



Evidence that bio-metallic mineral precipitation enhances the complex conductivity response at a hydrocarbon contaminated site

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ABSTRACT

The complex conductivity signatures of a hydrocarbon contaminated site, undergoing biodegradation, near Bemidji, Minnesota were investigated. This site is characterized by a biogeochemical process where iron reduction is coupled with the oxidation of hydrocarbon contaminants. The biogeochemical transformations have resulted in precipitation of different bio-metallic iron mineral precipitates such as magnetite, ferroan calcite, and siderite. Our main objective was to elucidate the major factors controlling the complex conductivity response at the site. We acquired laboratory complex conductivity measurements along four cores retrieved from the site in the frequency range between 0.001 and 1000 Hz. Our results show the following: (1) in general higher imaginary conductivity was observed for samples from contaminated locations compared to samples from the uncontaminated location, (2) the imaginary conductivity for samples contaminated with residual and free phase hydrocarbon (smear zone) was higher compared to samples with dissolved phase hydrocarbon, (3) vadose zone samples located above locations with free phase hydrocarbon show higher imaginary conductivity magnitude compared to vadose zone samples from the dissolved phase and uncontaminated locations, (4) the real conductivity was generally elevated for samples from the contaminated locations, but not as diagnostic to the presence of contamination as the imaginary conductivity; (5) for most of the contaminated samples the imaginary conductivity data show a well-defined peak between 0.001 and 0.01 Hz, and (6) sample locations exhibiting higher imaginary conductivity are concomitant with locations having higher magnetic susceptibility. Controlled experiments indicate that variations in electrolytic conductivity and water content across the site are unlikely to fully account for the higher imaginary conductivity observed within the smear zone of contaminated locations. Instead, using magnetite as an example of the bio-metallic minerals in the contaminated location at the site, we observe a clear increase in the imaginary conductivity response with increasing magnetite content. The presence of bio-metallic mineral phases (e.g., magnetite) within the contaminated location associated with hydrocarbon biodegradation may explain the high imaginary conductivity response. Thus, we postulate that the precipitation of bio-metallic minerals at hydrocarbon contaminated sites impacts their complex conductivity signatures and should be considered in the interpretation of complex conductivity data from oil contaminated sites undergoing intrinsic bioremediation.

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1. Introduction

Previous studies have suggested the use of geophysical methods as complementary, rapid, cost-effective, and minimally-invasive tools for detecting and monitoring the extent and fate of oil spills in the subsurface (Atekwana and Atekwana, 2010; Atekwana et al., 2004a; Che-Alota et al., 2009; Werkema et al., 2003). In our arsenal of geophysical tools,

complex conductivity has been suggested as a technique with high sensitivity to the presence of contaminants (Börner et al., 1993; Flores Orozco et al., 2012; Kemna et al., 2004; Olhoeft, 1985; Revil et al., 2011; Schmutz et al., 2010, 2012; Vanhala et al., 1992) as well as accompanying bio-physicochemical processes associated with hydrocarbon biodegradation (Abdel Aal et al., 2004, 2006). Nonetheless, the interpretation of complex conductivity data from field sites undergoing active microbial degradation remains challenging partly because several factors may contribute to the observed complex conductivity response including for instance the

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effect of the pore water composition and conductivity, temperature, the cation exchange capacity of the minerals, the presence of bacteria, non-wetting phases, and metallic particles.

The presence of oil stimulates microbial activity, resulting in biophysicochemical changes induced in the subsurface during the biodegradation of hydrocarbons by microbes (Cassidy et al., 2002; Cozzarelli et al., 1994, 2001). Microbes provided with an organic carbon source and nutrients can result in (1) an increase in cell density and the formation of biofilms on the grain surfaces and between pore openings in rocks and sediments that induce physical changes in the porous material itself (Abdel Aal et al., 2010; Atekwana and Atekwana, 2010; Atekwana and Slater, 2009; Clement et al., 1996; Thullner et al., 2002) and (2) the production of organic and carbonic acids that enhance the weathering of aquifer solids causing an increase in the surface roughness of the mineral grains and the ionic strength of the pore water (Abdel Aal et al., 2006; Atekwana et al., 2004b).

The presence of terminal electron acceptors (TEA's) governs nutrient utilization by microbes during the breakdown of organic carbon (Bekins et al., 2001; Cozzarelli et al., 2001). TEA's are sequentially utilized from O_2 , NO_3^- , Fe(III), Mn (IV), SO_4^{2-} , and CO_2 . Some iron(III)-reducing microorganisms can use hydrocarbons as a carbon source to reduce iron(III) to Fe(II) (Lovley et al., 1989). When hydrocarbon biodegradation is coupled to iron reduction it can lead to the formation of ferrous biominerals such as magnetite (Lovley et al., 1987; Rijal et al., 2010), pyrite (Prommer et al., 1999), ferroan calcite (Baedecker et al., 1992) and siderite (Tuccillo et al., 1999). For example, magnetite can be formed through either biologically induced (abiotic) mineralization or biologically controlled (biotic) mineralization. In the biologically induced mineralization magnetite can be nucleated and grow abiotically by chemical reactions involving byproducts as a result of biotic metabolic activity, while during biologically controlled mineralization, magnetite can be synthesized at a specific location within or on the cell (Bazylnski and Frankel, 2003). Following these two pathways, iron(III) can be converted to iron(II), then magnetite can be precipitated either by nucleation or growth that is controlled by ferrous iron concentration and/or pH (Hansel et al., 2005).

