

**National Water-Quality Assessment Program**

**Transport of Anthropogenic and Natural Contaminants (TANC)  
to Public-Supply Wells**

**An Excel<sup>®</sup> Workbook for Identifying Redox Processes in  
Ground Water**

Open-File Report 2009–1004

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By Bryant C. Jurgens, Peter B. McMahon, Francis H. Chapelle, and Sandra M. Eberts

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**U.S. Department of the Interior**  
**U.S. Geological Survey**

**U.S. Department of the Interior**  
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**U.S. Geological Survey**  
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U.S. Geological Survey, Reston, Virginia: 2009

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Suggested reference:

Jurgens, B.C., McMahon, P.B., Chapelle, F.H., and Eberts, S.M., 2009, An Excel® workbook for identifying redox processes in ground water: U.S. Geological Survey Open-File Report 2009-1004 8 p. Available at <http://pubs.usgs.gov/of/2009/1004/>

## Foreword

The U.S. Geological Survey (USGS) is committed to providing the Nation with credible scientific information that helps to enhance and protect the overall quality of life and that facilitates effective management of water, biological, energy, and mineral resources (<http://www.usgs.gov/>). Information on the Nation's water resources is critical to ensuring long-term availability of water that is safe for drinking and recreation and is suitable for industry, irrigation, and fish and wildlife. Population growth and increasing demands for water make the availability of that water, now measured in terms of quantity and quality, even more essential to the long-term sustainability of our communities and ecosystems.

The USGS implemented the National Water-Quality Assessment (NAWQA) Program in 1991 to support national, regional, State, and local information needs and decisions related to water-quality management and policy (<http://water.usgs.gov/nawqa>). The NAWQA Program is designed to answer: What is the condition of our Nation's streams and ground water? How are conditions changing over time? How do natural features and human activities affect the quality of streams and ground water, and where are those effects most pronounced? By combining information on water chemistry, physical characteristics, stream habitat, and aquatic life, the NAWQA Program aims to provide science-based insights for current and emerging water issues and priorities. From 1991–2001, the NAWQA Program completed interdisciplinary assessments and established a baseline understanding of water-quality conditions in 51 of the Nation's river basins and aquifers, referred to as Study Units (<http://water.usgs.gov/nawqa/studyu.html>).

Multiple national and regional assessments are ongoing in the second decade (2001–2012) of the NAWQA Program as 42 of the 51 Study Units are reassessed. These assessments extend the findings in the Study Units by determining status and trends at sites that have been consistently monitored for more than a decade, and filling critical gaps in characterizing the quality of surface water and ground water. For example, increased emphasis has been placed on assessing the quality of source water and finished water associated with many of the Nation's largest community water systems. During the second decade, NAWQA is addressing five national priority topics that build an understanding of how natural features and human activities affect water quality, and establish links between sources of contaminants, the transport of those contaminants through the hydrologic system, and the potential effects of contaminants on humans and aquatic ecosystems. Included are topics on the fate of agricultural chemicals, effects of urbanization on stream ecosystems, bioaccumulation of mercury in stream ecosystems, effects of nutrient enrichment on aquatic ecosystems, and transport of contaminants to public-supply wells. These topical studies are conducted in those Study Units most affected by these issues; they comprise a set of multi-Study-Unit designs for systematic national assessment. In addition, national syntheses of information on pesticides, volatile organic compounds (VOCs), nutrients, selected trace elements, and aquatic ecology are continuing.

The USGS aims to disseminate credible, timely, and relevant science information to address practical and effective water-resource management and strategies that protect and restore water quality. We hope this NAWQA publication will provide you with insights and information to meet your needs, and will foster increased citizen awareness and involvement in the protection and restoration of our Nation's waters.

The USGS recognizes that a national assessment by a single program cannot address all water-resource issues of interest. External coordination at all levels is critical for cost-effective management, regulation, and conservation of our Nation's water resources. The NAWQA Program, therefore, depends on advice and information from other agencies—Federal, State, regional, interstate, Tribal, and local—as well as nongovernmental organizations, industry, academia, and other stakeholder groups. Your assistance and suggestions are greatly appreciated.

