Characterization of the Effects of Redox Condition on Fe(III)/Fe(II) Transformation in a Small Karstic Aquifer: Poocher Swamp Freshwater Lens, South Australia

Nara Somaratne[1]

[1] South Australian Water Corporation, 250 Victoria Square, Adelaide, SA 5000, Australia

Correspondence: Nara Somaratne, South Australian Water Corporation, 250 Victoria Square, Adelaide, SA 5000, Australia. Tel: 618-7424-2379. E-mail: nara.somaratnef@sawater.com.au

Abstract

The presence of iron in potable water supply aquifers poses a major water quality problem and may render the supply unsuitable for domestic or industrial uses, unless appropriate treatments is undertaken. Evaluation of redox conditions in groundwater is a prerequisite for studies involving Fe(III)/Fe(II) transformation in aquifers. This study characterizes the redox conditions, geochemical evolution and distribution of iron in a small karstic freshwater aquifer, the Poocher Swamp freshwater lens, located in south-east of South Australia. The freshwater lens is formed as a result of flows from Tatiara Creek that enter Poocher Swamp and recharge the aquifer through two sinkholes located in the northwest section of the swamp. Stable isotopes of water molecules, δ^2H and $\delta^{18}O$, indicate that both Tatiara Creek and Poocher Swamp waters are isotopically more enriched due to evaporation than the pristine water of the aquifer. The Na^+/Cl^- ion ratio >0.85 for Tatiara Creek, Poocher Swamp and wells within the lens suggest additional sodium source(s) are involved in the evolution of groundwater chemistry. This study use redox potential, dissolved oxygen (DO) and dissolved organic carbon (DOC) contents to describe Fe(III)/Fe(II) transformation in the groundwater, and relate this to iron distribution within the lens. Three distinct redox zones are present in the freshwater lens; anoxic zone up to one kilometre from Poocher Swamp where dissolved oxygen (DO)   is <1 mg.L^{-1}, redox potential (Eh) <100 mV, and iron (Fe) in groundwater 2.3-9.3 mgL^{-1}. Following the anoxic zone is the suboxic zone (from 1to1.5 km from Poocher Swamp), where DO is <1 mg.L^{-1}, Eh is about 110-275 mV and Fe is 0.4-0.6 mg.L^{-1}. The oxic zone is 1.5 to 2.3 km from Poocher Swamp and is characterized by high DO (2-4 mg.L^{-1}), higher Eh (>300 mV) and low in Fe (<0.015 mg.L^{-1}). Only 0.4 km^2 of the 13 km^2 area of the freshwater lens is oxygenated, thus limiting further developments of the lens as potable water supply source.

Keywords: redox potential, iron reduction, DOC, DO, drinking water, fresh water lens, karstic aquifer

1. Introduction

In nature, iron occurs mostly in two oxidation states; ferrous (Fe^{+2}) and ferric (Fe^{+3}) depending on prevailing environmental physicochemical parameters, such as pH, oxygen concentration and redox potential (Hedrich et al., 2011 citing Stumm and Morgan, 1996). Ferrous iron is stable in anoxic environments, but is susceptible to spontaneous chemical oxidation by molecular oxygen (Hedrich et al., 2011). A high concentration of iron in groundwater is a concern for public water supply. Drinking water quality guidelines (WHO, 1996; ADWG, 2004) recommend a limit for iron concentration below 0.3 mg.L^{-1}, although colour may develop in piped systems at levels above 0.1 mg.L^{-1}. Laundry and sanitary ware will stain at iron concentrations above 0.3 mg.L^{-1} (WHO, 1996). Therefore, WHO (2008) recommends a range of 0.1 mg.L^{-1} and 0.3 mg.L^{-1} as highest desirable and maximum permissible limits. In groundwater systems, naturally occurring solid phase ferric (Fe^{3+} or Fe(III)) converts to more soluble ferrous form (Fe^{2+} or Fe(II)) through reduction dissolution mechanism in a reducing or anaerobic environment (Valcarce, undated). The most common cause of reducing reactions is organic matter decomposition; either in solid form or dissolved organic carbon (DOC) (Nelson, 2002). The redox potential can be correlated with the amount of dissolved oxygen as the decomposition of organic matter depletes dissolved oxygen. As the oxygen content drops, the environment becomes more reducing. All natural waters contain dissolved organic carbon and therefore is a very important component in the biogeochemical cycling of elements (Gooddy and Hinsby, 2008) that influence water quality and fuels microbial metabolism (Shen et al., 2015).

According to Nelson (2002) three factors; the temperature, pH, and redox potential define as the chemical state of groundwater. Redox reactions are facilitated by bacteria that are able to gain energy from the reactions. The oxidation of organic molecules contributes electrons, which can result in iron in a solid iron oxide mineral (Fe^{3+})(accepting electrons) being dissolved into the water as reduced iron, Fe^{2+} (Dimkic et al., 2011). Christensen et al. (2000) studied the redox conditions in a contaminant plume and show when sufficient organic matter and other reduced components leak into an aquifer, strongly reducing redox conditions will develop with a transversal redox gradient in the groundwater flow direction. In the outskirts of the lens, redox conditions will approach the redox conditions of the pristine aquifer. Seasonal recharge may result in a situation where the groundwater in the aquifer is oxygenated resulting in oxic condition. After recharge occurs, routine pumping may result in the bulk of the oxygenated water becoming depleted, leading to reducing conditions (Nelson, 2002). Therefore, understanding the processes involve in iron dissolution is a prerequisite in managing source water supply aquifers.

Microbial oxidation of organic compounds and H_2 with the reduction of Fe(III) is an important process in a variety of subsurface habitats (Lovley, 1997). Commonly, these organisms couple oxidation of organic matter or hydrogen to the reduction of iron oxides. In general, shallow unconfined aquifers are aerobic, but in certain circumstances anaerobic plumes may develop. Almost all aquatic organisms obtain their energy for metabolic processes from redox reactions (Banchuen, 2002). Citing Stumm and Morgan (1996) and Sigg (2000), Banchuan (2002) suggests that redox potentials in natural waters range from about -400 mV to +800 mV at pH 7 to 8. The sequence of microbial mediated redox processes may be seen in redox couples as: $MnO_2(s)/Mn^{2+}$ at +400 to +600 mV, $Fe(OH)_3(s)/Fe^{2+}$ at -200 to +200 mV, SO_4^{2-} /HS^- and CO_2/CH_4 below -200 mV. Thus solid iron, (Fe (III)) is reduced to Fe (II) when organic matter is mineralized. Dissimilatory iron-reducing bacteria couple the oxidation of organic matter or H_2 to the reduction of iron oxides (Frederickson et al., 1998; Lovely, 1997).

According to Lovely (1997), low redox potential is not a sufficient condition to bring about Fe(III) reduction but microorganisms that have the capacity to enzymatically reduce Fe(III) are also required. The extent of abiotic Fe(III) reduction is much less than the Fe(III) reduction that takes place when microorganisms completely oxidize the organics to carbon dioxide with Fe(III) serving as the electron acceptor (Lovley, 1997). Two most intensely studied genera of Fe(III) reducers are the *Geobacter* and *Shewanella* species (Lovley, 1997). Nevin and Lovely (2002) points out it is not necessary that Fe(III) reducing microorganisms come into direct contact with iron oxides in order to reduce them. Electron-shuttling compounds and/or Fe(III) chelators, either naturally present or produced by the Fe(III)-reducing microorganisms themselves, may alleviate the need for the Fe(III) reducers to establish direct contact with Fe(III) oxides in order to transfer electrons from the cell to the Fe(III) oxide surface.

