



# Thermal intensification of microbial Fe(II)/Fe(III) redox cycling in a pristine shallow sand aquifer on the Canadian Shield



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## ABSTRACT

This investigation evaluates spatial relationships between summer (July) groundwater temperatures and Fe(II)/Fe(III) biogeochemical cycling over a five year period in a shallow pristine sand aquifer at Meilleurs Bay near Deep River, Ontario, Canada. A warm subsurface thermal island of 12.5–16.1 °C, compared to background conditions of 10–11 °C, was manifest in contour maps of average groundwater temperature over the study period. The warm zone coincided with an area of convergent groundwater flow, implicating horizontal heat transfer by advective convection as the reason for elevated temperatures. Additionally, high concentrations of dissolved Fe(II) and Fe(III) overlapped the warm thermal island, indicative of increased rates of bacterial Fe(II)-oxidation and Fe(III)-reduction. A depletion in the modal abundance of Fe(II)-bearing minerals, notably amphibole and biotite, inside the area of the warm thermal island was also observed, suggesting enhanced mineral dissolution owing to chemoautotrophic Fe(II)-oxidation coupled to the reduction and fixation of dissolved inorganic carbon as biomass. Throughout the aquifer, redox conditions were poised in terms of Eh and pH close to equilibrium with respect to the Fe(II)/Fe(OH)<sub>3</sub> couple, feasibly enabling simultaneous bacterial Fe(II)-oxidation and Fe(III)-reduction with an adequate supply of electron acceptors and donors, respectively. The significance of higher groundwater temperature as a determinant of elevated dissolved Fe(II) and Fe(III) concentrations induced by thermal intensification of microbial biogeochemical activities yielded Pearson product-moment correlations in which temperature alone, as a single independent variable, explains almost 30 to nearly 60 percent of the variation in the measured dissolved Fe(II) and Fe(III) concentrations in the groundwater. These results emphasize the important influence of thermal conditions on biogeochemical processes in aquifers coupled to the development of steep gradients in groundwater quality over short distances in shallow unconfined groundwater systems.

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## 1. Introduction

The importance of groundwater systems as the most critical reservoir of freshwater storage on Earth cannot be understated (Taylor et al., 2013; Gleeson et al., 2015). On a global scale, groundwater is estimated to provide 36% of potable drinking water, 42% of irrigation water for agriculture, and 24% of direct-use industrial water; collectively, these groundwater withdrawals are estimated to be on the order of 900 km<sup>3</sup> per year (Foster et al., 2013). Most extractions are taken from recently recharged groundwater sources less than 50 years old, which are considered to be the most sensitive and vulnerable to anthropogenic

contamination and climate change (Gleeson et al., 2015; Taylor et al., 2013). Of particular concern is the prospect of global warming and increasing air temperatures bringing about warming in the shallow subsurface thereby affecting biogeochemical processes and, consequently, groundwater quality (Taylor and Stefan, 2009; Kurylyk et al., 2014; Menberg et al., 2014).

The acquisition of solutes and geochemical evolution of groundwater is determined foremost by the weathering rates of minerals along subsurface flow paths (Wilson, 2004; Glynn and Plummer, 2005). The kinetics of these reactions and their impact on groundwater quality are subject not only to acceleration by increasing temperature, but also a wide assortment of physical, chemical, and biological influences (Kump et al., 2000). Reduction-oxidation (redox) transformations are especially important as they are essential for bacterial energy metabolism and biogeochemical cycling, as well as the mobilization or immobilization of potentially

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toxic chemical species and degradation of anthropogenic contaminants (Groffman and Crossey, 1999; Chapelle et al., 2009; Barnes et al., 2011; Kumar and Riyazuddin, 2012; Lin et al., 2012; Parsons et al., 2013). Typically, solute concentrations and pH increase in response to longer periods of mineral weathering as redox conditions shift from oxidized recharge zones to more reducing conditions with increasing distance along groundwater flow paths (Kump et al., 2000; Wilson, 2004; Glynn and Plummer, 2005; McMahon and Chapelle, 2008). Although this type of behavior is especially pronounced in regional groundwater systems where residence times are long, local unconfined aquifers are susceptible to redox transitions over much shorter distances (<1.0 km) arising from upland recharge and discharge in adjacent topographic lows (Mitchell and Branfireun, 2005; Ulanowski and Branfireun, 2013).

The complex landscape of the Canadian Shield occupies nearly one-third of the North American landmass (Shilts et al., 1987). Shallow unconfined groundwater systems consisting of glacio-fluvial sands derived from reworked glacial sediments are important hydrogeological remnants left behind on the Canadian Shield in the aftermath of the Wisconsin glaciation and retreat of the Laurentide ice sheet (Catto et al., 1982; Singer and Cheng, 2002; Eyles, 2006). In some areas where their saturated thickness is adequate, the sand units constitute productive local aquifers that are used primarily for drinking-water supply (Montcoudiol et al., 2015). On a regional scale, they interact hydraulically with underlying bedrock aquifers, as well as neighbouring peatlands, wetlands, and lakes (Mitchell and Branfireun, 2005; Ulanowski and Branfireun, 2013; Richard et al., 2014). Hydrogeochemical surveys further indicate that groundwater in these shallow sand aquifers typically resembles recently infiltrated meteoric water with a chemical signature associated with relatively short subsurface residence times (Montcoudiol et al., 2015). Moreover, redox conditions tend to be thermodynamically poised by the Fe(II)/Fe(III) couple, implying an important biogeochemical role for Fe(II)-oxidizing and Fe(III)-reducing bacteria in Canadian Shield hydrogeochemical processes (Mitchell and Branfireun, 2005; Shirokova and Ferris, 2013; Gault et al., 2011, 2012).