Matthew C. Larsen  
Associate Director for Water

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# An Excel<sup>®</sup> Workbook for Identifying Redox Processes in Ground Water

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## Abstract

The reduction/oxidation (redox) condition of ground water affects the concentration, transport, and fate of many anthropogenic and natural contaminants. The redox state of a ground-water sample is defined by the dominant type of reduction/oxidation reaction, or redox process, occurring in the sample, as inferred from water-quality data. However, because of the difficulty in defining and applying a systematic redox framework to samples from diverse hydrogeologic settings, many regional water-quality investigations do not attempt to determine the predominant redox process in ground water. Recently, McMahon and Chapelle (2008) devised a redox framework that was applied to a large number of samples from 15 principal aquifer systems in the United States to examine the effect of redox processes on water quality. This framework was expanded by Chapelle and others (in press) to use measured sulfide data to differentiate between iron(III)- and sulfate-reducing conditions. These investigations showed that a systematic approach to characterize redox conditions in ground water could be applied to datasets from diverse hydrogeologic settings using water-quality data routinely collected in regional water-quality investigations.

This report describes the Microsoft<sup>®</sup> Excel<sup>®</sup> workbook, RedoxAssignment\_McMahon&Chapelle.xls, that assigns the predominant redox process to samples using the framework created by McMahon and Chapelle (2008) and expanded by Chapelle and others (in press). Assignment of redox conditions is based on concentrations of dissolved oxygen ( $O_2$ ), nitrate ( $NO_3^-$ ), manganese ( $Mn^{2+}$ ), iron ( $Fe^{2+}$ ), sulfate ( $SO_4^{2-}$ ), and sulfide (sum of dihydrogen sulfide [aqueous  $H_2S$ ], hydrogen sulfide [ $HS^-$ ], and sulfide [ $S^{2-}$ ]). The logical arguments for assigning the predominant redox process to each sample are performed by a program written in Microsoft<sup>®</sup> Visual Basic<sup>®</sup> for Applications (VBA). The program is called from buttons on the main worksheet. The number of samples that can be analyzed is only limited by the number of rows in Excel<sup>®</sup> (65,536 for Excel<sup>®</sup> 2003 and XP<sup>®</sup>; and 1,048,576 for Excel<sup>®</sup> 2007), and is therefore appropriate for large datasets.

## Introduction

The reduction/oxidation (redox) condition of ground water affects the mobility, degradation, and solubility of many contaminants in aquifers, including organic constituents such as solvents and gasoline compounds and inorganic constituents such as nitrate and arsenic. In addition, the quality of water can be aesthetically degraded by reaction products of redox processes, such as manganese ( $Mn^{2+}$ ), iron ( $Fe^{2+}$ ), hydrogen sulfide gas ( $H_2S_{(g)}$ ), and methane gas ( $CH_{4(g)}$ ). For these reasons, determining redox conditions in water is desirable for many water-quality investigations. However, many regional ground-water-quality investigations do not attempt to determine redox conditions in ground water because of the difficulty in defining and applying a systematic redox framework to samples from diverse hydrogeologic settings. Recently, a redox framework was devised using datasets from 15 principal aquifers in the United States (McMahon and Chapelle, 2008). Applying the framework to other large datasets and water-quality investigations could be aided by an easy-to-use, automated workbook program.

The precise determination of redox conditions in ground water is often difficult to ascertain because water is commonly not in redox equilibrium and multiple redox conditions may exist simultaneously as water progresses from more oxygenated states to more reduced states. For example, decreases in nitrate concentrations during denitrification can occur concomitant with increases in manganese concentrations as a result of solid-phase manganese (IV) reduction. In addition, ground-water samples are often mixtures of water from multiple parts of an aquifer that may have different redox conditions. Consequently, mixing within the well bore can produce chemistry results that suggest multiple redox conditions. Recognizing these limitations, several researchers have attempted to classify ground water on the basis of the predominant redox process or the terminal electron accepting process (TEAP) from concentrations of redox sensitive species (Chapelle and others, 1995; Christensen and others, 2000; Paschke and others, 2007; McMahon and Chapelle, 2008).

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Redox conditions are generally facilitated by microorganisms, which gain energy by transferring electrons from donors (usually organic carbon) to acceptors (usually inorganic species) (McMahon and Chapelle, 2008). Because some electron acceptors provide more energy than others, electron acceptors that yield the most energy are utilized first and species that yield less energy are utilized in order of decreasing energy gain. This process continues until all the available donors or acceptors have been used. If carbon sources are not a limiting factor, the predominant electron acceptor in water will usually follow an ecological succession from dissolved oxygen ( $O_2$ ), to nitrate ( $NO_3^-$ ), to manganese (IV), to iron (III), to sulfate ( $SO_4^{2-}$ ), and finally to carbon dioxide ( $CO_{2(g)}$ ) (table 1).