Studies of Konhauser (1998) show bacteria simply provide charged surfaces that bind metals and then excrete metabolic waste products into the surrounding environment that induce mineralization. The metabolic activity of Fe(II) –oxidizing bacteria can induce ferric hydroxide precipitation as a by-product. In reviewing literature, Konhauser (1998) further describes that when ferrous iron is transported into an oxygenated environment, it spontaneously reacts with dissolved oxygen at circumneutral pH (6.5-7.5) to precipitate rapidly as ferric hydroxides on available nucleation sites. Bacteria passively act as such sites. Liang et al. (1993) also examined the dynamics of dissolved, colloidal and deposited iron phases and observed under increased DO conditions, Fe(II) oxygenation was rapid, resulting in the formation of Fe(III) (hydr)oxide colloids. McMahon and Chapelle (2008) show that redox conditions and their impact on several water quality issues depends on ecological succession of electron acceptors ($O_2 > NO_3^- > Mn(IV) > Fe(III) > SO_4^{2-} > CO_2^-$) such as dissolved oxygen, nitrate and sulfate. Similarly, solid phase electron acceptors such as Fe(III) are indicated by production of dissolved iron. Those microbial processes that couple the most efficient electron donors to the most efficient electron acceptors have a competitive advantage (Dimkic, 2011). Dissolved and particulate organic carbon is often the common electron donors available in groundwater. Understanding the extent to which redox reactions occur and reduced species are present within the freshwater lens, is important with respect to drinking water supply. It is therefore essential to characterize the redox conditions in the Poocher Swamp freshwater lens.

The present investigation represents an extension of Somaratne and Mann (2016) and is a part of resource assessment efforts of Poocher Swamp fresh water lens. The study provides insight into the processes controlling occurrence of iron in groundwater, which is essential in management of the lens as a public water supply source. Study present stable isotopes within the fresh water lens, shown against the global meteoric water line and the local meteoric water line for Adelaide, to show the degree of evaporative enrichment and possible local recharge areas. Major ion chemistry of groundwater is analyzed to show groundwater mixing along flow paths. We use redox

potential, dissolved oxygen and dissolved organic carbon content to describe Fe(III)/Fe(II) transformation in the groundwater, and relate this to iron distribution within the freshwater lens.

2. Study Site: Poocher Swamp Freshwater Lens

The study site, Poocher Swamp freshwater lens, is located 275 km south-east from Adelaide (Figure 1) and is within the Tatiara catchment area that extends across the South Australian border into western Victoria and previously described by Somaratne (2014). For brevity, a succinct summary of the study freshwater lens is provided here. The Tatiara catchment area is approximately 500 km^2 (Herczeg et al., 1997) and features average annual rainfall ranging from 400 to 500 mm and pan evaporation of 2000 mm. The unconfined aquifer is Murray Group Limestone and contains brackish water with average total dissolved solids (TDS) > 1400 mg.L^{-1}. Freshwater with TDS < 1000 mg.L^{-1} occurs at locations where point recharge takes place through sinkholes. The Poocher Swamp freshwater lens, which is the largest of these freshwater plumes that float on brackish water, is a result of flows from Tatiara Creek that enter Poocher Swamp. The major recharge is through two sinkholes located in the northwest section of the swamp (Herczeg et al., 1997). The area encompassed by the 1000 mg.L^{-1} salinity contour comprises approximately 13 km^2 in 2016. Surface water flows in Tatiara Creek are highly irregular, with annual volumes of freshwater (0.05-2)×10^6 m^3 per year, but on rare occasions up to 19×10^6 m^3 per year. Groundwater flow direction is from east to west.
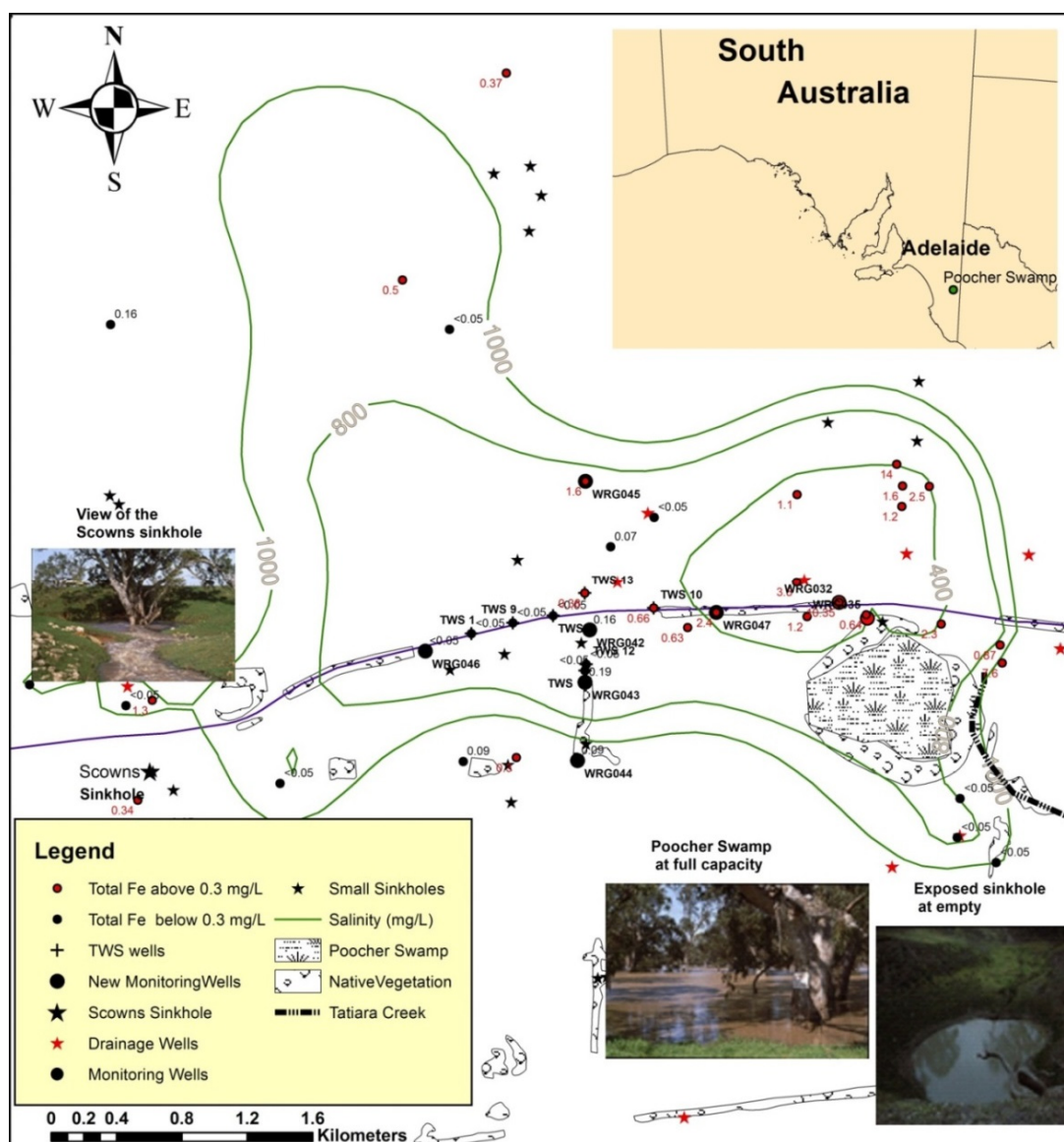

Figure 1. Iron distribution in Poocher Swamp freshwater lens

The study area is relatively flat terrain with ground elevations at WRG032 well near the Poocher Swamp (Figure 1) at 69.83 m AHD (Australian Height Datum) and most down gradient well WRG046 is at 66.24 m AHD. Depth to watertable varies, about 19 m at WRG032 and 15.6 m at WRG 046, and is on average about 17 m for the entire freshwater lens area. Currently, an annual volume of 0.6×10^6 m^3 of groundwater is extracted from the freshwater lens for town water supply to Bordertown, approximately 7 km east from the lens. The average salinity is about 490 mg.L^{-1}.

