, review and accept or reject dissolved oxygen concentrations in groundwater. The protocol includes using two methods to analyze dissolved oxygen in the field, comparing the dissolved oxygen concentrations to each other and to the USGS dissolved oxygen saturation tables for water. The protocol also includes comparing the field-measured dissolved oxygen to field-measured iron and sulphides results and includes consideration for the possibility of mixing groundwaters or uncommon redox conditions.

It should be understood that accepting geochemical results with known oxygen contamination may impact the concentration of dissolved species including the pH and alkalinity of the sample and it may cause remedial measures based on false dissolved oxygen positives to fail.

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