Although some redox processes overlap as water becomes progressively more reduced, there is usually one TEAP that dominates the chemical signature of the water. Consequently, the concentrations of soluble electron acceptors ( $O_2$ ,  $NO_3^-$ ,  $SO_4^{2-}$ ) and TEAP end products ( $Mn^{2+}$ ,  $Fe^{2+}$ ,  $H_2S_{(g)}$ ,  $CH_{4(g)}$ ) can be used to distinguish between redox processes. Because many water-quality investigations collect  $O_2$ ,  $NO_3^-$ ,  $Mn^{2+}$ ,  $Fe^{2+}$ , and  $SO_4^{2-}$ , a general framework for assessing redox processes was developed by McMahon and Chapelle (2008) using these parameters. Concentration thresholds were selected to apply broadly to regional ground-water-quality investigations. Although most water-quality studies analyze for total dissolved manganese and iron rather than the speciated forms of these elements, in samples that have been filtered ( $\leq 0.45\mu m$  [micrometer]) and acidified, the total dissolved concentrations are often accurate estimates of  $Mn^{2+}$  and  $Fe^{2+}$  above the threshold concentrations (50 and 100  $\mu g/L$  [microgram per liter], respectively) used by McMahon and Chapelle (2008) for pH ranges normally found in ground water (6.5–8.5) (Kennedy and others, 1974; Hem, 1989).

The framework of McMahon and Chapelle (2008) expanded on previous work (Chapelle and others, 1995; Paschke and others, 2007) by including both suboxic and methanogenic categories. Suboxic ground water in this framework indicates the sample has low  $O_2$  and low  $NO_3^-$ , but additional data is needed to further define redox processes. However, McMahon and Chapelle (2008) did not differentiate between iron (III)- and sulfate-reducing conditions because of the lack of sulfide data in their dataset. Chapelle and others (in press) found that iron- and sulfate-reducing conditions could be distinguished from one another on the basis of the ratio of  $Fe^{2+}$  to sulfide [the sum of dihydrogen sulfide (aqueous  $H_2S$ ), hydrogen sulfide ( $HS^-$ ), and sulfide ( $S^{2-}$ ) measured using colorimetric methods].

This report describes the Microsoft Excel® workbook, RedoxAssignment\_McMahon&Chapelle.xls, which assigns the predominant redox process to water-quality samples using the framework created by McMahon and Chapelle (2008) and extended by Chapelle and others (in press) (table 1).

Assignment of redox conditions is based on concentrations of dissolved  $O_2$ ,  $NO_3^-$ ,  $Mn^{2+}$ ,  $Fe^{2+}$ ,  $SO_4^{2-}$ , and sulfide (the latter being the sum of aqueous  $H_2S$ ,  $HS^-$ , and  $S^{2-}$ ). The logical arguments for assigning the predominant redox process to each sample are performed by a program written in Microsoft® Visual Basic® for Applications (VBA). This program is called from buttons on the main worksheet (“RedoxAssignment” worksheet) (fig. 1).

## Methods

The possible outcomes of redox categories and processes were differentiated by the number and type of parameters input into the program (table 2). Samples that had  $O_2$ ,  $NO_3^-$ ,  $Mn^{2+}$ ,  $Fe^{2+}$ , and  $SO_4^{2-}$  were considered complete and the possible outcomes of redox categories and processes were determined by the logic outlined in the upper-half of table 2. The possible outcomes for samples that have sulfide in addition to these five parameters are also included in the upper-half of table 2. NOTE: The actual implementation of the logic into VBA code is different than the simple “Yes,” “No” arguments in table 2. The logic used in the code was designed to execute more efficiently for a large number of samples. Table 2 is a reference for users to understand the general logic behind each redox assignment.

The redox categories listed in the upper-half of table 2 are the same or similar to the categories listed by McMahon and Chapelle (2008). The Mixed category was further defined to indicate whether the mixture had two anoxic redox processes [Mixed(anoxic)] or an oxic ( $O_2$ -reducing) and an anoxic redox process [Mixed(oxic-anoxic)]. The redox processes comprising the mixture is separated by a “-” (meaning *and*). For example, a redox process “ $NO_3$ - $Mn(IV)$ ” is a mixture of nitrate- *and* manganese-reducing ground water. Since both of these redox processes are anoxic, the redox category is “Mixed(anoxic).”