The Murray Group Limestone aquifer, comprises a consolidated, highly fossiliferous and fine to coarse bioclastic limestone. Saturated thickness of the limestone unconfined aquifer is approximately 50-60 m. During high flows in the Tatiara Creek, Poocher Swamp overflows through the outlet channel to Scowns sinkholes further west (Figure 1). Based on average annual flow data of Tatiara Creek for 1980-2010 periods, Somaratne (2014) suggested annual recharge to the lens through sinkholes at Poocher Swamp may be 2.5×10^6 m^3. In addition to the town water supply, groundwater is also extracted from the surrounding area for irrigated agriculture, mainly pasture, legumes and for viticulture. In addition, dryland grazing is common within the lens area and surroundings. Therefore, prudent management of the Poocher Swamp fresh water lens is vital for economic development.

3. Method

Water samples were collected from Tatiara Creek, Poocher Swamp, aquifer monitoring wells and town water supply wells in 2012 and 2014. Groundwater samples from monitoring wells were collected using micro-purge (low-flow) sampling procedure (Vail, 2011). The micro sampling is employed to gain representative groundwater samples within open-hole sections of monitoring wells. Water samples were preserved according to the standard methods specified in Australia/New Zealand standard, AS/NZS 5667.5 (1998) guidelines and chemical analyses were performed at the Australian Water Quality Centre, Adelaide. Analysis of Ca, Mg, Na, K and SO_4 is based on Method 3120B-Metals by plasma emission spectroscopy (APHA/AWWA/WEF Method 3120B, 1999). The following methods described in APHA/AWWA/WEF Methods (2012) were used for analyses of: for chloride, Method 4500-Cl Chloride-E (automated ferricyanide method); for analysis of HCO_3, Method 2320 Alkalinity-B using radiometer autotitrator; and analysis of DOC is based on the Method 5310 C; for nitrogen Method 4500; for iron and sulphate reducing bacteria Method 9240-E. For the analyses of sulphide, EPA Method 376.2 (1978) and for Fe-total EPA Method 200.8 (1994) were used. In addition, redox couples; nitrate/nitrite, sulphate/sulphide along with free carbon dioxide in groundwater, total iron, iron reducing bacteria and sulphate reducing bacteria were analysed. Following methods described in APHA/AWWA/WEF Standard Methods (2012) were used: for nitrate Method 4500-NO_3, nitrite Method 4500-NO_2, sulphide Method 4500-D, iron Method 3500-Fe, iron reducing bacteria 9240-B and sulphate reducing bacteria Method 9240-C. Redox potential and dissolved oxygen were obtained from the field using YSI pro plus (https://www.ysi.com/proplus?Professional-Plus-18) multiparameter probe. The probe was calibrated on the day with ZoBell's ORP/Redox standard solution (http://www.hach.com/zobell-s-orp-redox-standard-solution-500-ml/product?id=7640206194) and readings were taken within a flow cell.

Water samples for stable isotope analysis were collected in 30 mL McArtney glass bottles with metal screw top lids with rubber insert. In order to reduce evaporation, samples were stored and transported inverted. Stable isotope (δ^2H and δ^{18}O) samples were analysed at the Flinders University of South Australia isotope analytical laboratory in Adelaide. The standard procedure for analysis of the Deuterium and Oxygen-18 composition of water is that described by PICARRO (2015).

4. Results and Discussion

4.1 Stable Isotope Signatures

Distinct stable isotopic compositions allow us to distinguish the contribution from various recharge sources such as surface water subject to evaporation or direct recharge of the aquifer. The use of empirical relationship of δ^2H = $8\delta^{18}$O + 10 (Craig, 1961) for meteoric water on a global scale is a common reference. However, the global meteoric water line (GMWL) relationship varies depending on location and it is necessary to define a local meteoric water line (LMWL) relationship derived from the annual weighted mean of δ^2H and δ^{18}O in local rainfall (Somaratne et al., 2016). Due to the lack of sufficient data for the study area, the Adelaide LMWL is taken as the reference in this study. Both GMWL and LMWL are presented in Figure 2.

While there are varying degrees of overlap, the majority of groundwater samples are plotted with the Adelaide winter average, with two observations (TWS 10 and WRG047) around the summer average isotope. A majority of the results show good conformance with the MWL indicating that recharge occurred predominantly during winter months and aquifer received vertical recharge downgradient from TWS 10 well.
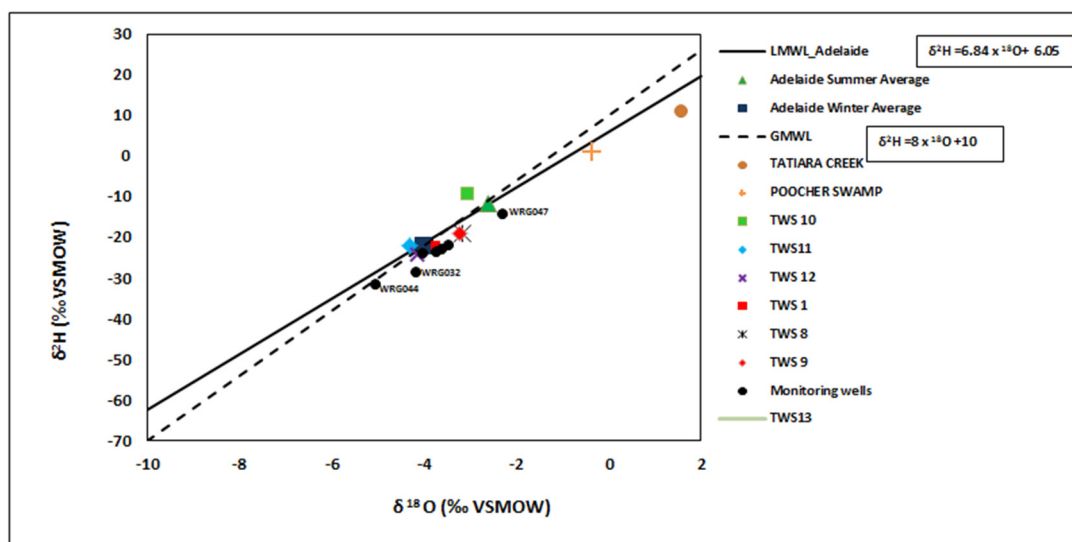
Figure 2. Relationship of δ^2H and δ^{18}O within the Poocher Swamp freshwater lens

This observation is consistent with gradual decrease of δ^{18}O enrichment from Poocher Swamp (−0.34‰ VSMOW-Vienna Standard Mean Ocean Water) to Adelaide winter average -4.19‰ in TWS 8 (Figure 2). The increases of DO (Table 1) in this zone from TWS 8 to WRG046 further support the view that the influence of diffuse rainfall recharge appears downgradient to TWS 10 well, as there are no other significant point recharge sources. This indicates that evolution of groundwater is a complex mixing of Poocher Swamp water, ambient groundwater and local rainfall recharge that occurs over the distance between the point recharge source and ambient regional groundwater, forming a non-homogeneous freshwater plume.