In several recent studies, magnetic susceptibility data from hydrocarbon contaminated sites have documented zones of enhanced magnetic susceptibility within the smear zone coincident with the free phase hydrocarbon plume (Mewafy et al., 2011; Rijal et al., 2010, 2012). In these studies, magnetite was documented as the dominant mineral within the

enhanced zone of magnetic susceptibility, suggesting biomineralization due to iron reduction. This raises an important question regarding the contribution of bio-metallic mineral phases such as magnetite to the complex conductivity response at hydrocarbon contaminated sites.

In this study, we acquired laboratory complex conductivity measurements on core sediments retrieved from a hydrocarbon contaminated site where hydrocarbon biodegradation has been extensively documented. Additionally, we conducted several controlled experiments simulating the field conditions to aid interpretation of our results. Our specific objective was to elucidate the major factors controlling the complex conductivity response at hydrocarbon contaminated sites undergoing biodegradation.

2. Site history

The National Crude Oil Spill Fate and Natural Attenuation Research Site at Bemidji, MN (Fig. 1) is a natural laboratory available for investigating bio-physicochemical processes associated with the intrinsic bioremediation of a crude oil spill (Cozzarelli et al., 2001; Eganhouse et al., 1993). In August 1979, a high pressure crude oil pipeline ruptured, releasing 1,700,000 L of crude oil. Oil pooled in low-lying areas (~2000 m²) over a total area of 6500 m² (Fig. 1). According to Essaid et al. (2011), a maximum oil saturation of 0.74 was measured in the down gradient part of the oil body with a smear zone (dominated by residual and free phase hydrocarbon) extending more than 2 m around the water table with ~1 m seasonal fluctuation. This smear zone can be divided into lower and upper parts located below and above the water table elevation, respectively. The time averaged water table is observed at approximately 8 m below land surface (Delin and Herkelrath, 1999).

The site geology consists of pitted sand and gravel outwash and moderately calcareous silty sand (about 20 m thick) and outwash glacial deposits overlying clayey till of unknown thickness (Bennett et al., 1993). The site has been the focus of intensive geochemical (Cozzarelli et al., 2010) and microbiological studies (Bekins et al., 2001). The uncontaminated groundwater is aerobic with dissolved oxygen concentrations between 8 and 9 mg/L, dissolved organic carbon of 2.8 mg/L as C, and low levels of nitrate at 44.8 µg/L as N₂ and sulfate at 2.9 mg/L (Bennett et al., 1993).

Geochemical and microbial studies suggest that iron reduction is an important terminal electron acceptor process occurring within the anaerobic plume (e.g., Baedecker et al., 1993). In addition, iron-reducing

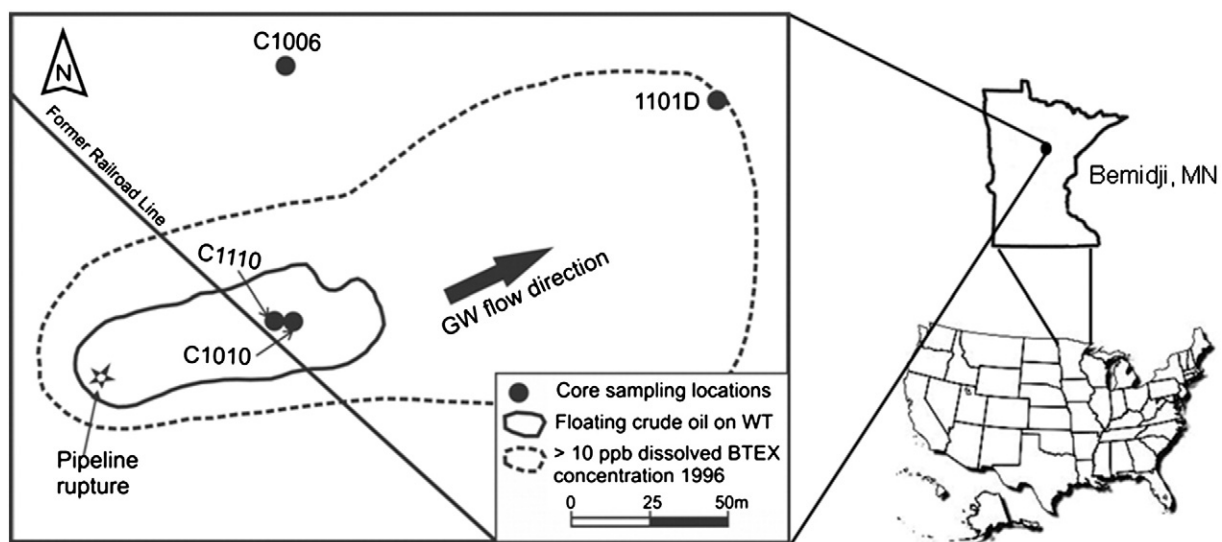


Fig. 1. Plan view of the Bemidji oil spill site showing locations of the cores retrieved from the free phase plume (C1010 and C1110), dissolved phase plume (1101D) and uncontaminated (C1006).

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