Samples that have fewer than the five parameters listed above were considered incomplete, and the possible outcomes of redox categories and processes are listed in the bottom-half of table 2. These samples were further differentiated into two groups: (1) samples that have measured  $O_2$ , but are missing one or more of the other four redox constituents, and (2) samples missing  $O_2$ , but have  $NO_3^-$ ,  $Mn^{2+}$ ,  $Fe^{2+}$ , and  $SO_4^{2-}$ . Samples collected for regulatory compliance purposes are often analyzed for major ions, trace elements, and nutrients, but usually not for dissolved  $O_2$ . Redox processes for these samples would be assigned using the logic of the second group. However, water-quality samples collected for compliance purposes may not have been filtered or preserved (acidified), and (or) may have been treated or blended. Users should always evaluate the source and quality of data to determine if the data are suitable for redox classification.

**Table 1.** Criteria and threshold concentrations used to identify redox processes in ground water.

[Table was modified from McMahon and Chapelle, 2008. Redox process: O<sub>2</sub>, oxygen reduction; NO<sub>3</sub>, nitrate reduction; Mn(IV), manganese reduction; Fe(III), iron reduction; SO<sub>4</sub>, sulfate reduction; CH<sub>4</sub>gen, methane genesis. Chemical species: O<sub>2</sub>, dissolved oxygen; NO<sub>3</sub><sup>-</sup>, dissolved nitrate; MnO<sub>2(s)</sub>, manganese oxide with manganese in 4+ oxidation state; Fe(OH)<sub>3(s)</sub>, iron hydroxide with iron in 3+ oxidation state; FeOOH<sub>(s)</sub>, iron oxyhydroxide with iron in 3+ oxidation state; SO<sub>4</sub><sup>2-</sup>, dissolved sulfate; CO<sub>2(g)</sub>, carbon dioxide gas; CH<sub>4(g)</sub>, methane gas. Abbreviations: mg/L, milligram per liter; —, criteria do not apply because the species concentration is not affected by the redox process; ≤, less than or equal to; ≥, greater than or equal to; <, less than; >, greater than]

Redox category	Redox process	Electron acceptor (reduction) half-reaction	Criteria for inferring process from water-quality data					
			Dissolved oxygen (mg/L)	Nitrate, as Nitrogen (mg/L)	Manganese (mg/L)	Iron (mg/L)	Sulfate (mg/L)	Iron/sulfide (mass ratio)
Oxic	O <sub>2</sub>	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	≥0.5	—	<0.05	<0.1	—	—
Suboxic	Suboxic	Low O <sub>2</sub> ; additional data needed to define redox process	<0.5	<0.5	<0.05	<0.1	—	—
Anoxic	NO <sub>3</sub>	$2NO_3^- + 12H^+ + 10e^- \rightarrow N_{2(g)} + 6H_2O$ ; $NO_3^- + 10H^+ + 8e^- \rightarrow NH_4^+ + 3H_2O$	<0.5	≥0.5	<0.05	<0.1	—	—
Anoxic	Mn(IV)	$MnO_{2(s)} + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	<0.5	<0.5	≥0.05	<0.1	—	—
Anoxic	Fe(III)/SO <sub>4</sub>	Fe(III) and (or) SO <sub>4</sub> <sup>2-</sup> reactions as described in individual element half reactions	<0.5	<0.5	—	≥0.1	≥0.5	no data
Anoxic	Fe(III)	$Fe(OH)_{3(s)} + H^+ + e^- \rightarrow Fe^{2+} + H_2O$ ; $FeOOH_{(s)} + 3H^+ + e^- \rightarrow Fe^{2+} + 2H_2O$	<0.5	<0.5	—	≥0.1	≥0.5	>10
Mixed(anoxic)	Fe(III)-SO <sub>4</sub>	Fe(III) and SO <sub>4</sub> <sup>2-</sup> reactions as described in individual element half reactions	<0.5	<0.5	—	≥0.1	≥0.5	≥0.3, ≤10
Anoxic	SO <sub>4</sub>	$SO_4^{2-} + 9H^+ + 8e^- \rightarrow HS^- + 4H_2O$	<0.5	<0.5	—	≥0.1	≥0.5	<0.3
Anoxic	CH <sub>4</sub> gen	$CO_{2(g)} + 8H^+ + 8e^- \rightarrow CH_{4(g)} + 2H_2O$	<0.5	<0.5	—	≥0.1	<0.5	<0.5