Two isotopic end members within the lens are the groundwater at WRG044 and the Poocher Swamp. The stable isotope values of WRG044 are below the Adelaide winter average as the study site is about 100 km from the nearest coastline and rainfall is to some extent depleted with respect to heavy isotopes due to continental effect. This represents the pristine water isotopes of the lens. The other end member Tatiara Creek-Poocher Swamp system shows enriched isotope values due to evaporation during sampling period in October, 2012. Herczeg et al. (1997) show dynamic nature of stable isotope and salinity variation in the Poocher Swamp; with annual variation of ^{2}H range from 10 to -40‰ VSMOW, and variation of chloride about 10-40 mg.L^{-1}. The evaporative enrichment of stable isotopes diminishes along the flow paths, up to WRG047 and TWS 10 wells, due to mixing. Constructed in 1960, WRG032 well is 150 m downgradient of the Poocher Swamp and shows isotopic composition of water, close to Adelaide winter average. This is possibly due to more recent winter recharge water received from the Poocher Swamp. The lower chloride values (29-35 mg.L^{-1}) in WRG032 is similar to the Poocher Swamp (27-44 mg.L^{-1}) supports this suggestion.

4.2 Groundwater Mixing

Understanding of the geochemical compositions, nature and extent of a groundwater mixing zone in a karstic system can help determine the relative importance of non-homogeneity in an aquifer system and its potential impact on the resource estimate. The results of chemical analyses of groundwater in the fresh water lens (from monitoring wells WRG 35 and WRG 32 located adjacent to Poocher Swamp, town water supply wells, and new monitoring wells within and just outside the fresh water lens and the surface water samples taken from Tatiara Creek and Poocher Swamp) are shown in the Piper diagram (Figure 3). The major ion chemistry results show no dominant cations in Tatiara Creek, Poocher Swamp and town water supply (TWS) wells: TWS 10, TWS 8, TWS 9 and TWS 1. However, alteration of water chemistry of Tatiara Creek (Na-Ca-Mg-HCO$_3$-Cl) and Poocher Swamp (Na-Ca-HCO$_3$-Cl) water types to calcium dominant water: Ca-Na-HCO$_3$, in WRG035 well is the result of dissolution of calcite. Ca and HCO$_3$ dominant water type (Ca-Na-HCO$_3$-Cl) found along the flow path (Somaratne and Mann, 2016) that intercepts WRG047,TWS 10, TWS 8 and TWS 9. Higher salinity wells are located outside the freshwater lens, WRG044 with Na-HCO$_3$-Cl type water and WRG045 well with Na-Ca-Cl-HCO$_3$ water type. Hence, groundwater in the lens can be divided into two types based on the dominant cation, i.e., Ca-dominant and Na-dominant types (Somaratne, 2014).
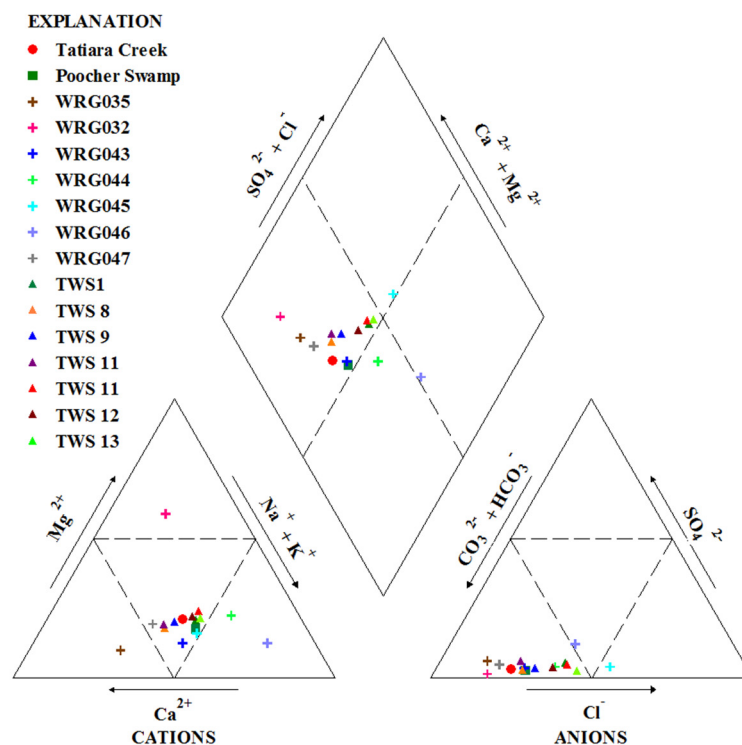
Figure 3. Piper plot of the groundwater samples of freshwater lens

Table 1. Well details, physical and chemical parameters

Source	Depth (m)	Prod. Interval (m)	SWL (m)	Sample Depth (m)	Ca (mg.L⁻¹)	Mg (mg.L⁻¹)	Na (mg.L⁻¹)	K (mg.L⁻¹)	HCO₃ (mg.L⁻¹)	SO₄ (mg.L⁻¹)	Cl (mg.L⁻¹)	EC (µS.cm⁻¹)	pH	Temp. (⁰C)	DOC (mg.L⁻¹)	DO (mg.L⁻¹)	ORP (mV)	Eh (mV)	Total Fe (mg.L⁻¹)
Tatiara Creek	n/a	n/a	n/a	n/a	37.5	13	45.1	7.9	245	8.1	46	525	8.3	dry	dry	dry	dry	dry	dry
Poocher Swamp	n/a	n/a	n/a	n/a	28.2	8.6	40.8	6.6	186	5.1	27-44	421	8.2	dry	dry	dry	dry	dry	dry
WRG035	18	12-18	dry	dry	89.6	8.8	42.2	9.6	370	22.2	40	699	7.4	dry	dry	dry	dry	dry	dry
WRG032	38.7	19.3-38.7	19.1	21	53.9	6.3	32.4	7.2	225	3	29-35	612	6.91	16.1	5.9	0.88	-112.3	87.7	9.3
				25	-	-	-	-	-	-	-	612	6.98	16.7	-	0.85	-106.1	93.9	-
				30	-	-	-	-	-	-	-	612	6.95	16.7	-	0.73	-103.7	96.3	-
				35	-	-	-	-	-	-	-	612	6.95	16.7	-	0.6	-103.8	96.2	-
WRG047	40	16-40	18.3	21	45.5	11.4	34.2	6.2	278	12.9	35-40	670	6.8	17	2.2	0.59	-88.6	111.4	2.39
TWS 10	40	16-40	-	pump	76.2`	20	71	6	378	24.3	81	962	7.1	18	1.2	0.41	-5.8	194.2	0.66
TWS 8	26.3	16-26.3	-	pump	66.2	16	64.2	4.1	329	9	73	739	7.1	17.9	0.7	2.62	107.7	307.7	0.005
TWS 9	45	20-45	-	pump	67.5	19.9	75.3	4.3	342	12.6	93.3	1054	7.01	18	0.7	3.85	132.8	332.8	0.005
TWS 1	40	19-40	-	pump	71.5	27.1	114	4.9	371	27	149	805	7	18.1	1.7	4.09	136.7	336.7	0.001
WRG046	40	16-40	15.5	20	28	14.3	148	16.6	371	70.8	173	1326	11.6	17.8	3.9	1.16	-186	14	0.048
WRG045	40	16-40	15.3	20	89.1	24.3	140	6.1	331	24	242	2032	6.7	18.1	0.7	1.6	12.7	212.7	1.11
TWS 13	40	25-40	16.7	20	62.2	24.6	104	5.4	358	12	171	808	7.1	17.6	0.7	0.35	-61.3	138.7	0.43
WRG042	40	16-40	17.8	21	-	-	-	-	-	19.2	-	888	6.9	17.4	0.8	3.6	75.4	275.4	0.16
TWS 12	37	25-37	-	pump	58.5	23.3	87.1	4.8	357	16.5	124	907	7	18	0.7	2.38	137	337	0.015
TWS 11	37	25-37	-	pump	56.5	26.3	93.7	5.3	354	20.4	150	805	7	17.8	0.6	2.45	133.2	333.2	0.015
WRG043	36	28.8-36	16.6	30	58	10.4	73.3	3.8	305	11.4	70	733	7.1	16.5	2.2	1.03	-116.9	83.1	0.192
WRG044	40	16-40	16.3	20	89.3	58	275	7	1350	70.5	487	2849	6.8	17.3	0.8	6.53	117.4	317.4	0.089