This investigation focuses on spatial relationships between groundwater temperature and Fe(II)/Fe(III) biogeochemical cycling in a shallow pristine Canadian Shield groundwater system (Shirokova and Ferris, 2013). Several studies have considered the biogeochemical impact of groundwater warming on groundwater quality associated with urban heat islands and artificial aquifer thermal storage systems (Bonte et al., 2013a, 2013b; Jesušek et al., 2013; Zhu et al., 2015); however, few have been conducted on the extent to which natural horizontal temperature variations associated with groundwater flow impact biogeochemical processes, particularly with respect to shifts in redox conditions and changing rates of mineral weathering. As such, the main objective of this research is to use measurements of groundwater chemistry and temperature from a high-resolution spatial network of piezometers for physicochemical mapping of thermal impacts on microbial Fe(II)/Fe(III) cycling.

## 2. Methods

### 2.1. Site description

The study site is a shallow unconfined pristine aquifer in a small forested catchment at Meilleurs Bay on the south bank of the Ottawa River, approximately 10 km west of Deep River in central Ontario, Canada (46°09'42.8"N 77°37'09.5"W) (Catto et al., 1982). The mean annual temperature in the region averages 4.9 °C, ranging from –10.5 °C in January to 18.4 °C in July (Fu et al., 2014;

Montcoudiol et al., 2015). Bedrock in the region is Precambrian in age, consisting of faulted and fractured monzonitic gneiss that is typical of the Grenville Province of the Canadian Shield (Carr et al., 2000). A variety of unconsolidated sediments, predominantly glacial till and post-glacial fluvial sands, overlie bedrock in the region; in some areas thin layers of clay occur on top of the till (Singer and Cheng, 2002; Richard et al., 2014). At the study site itself, aquifer sands were deposited by the Ottawa River between 6000 and 11,200 years ago when the precursors of the Great Lakes drained through the Mattawa and Ottawa Rivers (Lewis et al., 2008). These sands grade into surface exposures of sandy washed till and coarse gravel.

### 2.2. Hydrogeology and groundwater geochemistry

The aquifer was instrumented with a network of standpipe piezometers to provide repeatable, spatially consistent, measurements over time. The piezometers were constructed from 2.5 cm outer diameter PVC conduit glued to 15 cm length Solinst Model 601 perforated PVC screens fitted with 60 µm polyethylene mesh inserts. The piezometers were inserted into boreholes hand-augered with 5.0 cm outer diameter stainless steel sand corers (AMS). Samples of aquifer sand were collected during installation for mineral identification and modal abundance determinations using X-ray diffraction and petrographic thin-sections (Klein and Philpotts, 2013), and for grain size analyses by sieving to estimate porosity and hydraulic conductivity (Vienken and Dietrich, 2011). Measurements of water depth at each piezometer were done using a Solinst 102 M water level meter.

A Solinst 410 peristaltic pump was used to recover groundwater samples for geochemical analysis; sampling at each piezometer was repeated annually in July from 2010 to 2015. Before sampling, piezometers were bailed completely and allowed to recover at least twice to remove standing water and any silt that may have collected in the piezometer. In order to avoid contact with atmospheric oxygen, groundwater was pumped into a closed 1.5 L flow-through sample cell equipped with a YSI 600 QS multi-electrode sonde for measurement of pH, Eh, temperature, conductivity, and dissolved oxygen. Groundwater samples were vacuum filtered immediately after sampling using 0.22 µm-pore-size membrane filters. Concentrations of dissolved total Fe, Fe(II), and dissolved silica were measured upon filtration using a HACH DR/2500 spectrophotometer with FerroVer<sup>®</sup>, 1,10 phenanthroline, and heteropoly blue reagents (HACH), respectively. Concentrations of Fe(III) were calculated afterwards as the difference between measured total Fe and Fe(II) concentrations.

### 2.3. Data analyses

In order to assess spatial relationships between aquifer hydrogeology and groundwater geochemistry, a series of contour maps were constructed using Surfer 11 (Golden Software) including water table elevation, temperature, pH, Eh, and dissolved Fe(II) and Fe(III) concentrations, as well as mineral saturation states for hydroxy-green rust and hydrous ferric oxide. Water table elevation contours were used to infer groundwater flow direction with indicator vector lengths proportional to the slope of the water table surface (i.e., hydraulic gradient) at their location. Statistical analyses were done using STATISTICA 6.0 (StatSoft).

Geochemical modeling was carried out using PHREEQC 3.1.4 to determine the relative saturation state of representative Fe(II) and Fe(III) bearing minerals taken to be plausible constituents of aquifer sand; specifically, hydroxy-green rust Fe<sub>3</sub>O<sub>2</sub>(OH)<sub>4</sub>, grunerite (amphibole Fe(II) end-member) Fe<sub>7</sub>Si<sub>8</sub>O<sub>22</sub>(OH)<sub>2</sub>, annite (biotite Fe(II) end-member) KFe<sub>3</sub>AlSi<sub>3</sub>O<sub>10</sub>(OH)<sub>2</sub>, and hydrous ferric oxide

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