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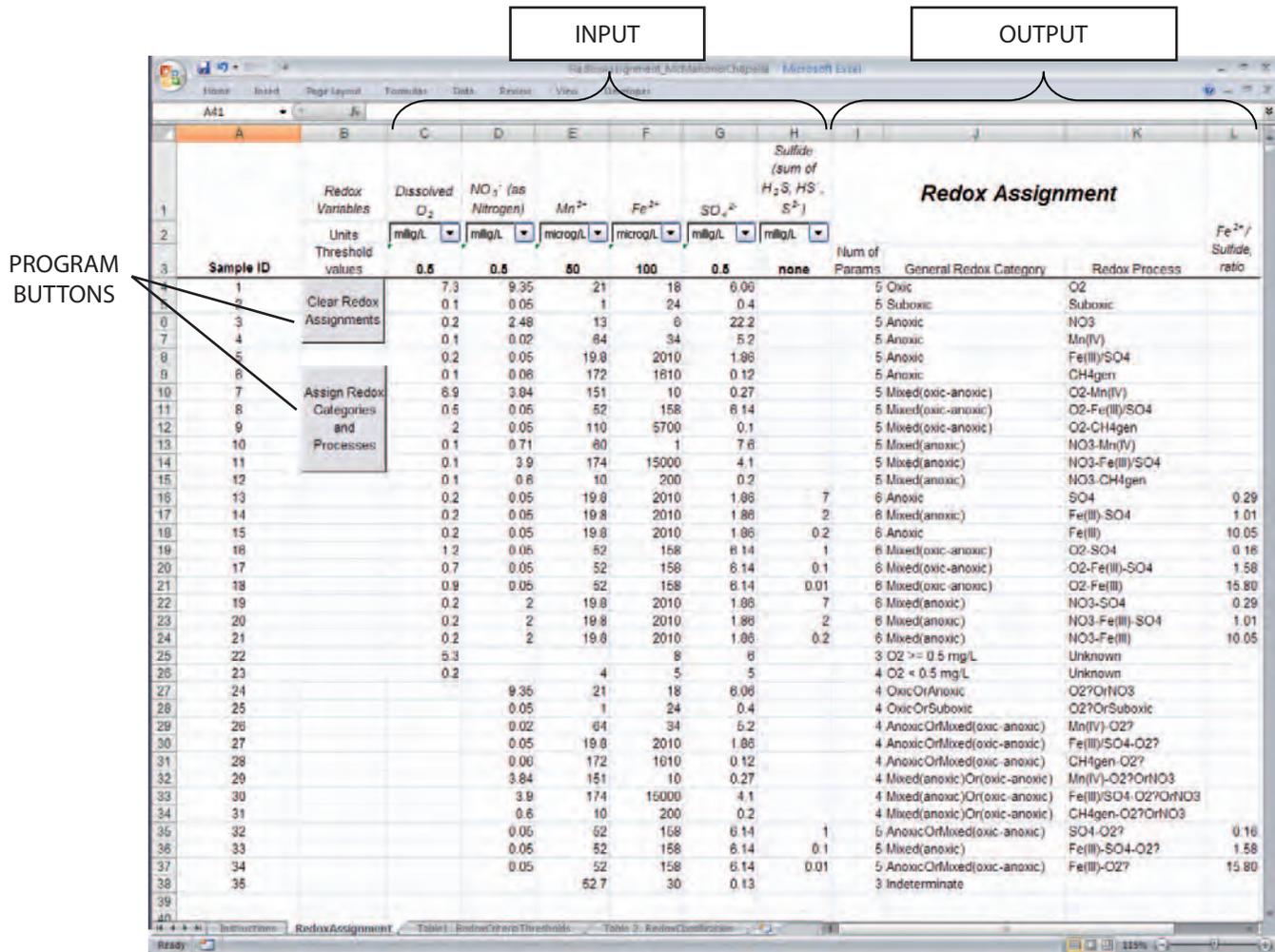


Figure 1. View of the worksheet used for assigning redox processes to ground-water analyses.