Note: *Tatiara Creek, Poocher Swamp and WRG035 well were dry during May 2016 sampling round. Major ions, EC and pH data collected in 2012 and 2014, ORP=Oxidation-reduction potential.*

Town water supply wells TWS 1, TWS 11, TWS 12 and TWS 13 and monitoring wells WRG043 and WRG046 water types are either Na-Ca-HCO_3-Cl or Na-Ca-Mg-HCO_3-Cl (TWS 11, TWS 12) as a result of different degrees of mixing along flow paths between two end member (Poocher Swamp and WRG044 well) water types in the fresh water lens. Apart from WRG044 (0.46), WRG045 (0.47), TWS 11 (0.49) and TWS 13 (0.48) wells, ionic ratios of $Na^+/(Na^+ + Cl^-)$ are >0.5 indicating another sodium source, such as dissolution of albite (*sodium aluminium silicate*) (Hem, 1985), or cation exchange taking place when fresh recharge water, with Ca^{2+} and HCO_3^- ions reaches the aquifer. The Na^+/Cl^- ion ratio >0.85 (sea water ratio) for all wells except WRG044 (0.86) and WRG045 (0.88), supports the suggestion of additional sodium source(s) involved in evolution of the groundwater chemistry. The highest ratio Na^+/Cl^- ion ratio is found in Tatiara Creek, Poocher Swamp, WRG035 and WRG032 and the ratio decreases along flow paths to the meteoric origin (0.85) at WRG044 to about 0.86 (outside the lens to the south) and at WRG045 to about 0.88 at the boundary to the north of the lens. This indicates, additional sodium may have been derived from sources outside the lens and distributed as the plume spreads.

4.3 Redox Control on Fe(III)/Fe(II) Transformation

In order to understand the Fe(III)/Fe(II) transformation, it is essential to consider physical, chemical and biological processes that occur within the Tatiara Creek-Poocher Swamp surface water and the shallow groundwater system. The main chemical changes that influence the iron transformation is the organic matter decomposition that depletes the oxygen in groundwater, leading to reducing condition (Matsunaga et al., 1993).
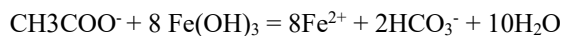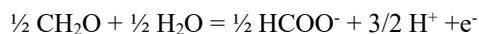
$$CH_2O + O_2 = CO_2 + H_2O$$
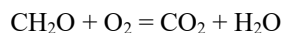
Typically, the oxidation-reduction state is plotted in Eh-pH diagram, but a broad classification of redox potentials from oxic to anoxic conditions are given in GES166/266n (2000) as:

Oxic	$Eh > 400$ mV
Suboxic	$100 < Eh < 400$ mV
Anoxic	$Eh < 100$ mV

Studies of different forms of iron in waterlogged soil over a wide range of closely controlled redox potential and pH conditions (Gotoh and Patrick, 1974) show critical redox potentials (Eh) for iron reduction and consequent dissolution was between +300 mV and +100 mV at pH 6 and 7, and −100 mV at pH 8. According to Sigg (2000), iron reduction can occur at redox potential -100 mV at pH 8 and up to +100 mV at pH 7.

Thus, with respect to iron reduction in this study, three distinct zones are identified: from WRG035 to WRG047 wells, Eh range from +87.7 to +111.4 (Table 1) indicating predominantly anoxic conditions; in the east-west direction from TWS 8 to TWS 1 and north-south direction from TWS 12 to WRG044 showed predominantly oxic (Eh>+300) conditions; and in between areas sub-oxic conditions with both iron reduction and oxidation is possible. Under anoxic or reducing conditions, organic matter breakdown is mediated by bacteria (Lovley, 1997). Appelo and Postma (2007) describe the process as follows: 'in the first step, fermenting bacteria excrete enzymes that hydrolyze the polysaccharides and break them down to alcohols, fatty acids and H_2. In the next step, other bacteria degrade the alcohols and long chained fatty acids further to acetic acid (CH_3COOH), formic acid ($CHOOH$), H_2 and CO_2. In the last step, the fermentative intermediate acetate, formate and H_2 are oxidized by oxidants or terminal electron accepting processes'. Thus:

$$\frac{1}{2} CH_2O + \frac{1}{2} H_2O = \frac{1}{2} HCOO^- + 3/2 H^+ + e^-$$

$$3CH_2O + H_2O = 2CH_3COO^- + 2H^+ + e^-$$

$$FeOOH + HCO_3^- + 2H^+ + e^- = FeCO_3 + 2H_2O$$

$$CH3COO^- + 8 Fe(OH)_3 = 8Fe^{2+} + 2HCO_3^- + 10H_2O$$

If the aquifer receives fresh recharge, groundwater is oxygenated increasing dissolved oxygen content. This is seen in the Poocher Swamp fresh water lens. The main mechanism of bacterial oxidation of ferrous iron, with oxygen as the electron acceptor, is according to the reaction (Meruane & Vargas, 2003):

$$Fe^{2+} + \frac{1}{4} O_2 + H^+ = Fe^{3+} + \frac{1}{2} H_2O$$

This process is schematically shown in Figure 4 in a conceptual diagram. In the sub-oxic zone from WRG047 to TWS 8 where redox potential is $100<Eh<300$ mV, both oxidation and reduction is possible. Mejia et al. (2016) describe the process as oscillations between reducing and oxidizing conditions at the interface of anaerobic/oxic and anaerobic/anoxic environments, and are often stimulated by an alternating flux of electron donors (e.g., organic carbon) and electron acceptors (e.g., O_2 and NO_3^-). In the iron (Fe) rich sediments of the Murray Group Limestone in the freshwater lens, these oscillations may stimulate the growth of both Fe-reducing bacteria (Table