Samples that have dissolved O<sub>2</sub>, but are missing one or more of the other four constituents, will have a general redox category of either “O2 ≥ 0.5 mg/L” or “O2 < 0.5 mg/L”. These two categories are used to distinguish between predominately oxic and anoxic conditions.

Samples that are missing dissolved O<sub>2</sub>, but have measured NO<sub>3</sub><sup>-</sup>, Mn<sup>2+</sup>, Fe<sub>2+</sub>, and SO<sub>4</sub><sup>2-</sup>, will be assigned a redox category and process that is consistent with the framework in table 1. However, each redox process is amended with a prefix or suffix of “O2?” or “O2?OrNO3” to indicate that dissolved oxygen was not measured and could be present above the threshold concentration (table 2). The general redox category is also amended to indicate the two possible redox categories for O<sub>2</sub> above or below the threshold. The first redox category indicates the predominant redox category that would be consistent with the other measured data, and the second category indicates the less likely category. For example, a sample that has low nitrate (<0.5 mg/L

[milligrams per liter]) and high iron and sulfate (>100 µg/L and >0.5 mg/L, respectively) is consistent with an Fe(III)/SO<sub>4</sub><sup>2-</sup> reducing redox environment, so the presence of oxygen would not be expected. Therefore, the general redox category for this sample would be “AnoxicOrMixed(oxic-anoxic)” to indicate this sample is most likely anoxic but would be a mixed sample if dissolved O<sub>2</sub> was greater than 0.5 mg/L. Conversely, a sample containing high NO<sub>3</sub><sup>-</sup> and low Mn<sup>2+</sup> and Fe<sup>2+</sup> is consistent with both an O<sub>2</sub><sup>-</sup> and a NO<sub>3</sub><sup>-</sup> reducing environment, as indicated by the “O2?OrNO3” designation in table 2. McMahon and Chapelle (2008, table 2) showed that most ground-water samples (greater than 50 percent) tend to be O<sub>2</sub> reducing while only a small percentage (less than 4 percent) tend to be NO<sub>3</sub><sup>-</sup> reducing for many hydrogeologic settings. Consequently, these samples are assigned a general redox category of “OxicOrAnoxic” to indicate that the oxic condition is more likely than the anoxic condition, although this assumption may not be valid in some settings.

**Table 2.** Classification of redox categories and processes assigned on the basis of water-quality data.

[Redox category: O<sub>2</sub> ≥ 0.5 mg/L, dissolved oxygen greater than or equal to 0.5 mg/L; O<sub>2</sub> < 0.5 mg/L, dissolved oxygen less than 0.5 mg/L. Redox process: O<sub>2</sub>, oxygen reduction; NO<sub>3</sub>, nitrate reduction; Mn(IV), manganese reduction; Fe(III), iron reduction; SO<sub>4</sub>, sulfate reduction; CH<sub>4</sub>gen, methanogenesis. Abbreviations: mg/L, milligram per liter; <, less than; ≤, less than or equal to; ≥, greater than or equal to; >, greater than; Y, yes; N, no; —, criteria do not apply because the species concentration is not affected by the redox process; ?, insufficient data to determine whether process is occurring or not; /, and (or); -, and; x, not applicable]