2) and Fe-oxidizing bacteria (Meija et al., 2016), and their metabolism may induce cycling between Fe(II) and Fe(III). In contrast, introduction of O_2 with recharge water results in increased Fe(II) oxidation and so reduces iron in groundwater as observed in TWS 8 to TWS 1. According to Konhauser (1998), in oxygenated waters, iron hydroxides are a common precipitate and can form passively through the binding of dissolved ferric species to negatively charged polymers, or when soluble ferrous iron spontaneously reacts with dissolved oxygen to precipitate as ferric hydroxide on available nucleation sites (e.g., bacteria).
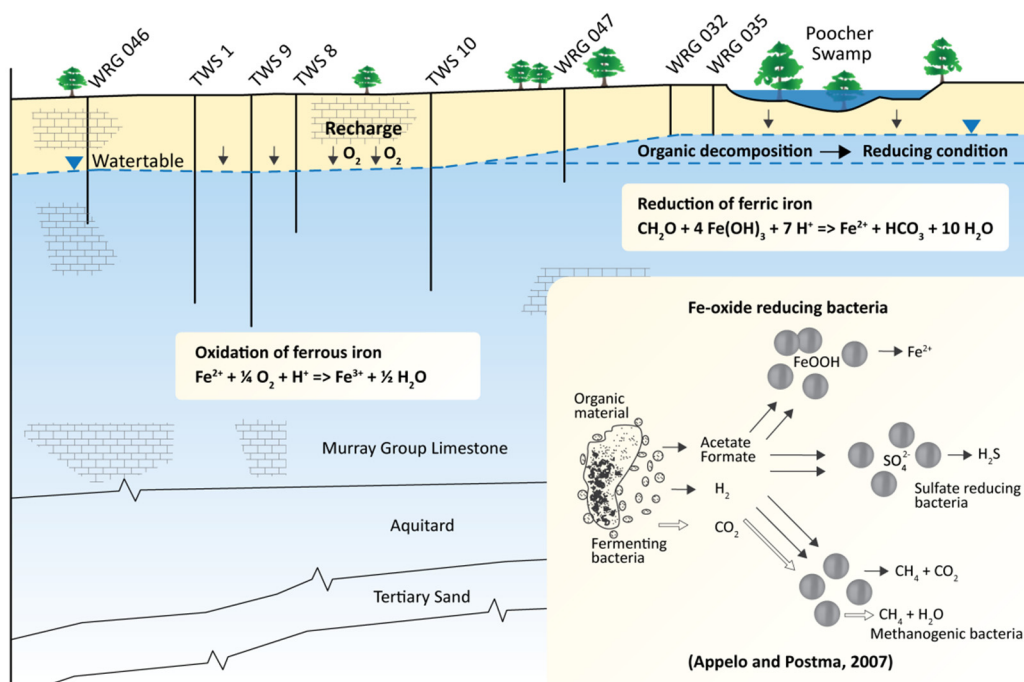

Figure 4. Organic decomposition, reducing condition and Fe(III)/Fe(II) transformation in the Poocher Swamp fresh water lens

Typically, the presence of Fe^{2+} is a result of iron reduction and indicates anoxic conditions of groundwater. The presence of NO_3^- indicates aerobic or nitrate reducing conditions. The presence of nitrite, NO_2^- indicates nitrate reduction. The presence of low SO_4^2 under anoxic conditions indicates sulfate reduction. The study analysed two other redox couples; NO_3^-/NO_2^- and SO_4^{2-}/H_2S in order to gain an understanding of other possible redox reactions competing with Fe(III)/Fe(II) transformation. Results show negligible concentrations of reduced forms of nitrate and sulphate within the freshwater lens, thus Fe(III) may be used preferentially by subsurface microorganisms in the anoxic zone, in the absence of oxygen and nitrate. The threshold concentration (McMahon & Chapelle, 2008) for nitrate- (NO_3^--N) reduction is ≥ 0.5 mg.L^{-1}, but in our study, nitrate concentrations at all sampling points are <0.5 mg.L^{-1} (Table 2). Nitrate reduction has occurred in the Tatiara Creek-Poocher Swamp system ($NO_3 < 0.1$ mg.L^{-1}), possibly as a part of organic matter decomposition according to (Vance, 1996):

$$5CH_2O + 4NO_3^- + 4H^+ = 5CO_2 + N_2 + 7H_2O$$

In the oxic zone, nitrate content is low but varies between 0.1-0.3 mg.L^{-1}. According to the redox sequence, ($O_2 > NO_3^- > Mn(IV) > Fe(III) > SO_4^{2-} > CO_2^-$), lack of O_2 and NO_3^- in the anoxic and sub-oxic zones (up to 1.5 km from the Poocher Swamp) causes Fe(III) to be the sole electron acceptor. Hence redox couples NO_3^-/NO_2^- and SO_4^{2-}/H_2S show no evidence to whether they act as electron acceptors. Nitrate is a common inorganic pollutant in shallow groundwater aquifers and drinking water abstraction wells and is often seen as a pollutant linked to agricultural sources (Jorgenesen et al., 2009). Despite the study area being an agricultural catchment, marked reduction in nitrate levels present in the Tatiara Creek-Poocher Swamp systems and groundwater within the freshwater lens suggest denitrification is taking place.
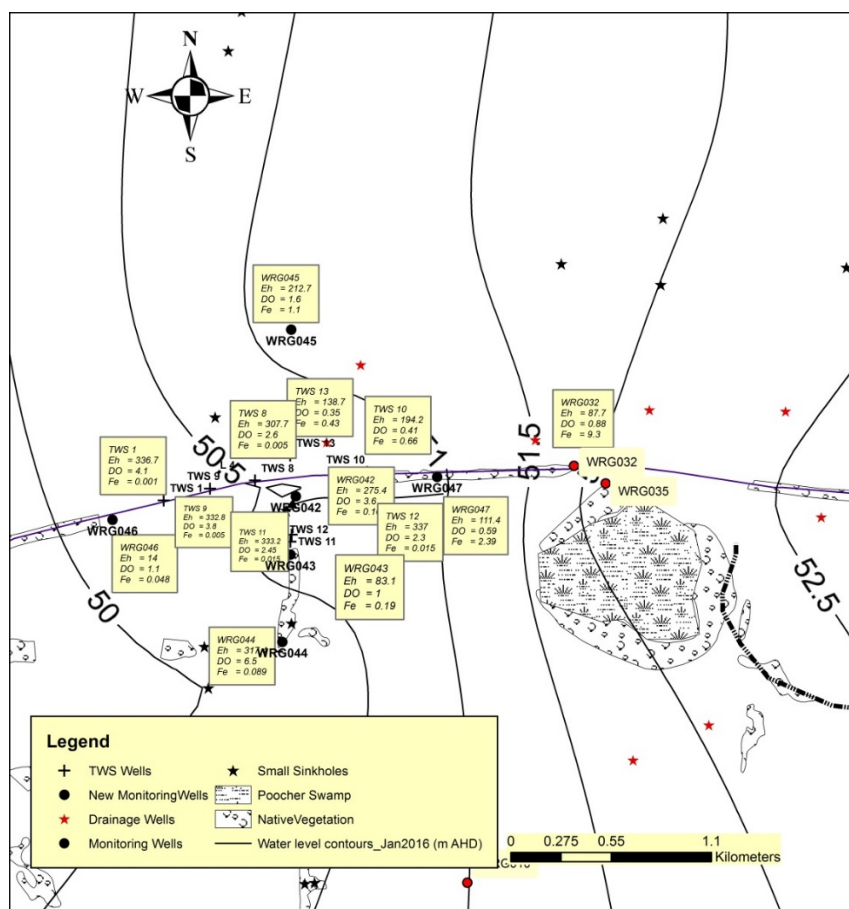
Figure 5. Redox potential (ORP), DO and Fe distribution in the freshwater lens

Table 2. Iron reducing bacteria, sulphate reducing bacteria and redox couples

Source	Iron Bacteria-Heterophic (MPN/100mL)	Sulphate Reducing Bacteria (MPN/100 mL)	Carbon Dioxides-Free (mg/L)	Nitrate Reduction		Sulphate Reduction		Iron-Total (mg/L)
				Nitrate as N (mg/L)	Nitrate + Nitrite as N (mg/L)	Sulphate (mg/L)	Sulphide-Total (mg/L)	
Tatiara Creek	-	-	-	<0.1	<0.1			
Poocher Swamp	-	-	-	<0.1	<0.1			
WRG035	-	-	-	<0.1	<0.1			
WRG032	2000	>4800	82	<0.1	<0.1	3	0.2	9.3
WRG047	80	1200	73	<0.1	<0.1	12.9	<0.1	2.39
TWS 10	<10	44	48	<0.1	<0.1	24.3	<0.1	0.66
TWS 8	<10	340	40	0.105	<0.1	9	<0.1	0.005
TWS 9	<10	0	43	0.196	<0.1	12.6	<0.1	0.005
TWS 1	30	60	59	0.332	0.332	27	<0.1	0.001
WRG046	<10	>4800	-	<0.1	<0.1	70.8	1.6	0.048
WRG045	210	>4800	112	0.304	0.304	24	<0.1	1.11
TWS 13	3300	1700	39	<0.1	<0.1	12	0.4	0.43
WRG042	200	650	107	<0.1	<0.1	19.2	<0.1	0.16
TWS 12	<10	20	55	<0.1	<0.1	16.5	<0.1	0.015
TWS 11	<10	0	58	<0.1	<0.1	20.4	<0.1	0.015
WRG043	380	1000	39	<0.1	<0.1	11.4	0.3	0.192
WRG044	530	2	113	1.81	1.81	70.5	<0.1	0.089

Water sources; Tatiara Creek, Poocher Swamp and WRG035 well were sampled in 2012; MPN=Most Probable Number.

It is essential to understand the physical, chemical and biological processes that could lead to distribution of iron within the freshwater lens. In this regard, accurate mapping of DO, DOC and redox potential of groundwater is important in delineating the exploitable freshwater for public water supply. Results imply that redox conditions of groundwater change from anoxic to suboxic and to oxic through the east-west trending flow path.

The Fe^{2+}, once mobilized from the anoxic zone is eventually reoxidized on reaching a zone of higher Eh, forming Fe(III) oxides. The reoxidation of ferrous iron in oxygen rich, circum-neutral pH waters is usually rapid and abiotic (Hedrich et al., 2011). Despite an oxic environment in the wellfield area (area covering TWS 8 to TWS 1, and TWS 11 and TWS 12), that is favorable for self-purification of iron in groundwater, a small oxygenated area (about 0.4 km^2) limits further groundwater development for town water supplies.

5. Conclusions

This study shows that combined interpretation of hydrochemical data with dissolved oxygen, dissolved organic carbon and redox potential in the freshwater lens enabled the assessment of the mechanism of iron distribution within the lens. The direct conduit flow paths from the Poocher Swamp carry anoxic water and should be avoided for future well developments. The hydrogeochemical characteristics of groundwater in the freshwater lens comprise two main water types; Na-Ca-HCO$_3$-Cl and Ca-Na-HCO$_3$-Cl. Excess Na$^+$ ion within the freshwater lens is derived from outside the lens. Stable isotopic composition of δ^{2}H and δ^{18}O increases of DO in groundwater indicate the wellfield area receives localised diffuse rainfall recharge as there are no other significant point recharge sources. This indicates that the evolution of groundwater is from complex mixing of Poocher Swamp water, ambient groundwater and local rainfall recharge, making a non-homogeneous freshwater plume. Microbial decomposition of organic matter within the Tatiara Creek-Poocher Swamp system has led to depleted oxygen in recharge water, creating strong reducing environments. Results imply that redox conditions of groundwater change from anoxic to suboxic and to oxic through east-west trending flow path. Management strategies are pursued to achieve long-term sustainable water supply from the freshwater lens. It is apparent that abstractions need to balance both, the recharge water from the Poocher Swamp for low salinity groundwater, and diffuse recharge for oxygenation of ferrous iron. A water balance study using a numerical groundwater model may provide useful information on through flow and vertical recharge to the wellfield area. As groundwater extraction may also remove dissolved oxygen, well abstraction practice need to follow pumping and recovery cycles allowing fresh oxygenated groundwater to flow into the wellfield. As biogeochemical processes in the freshwater lens are dynamic, periodic monitoring of DO, DOC, redox potential, nitrate and iron in groundwater is a necessity.

Acknowledgments

References

ADWG. (2004). Australian drinking water guidelines, 6, National water quality management strategy, National Health and Medical Research Council, Australian Government, pp. 511.

APHA/AWWA/WEF Method 3120B. (1999). In *Standard Methods for the Examination of Water and Wastewater* （20th ed.). American Public Health Association, Washington, DC, USA.

APHA/AWWA/WEF Methods. (2012). In *Standard Methods for the Examination of Water and Wastewater* (22nd ed.). American Public Health Association, Washington, DC, USA.

Appelo, C. A. J., & Postma, D. (2007). *Geochemistry, groundwater and pollution* (2nd ed.). A. A. Balkema Publishers, Leiden, The Netherlands.

AS/NZ 5667.5. (1998). Water Quality Sampling-Guidance on the Design of Sampling Programs, Sampling Techniques and the Preservation and Handling of Samples; AS/NZS 5667.5; Australia/New Zealand Standard: Homebush, Australia.

Banchuen, T. (2002). Oxydation-Reduction (Redox) reactions and potentials. Retrieved March 24, 2016, from https://theses.lib.vt.edu/theses/available/etd-01102003-162857/unrestricted/(08)Lit_Rev_2.pdf

Christensn, T. H., Bjerg, P., Banwart, S. A., Jakobsen, R., Heron, G., & Albrechtsen, H.-J. (2000). Characterization of redox conditions in groundwater contaminant plumes. *Journal of Contaminant Hydrology, 45*, 165-241.

Craig, H. (1961). Isotopic variations in meteoric waters. *Science, 133*, 1702-1703.

Dimkic, M., Pusic, M., MAjkic-Dursun, B., & Obradovic, V. (2011). Certain implications of oxic conditions in alluvial groundwater. *Water Research and Management, 1*(2), 27-43.

EPA Method 376.2. (1978). Methods for the chemical analysis of water and wastes (MCAWW), EPA/600/4-79/020, U.S. EPA, Office of Research and Development, Environmental Monitoring Support Laboratory, Ohio.