Redox Category	Redox Process	Dissolved oxygen >0.5 mg/L	Nitrate, as Nitrogen >0.5 mg/L	Manganese >0.05 mg/L	Iron >0.01 mg/L	Sulfate >0.5 mg/L	Iron/sulfide mass ratio >0.3	Iron/sulfide mass ratio >10
Water-quality data complete								
Oxic	O <sub>2</sub>	Y	—	N	N	—	x	x
Suboxic	Suboxic	N	N	N	N	—	x	x
Anoxic	NO <sub>3</sub>	N	Y	N	N	—	x	x
Anoxic	Mn(IV)	N	N	Y	N	—	x	x
Anoxic	Fe(III)/SO <sub>4</sub>	N	N	—	Y	Y	no data	no data
Anoxic	CH <sub>4</sub> gen	N	N	—	Y	N	x	x
Mixed(oxic-anoxic)	O <sub>2</sub> -Mn(IV)	Y	—	Y	N	—	x	x
Mixed(oxic-anoxic)	O <sub>2</sub> -Fe(III)/SO <sub>4</sub>	Y	N	—	Y	Y	no data	no data
Mixed(oxic-anoxic)	O <sub>2</sub> -CH <sub>4</sub> gen	Y	N	—	Y	N	x	x
Mixed(anoxic)	NO <sub>3</sub> -Mn(IV)	N	Y	Y	N	—	x	x
Mixed(anoxic)	NO <sub>3</sub> -Fe(III)/SO <sub>4</sub>	N	Y	—	Y	Y	no data	no data
Mixed(anoxic)	NO <sub>3</sub> -CH <sub>4</sub> gen	N	Y	—	Y	N	x	x
Anoxic	SO <sub>4</sub>	N	N	—	Y	Y	N	N
Mixed(anoxic)	Fe(III)-SO <sub>4</sub>	N	N	—	Y	Y	Y	N
Anoxic	Fe(III)	N	N	—	Y	Y	Y	Y
Mixed(oxic-anoxic)	O <sub>2</sub> -SO <sub>4</sub>	Y	N	—	Y	Y	N	N
Mixed(oxic-anoxic)	O <sub>2</sub> -Fe(III)-SO <sub>4</sub>	Y	N	—	Y	Y	Y	N
Mixed(oxic-anoxic)	O <sub>2</sub> -Fe(III)	Y	N	—	Y	Y	Y	Y
Mixed(anoxic)	NO <sub>3</sub> -SO <sub>4</sub>	N	Y	—	Y	Y	N	N
Mixed(anoxic)	NO <sub>3</sub> -Fe(III)-SO <sub>4</sub>	N	Y	—	Y	Y	Y	N
Mixed(anoxic)	NO <sub>3</sub> -Fe(III)	N	Y	—	Y	Y	Y	Y



## Description of Spreadsheet Program

The Microsoft® Excel® workbook, RedoxAssignment\_McMahon&Chapelle.xls, consists of two worksheets and a VBA program that determines the predominant redox process in each sample according to [table 2](#). The first worksheet, named “Instructions,” provides brief instructions on the use of the program. The second worksheet, named “Redox Assignment,” is the main worksheet where data are entered and redox processes and categories are assigned. The workbook includes a set of 32 example analyses, each representing one of the unique redox assignments listed in [table 2](#). NOTE: Because this workbook contains a VBA program, the program will not operate unless macros are enabled in Microsoft® Excel®.

The Sample ID, and concentrations of dissolved  $O_2$ ,  $NO_3^-$ ,  $Mn^{2+}$ ,  $Fe^{2+}$ , and  $SO_4^{2-}$  are required for a redox assignment using the classification scheme by McMahon and Chapelle (2008). Samples that have measured sulfide concentrations will be further defined to distinguish iron(III)-reducing from sulfate-reducing conditions, as described by Chapelle and others (in press). Samples having only dissolved  $O_2$ , or are missing one or more of the other redox species, will be classified as either “ $O_2 \geq 0.5$  mg/L” or “ $O_2 < 0.5$  mg/L.” A redox process will also be assigned to samples lacking  $O_2$  data but having  $NO_3^-$ ,  $Mn^{2+}$ ,  $Fe^{2+}$ , and  $SO_4^{2-}$  data. The redox process determined for these samples is consistent with the framework created by McMahon and Chapelle (2008), but, as noted above, is amended with an “O2?” or “O2?OrNO3” to include the possibility that dissolved oxygen could be present at concentrations above the threshold. Without  $O_2$  data, oxygen-reducing and nitrate-reducing ground water cannot be distinguished.

### Input

Data can be copied from other spreadsheets or programs into the corresponding constituent columns on the main spreadsheet (“RedoxAssignment” worksheet, [fig. 1](#)). The program accepts constituent concentrations in either milligrams per liter (mg/L) or micrograms per liter ( $\mu$ g/L). The concentration units can be changed using the pull down menu in row 2 below each constituent and must be defined before running the program to ensure the use of accurate thresholds and ratios of  $Fe^{2+}$  to sulfide. Input concentrations should be formatted as a number and preferably should not contain text characters. The program will accept 3 types of mixed character-number formats. The first character must be either a “<,” “E” (case sensitive), or “>,” and must be

followed by a number—for example, “<0.2,” “E10.5,” or “>50.” In general, the first mixed character-number format indicates the value is less than the laboratory reporting limit, the second an estimated value, and the third a value greater than the analytical limit. Once the program identifies a mixed character-number formatted value, the text character, either the “<,” “E,” or “>,” will be removed and the number retained before the program assigns a redox state.

All constituents used for determining redox processes should be analyzed with method reporting levels equal to or, preferably, lower than the threshold concentrations listed in [tables 1](#) and [2](#). The use of analyses with higher reporting levels will likely result in incorrect redox classifications.

Total manganese and total iron concentrations above the threshold concentrations (50 and 100  $\mu$ g/L) from samples that have been filtered ( $\leq 0.45$   $\mu$ m) and acidified and are often accurate measurements of dissolved  $Mn^{2+}$  and  $Fe^{2+}$  at pH ranges normally measured in ground water (6.5–8.5) (Kennedy and others, 1974; Hem, 1989). Consequently, it may be acceptable to use total dissolved concentrations of manganese and iron as substitutes for  $Mn^{2+}$  and  $Fe^{2+}$ . Other data may be equally acceptable; however, all water-quality data should be evaluated to determine if the data are suitable for redox classification.

### Redox Assignment

The program is operated by two buttons located in the second column on the left-hand side of the main worksheet ([figure 1](#)). These two buttons control the contents of the cells in columns I thru L. The number of samples to be analyzed is determined by the number of non-null cells in column A, so a Sample ID must be assigned to every sample before running the program. The number of samples that can be analyzed is only limited by the number of rows in Excel® (65,536 for Excel® 2003 and XP and 1,048,576 for Excel® 2007). The “Clear Redox Assignments” button clears the contents of cells in columns I thru L. The “Assign Redox Categories and Processes” button assigns a redox process and category to each sample according to the logic in [table 2](#).

Column I is a count of the number of constituents. Column J is the general redox category defined in [table 2](#), and column K is the redox process defined in [table 2](#). Column L is the calculated  $Fe^{2+}$  to sulfide ratio for samples having sulfide in addition to the five required parameters. Mixed samples are identified in the General Redox Category column and a hyphen, “-,” is added to separate the two redox processes of the mixture in the Redox Process column.

## Limitations

The redox framework described by McMahon and Chapelle (2008) has some limitations and inherent uncertainty. These limitations are described more fully by McMahon and Chapelle (2008) and Chapelle and others (in press). In general, most of the uncertainty is derived from defining appropriate thresholds that accurately identify the predominant terminal electron acceptor process for many water analyses with varied chemistry from diverse hydrogeologic settings. The thresholds used here were defined to be broadly applicable to large datasets for regional studies across different hydrogeologic settings. Threshold concentrations and the relative importance of each redox process could be further refined using site-specific information. To change threshold concentrations, users can change the threshold values listed in row 3 on the main worksheet (“RedoxAssignment” worksheet, [fig. 1](#)). NOTE: The cells containing the original threshold concentrations in row 3 contain a formula that will be lost after manually changing the values in these cells. It is suggested that the user save any altered version of the workbook separately from the original workbook.

## Example Dataset

The workbook includes a sample dataset (“RedoxAssignment” worksheet, [fig. 1](#)) that is a subset of samples from wells used in the report by McMahon and Chapelle (2008). Each sample well has a chemistry analysis representing one of the redox categories and the corresponding redox process given in [table 1](#). Some of the samples were duplicated to illustrate how sulfide concentrations may affect the redox assignment, using the criteria described by Chapelle and others (in press). The sulfide concentrations from these samples are not actual measured data. Other samples were duplicated, and dissolved O<sub>2</sub> data was removed to demonstrate the redox process assignments and general redox categories for samples lacking O<sub>2</sub> data. The redox process assignments for these samples were amended with an “O<sub>2</sub>?” or “O<sub>2</sub>?OrNO<sub>3</sub>.”

## Acknowledgments

The funding for this report and development of this program was provided by the U.S. Geological Survey’s National Water-Quality Assessment (NAWQA) program’s “Transport of Anthropogenic and Natural Contaminants (TANC) to supply wells” topical team.

## Disclaimer

This program contains Microsoft® Visual Basic® code that was written to determine the predominant redox process in ground-water samples based on the work of McMahon and Chapelle (2008) and Chapelle and others (in press). All efforts have been made to ensure the program makes accurate determinations; however, it is possible that errors within the code may exist or that certain formats of input data could cause a redox process to be assigned in error or not at all. Users are encouraged to keep an original copy of the workbook and notify the author if any errors are found.

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