EPA Method 200.8. (1994). Determination of trace elements in water and waste by inductively coupled plasma mass spectrometry. *Revision 5.4, Methods for Determination of Metals in Environmental Samples-Supplement I*, EPA/600/R-94-111, U.S.EPA.

Fredickson, J. K., Zachara, J. M., David, K., Dong, H., Onstott, T., Hinman, N., & Li, S. (1998). Biogenic iron mineralization accompanying the dissimilatory reduction of hydrous ferric oxide by a groundwater bacteruium. *Geochimica et Cosmochimica Acta, 62*(19/20), 3239-3257.

GES166/266. (2000). *Soil Chemistry Lecture 4: Oxydation and Reduction (Redox) reactions*. Retrieved April 30, 2016, from http://soils.stanford.edu/classes/GES166_266items/HO4_Redox.doc

Gotoh, S., & Patrick, W. H. (1974). Transformation of iron in a waterlogged soil as influenced by redox potential and pH. *Soil Science Society of America, 38*(1), 66-71.

Gooddy, D. C., & Hinsby, K. (2008). Organic quality of groundwaters. In W. M. Edmunds, & P. Shand (Eds.), *Natural groundwater quality* (pp. 59-70). Oxford, Blackwell.

Hedrich, S., Schlomann, M., & Johnson, D. B. (2011). The iron-oxidizing proteobacteria. *Microbiology, 157*, 1551-1564. http://dx.doi.org/10.1099/mic.0.045344-0

Hem, J. D. (1985). *Study and interpretation of the chemical characteristics of natural waters*. U.S Geological Survey Water Supply paper 2254, U.S Geological Survey, U.S.A.

Herczeg, A. L., Leaney, F. W. J., Stadter, M. F., Allan, G. L., & Fifeld, L. K. (1997). Chemical and isotope indicators of point source recharge to karst aquifers, South Australia. *J. Hydrol., 192*, 271-299.

Jorgensen, C. J., Jacobsen, O. S., Elberling, B., & Aamand, A. A. (2008). Microbial oxidation of Pyrite coupled to nitrate reduction in anoxic groundwater sediment. *Environ. Sci. Technol., 43*, 4851-4857.

Konhauser, K. O. (1998). Diversity of bacteria iron mineralization. *Earth Science Reviews, 43*, 91-121.

Liang, L., McCarthy, J. F., Jolley, L. W., McNabb, J. A., & Mehlhorn, T. L. (1993). Iron dynamics: Transformation of Fe(II)/Fe(III) during injection of natural organic matter in a sandy aquifer. *Geochimca et Cosmochimca Acta, 57*, 1987-1999.

Lovley, D. R. (1997). Microbial Fe (III) reduction in subsurface environments. *FEMS Microbiology Reviews, 20*, 305-313.

Matsunaga, T., Karametaxas, G., von Gunten, H. R., & Lichtner, P. C. (1992). Redox chemistry of iron and manganese minerals in river-recharged aquifers: A model interpretation of a column experiment. *Geochimca et Cosmochimca Acta, 57*, 1691-1704.

McMahon, P. B., & Chapelle, F. H. (2008). Redox processes and water quality of selected principal aquifer systems. *Ground Water, 46*(2), 259-271.

Mejia, J., Roden, E. E., & Ginder-Vogel, M. (2016). Influence of oxygen and nitrate on Fe (Hydr)oxide mineral transformation and soil microbial communities during redox cycling. *Environ. Sci. Techol., 50*(7), 3580-3588.

Meruane, G., & Vargas, T. (2003) Bacteria oxidation of ferrous iron by *Acidithiobacillus ferroooxidans* in the pH range 2.5-7.0. *Hydrometallurgy, 71*, 149-158.

Nelson, D. (2002). Natural variations in the composition of groundwater. Presentation at Groundwater Foundation Annual Meeting, November, 2002, Oregan Department of Human Services, Springfield, Oregan, USA. Retrieved March 30, 3016, from https://public.health.oregon.gov/HealthyEnvironments/DrinkingWater/SourceWater/Documents/gw/chem.pdf

Nevin, K. P., & Lovley. (2002). Mechanismsfor Fe(III) oxide reduction in sedimentary environments. *Geomicrobiology Journal, 19*, 141-159.

PICARRO. (2015). PICARRO L2130-i δD and δ^{18}O High Precision Isotopic Water Analyser, PICARRO Inc, Santa Clara, USA. Retrieved April http://www.picarro.com/products_solutions/peripherals/for_h2o/ih2o_solids_liquids_and_vapor

Shen, Y., Chapelle, F. H., Storm, E. W., & Benner, R. (2015). Origins and bioavailability of dissolved organic matter in groundwater. *Biogeochemistry, 122*, 61-78. http://dx.doi.org/10.1007/s10533-014-0029-4

Sigg, L. (2000). Redox potential measurements in natural waters: Significance, concepts and problems. In J. Schring, H. D. Schulz, W. R. Fischer, J. Bottcher, & W. H. M. Duijnisveld (Eds.), *Redox: Fundamentals, processes and applications* (pp. 1-12). http://dx.doi.org/10.1007/978-3-662-04080-5_1

Somaratne, N. (2014). Characteristics of point recharge in karst aquifers. *Water,* 2014(6), 2782-2807. http://dx.doi.org/10.3390/w6092782.

Somaratne, N., Mustafa, S., & Lawson, J. (2016). Use of hydrochemistry, stable isotope, radiocarbon, ^{222}Rn and terrigenic ^{4}He to study the geochemical processes and the mode of vertical leakage to the Gambier Basin Tertiary confined sand aquifer, South Australia. *Water, 2016*(8), 180. http://dx.doi.org/10.390/w8050180

Somaratne, N., & Mann, S. (2016). Integrated use of geological, geophysical, radiocarbon and stable isotopes data for tracing the conduit flow paths in a small karstic aquifer-Poocher Swamp ftreshwater lens, South Australia. *Environment and Natural Resources Research, 6*(3).

Stumm, W., & Morgan, J. J. (1996). *Aquatic Chemistry* (3rd ed.). New York: Wiley-Interscience.

Tuhela, L., Carlson, L., & Tuovien, O. H. (1997). Biogeochemical transformation of Fe and Mn in oxic groundwater and well water environment. *Environ. Sci. Health, A32*(2), 407-426.

Valcarce, C. (n.d.). Factors affecting iron mobilization in surface and groundwater sites near Florida landfills, College of Enginnering, University of Florida. Retrieved March 24, 2016 from http://www.honors.ufl.edu/apps/Thesis.aspx/Download/577

Vance, D. B. (1996) Redox reactions in remediations. *Environmental Technology, July/Aug. 1996, 6*(4), 24-25. Retrieved August 3, 2016 from http://2the4.net/redox.htm

Vail, J. (2011) *Groundwater Sampling*; SESDRPROC-301-R3. U.S. Environmental Protection Agency, Science and Ecosystem Support Division: Athens, GA, USA.

WHO. (1996). Iron in drinking water. In *Guidelines for drinking water quality* (2nd ed. Vol. 2). Health criteria and other supporting information, World Health Organization, Geneva, p. 9.

WHO. (2008). *Guidelines for drinking water quality 2*. World Health Organization, Geneva, pp.67.

Copyrights