Journal of Contaminant Hydrology 108 (2009) 89–106

Contents lists available at ScienceDirect

Journal of Contaminant Hydrology

journal homepage: www.elsevier.com/locate/jconhyd

A detailed field-based evaluation of naphthenic acid mobility in groundwater

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ARTICLE INFO

Article history:
Received 15 February 2008
Received in revised form 2 June 2009
Accepted 19 June 2009
Available online 30 June 2009

Keywords:
Naphthenic acid
Groundwater
Arsenic
Oil sand

ABSTRACT

An anaerobic plume of process-affected groundwater was characterized in a shallow sand aquifer adjacent to an oil sands tailings impoundment. Based on biological oxygen demand measurements, the reductive capacity of the plume is considered minimal. Major dissolved components associated with the plume include HCO_3, Na, Cl, SO_4, and naphthenic acids (NAs). Quantitative and qualitative NA analyses were performed on groundwater samples to investigate NA fate and transport in the subsurface. Despite subsurface residence times exceeding 20 years, significant attenuation of NAs by biodegradation was not observed based on screening techniques developed at the time of the investigation. Relative to conservative tracers (i.e., Cl), overall NA attenuation in the subsurface is limited, which is consistent with batch sorption and microcosm studies performed by other authors. Insignificant biological oxygen demand and low concentrations of dissolved As ($<10\ \mu g\ L^{-1}$) in the plume suggest that the potential for secondary trace metal release, specifically As, via reductive dissolution reactions driven by ingress of process-affected water is minimal. It is also possible that readily leachable As is not present in significant quantities within the sediments of the study area. Thus, for similar plumes of process-affected groundwater in shallow sand aquifers which may occur as oil sands mining expands, a reasonable expectation is for NA persistence, but minimal trace metal mobilization.

1. Introduction

The Athabasca Oil Sands deposit (Alberta, Canada) is a vast resource, with crude oil reserves of 174 billion barrels (Government of Alberta, 2006). Oil sand in its natural state is a combination of mineral matter (sand with some silt and clay), connate water and bitumen. After stripping surficial materials, the oil sand is mined and the bitumen is separated from the oil sand based on the Clark hot water process or a variation of this method, involving aeration while mixing with warm water and a caustic agent (e.g. NaOH; Schramm et al., 2000). Using this method, the production of 1 m^3 (6.25 US barrel) of bitumen yields approximately 16 m^3 of water saturated mineral matter, collectively referred to as tailings (Scott et al., 1985).

Currently, oil sand mining operations maintain saturated tailings onsite in abandoned open pit mines or in above grade tailings impoundments constructed using sand-based dykes. These dykes are constructed by hydraulic emplacement of saturated tailings. Seepage plumes which may form adjacent to tailings impoundments are thought to originate from drainage of the fluid phase of these tailings used in construction of the dykes (e.g., Ferguson et al., 2009). Within the tailings impoundment, the fluid phase of tailings is believed to be largely contained by the presence of fine grained tailings which settle at the bottom, and bitumen mats which form on the sides of the impoundment (Ferguson et al., 2009). MacKinnon (1989) provides a more detailed description of

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doi:10.1016/j.jconhyd.2009.06.003

the construction and layout of oil sand tailings impoundments. The fluid phase consists mainly of a mixture of oil sand connate water, relatively fresh river water, and recycled process water, containing caustic (NaOH) in addition to other process aids (e.g., SO_4-based additives used for water treatment) used during the extraction process (MacKinnon, 1989; Kasperski, 1992), and are herein termed process waters. Processing also enhances the concentrations of SO_4, Na and alkalinity, the latter two derived from the caustic addition (Schramm et al., 2000).

The primary source of aquatic toxicity in process water is a complex mixture of methyl substituted, aliphatic and cycloaliphatic organic acids termed naphthenic acids or NAs (MacKinnon and Boerger, 1986). NAs have the general chemical formula $C_nH_{2n+Z}O_2$, where n refers to the number of carbon atoms, and Z is a negative number that refers to the hydrogen atom deficiency caused by ring formation (Holowenko et al., 2002). Scott et al. (2008) indicates that hydroxy-NAs with the general chemical formula $C_nH_{2n+Z}O_3$ also form a significant portion of the mixture. To date, the study of the environmental properties of NAs has focused on the collective mixture of $C_nH_{2n+Z}O_2$ and $C_nH_{2n+Z}O_3$, herein referred to as NAs. No information exists on the relative fate and transport, or toxicity of these two types of NAs. NAs are ubiquitous in petroleum deposits, but are of particular concern in the case of oil sands tailings, as they become concentrated in the process waters during bitumen extraction (Schramm et al., 2000), in part due to dissociation of NAs at circumneutral pH into anions of high solubility and low volatility (Headley and McMartin, 2004; Clemente and Fedorak, 2005). NAs are common constituents of oil sand, such that concentrations of a few mg L^{-1} may naturally occur in surrounding surface water bodies (Schramm et al., 2000). With the exception of NAs, other organic compounds are generally present only in trace quantities or below detection limits within the tailings water (MacKinnon, 1989).

To date, much of the research regarding the environmental fate of naphthenic acids (NAs) has been restricted to surface water (MacKinnon and Boerger, 1986) or laboratory investigations (Herman et al., 1993, 1994; Lai et al., 1996; Zou et al., 1997; Headley et al., 2002; Holowenko et al., 2001; Peng et al., 2002; Clemente et al., 2003, 2004; Gervais, 2004; Scott et al., 2005; Marsh 2006). Thus far, numerous laboratory microcosm experiments have demonstrated some degree of aerobic degradation of NAs extracted from oil sand process water (Herman et al., 1994; Clemente et al., 2003; Gervais, 2004; Bataineh et al., 2006). However, attempts at stimulating anaerobic degradation of these same NAs in the lab have been unsuccessful (Holowenko et al., 2001; Gervais, 2004).

Only two studies of NAs in groundwater have been reported. MacKinnon et al. (2004) describes the attenuation of NAs and inorganic components present in process-affected groundwater based on water samples collected from surface water bodies and groundwater discharge from hillsides near tailings impoundments. Decreases in NA concentration were mirrored by a decrease in the relative abundance of lower-molecular weight NAs and Microtox toxicity, characteristic of NAs which have undergone aerobic biotransformation (Clemente et al., 2004). Gervais and Barker (2004) and Gervais (2004) assessed three NA plumes at a screening level. They reported significant decreases in NA concentrations due to dispersive dilution at all three sites, but evidence for significant attenuation by sorption was not found. However, one of the plumes, consisting of NAs solubilized from a natural oil sand source, showed decreases in the relative abundance of lower molecular weight NAs coupled with a decreased ratio of NA to Cl near the leading edge of the plume, suggesting aerobic biodegradation. Of the two remaining plumes, one plume showed decreased NAs:Cl ratios near the base of the plume coupled with decreased SO_4 concentrations and the occurrence of $CH_{4(aq)}$, suggesting anaerobic biotransformation of NAs might have occurred (Gervais and Barker, 2004). However, definitive confirmation of anaerobic degradation was not possible, as detailed (qualitative) NA analysis was unavailable. Because groundwater samples were collected with the Waterloo profiling tool (Pitkin et al., 1999), data regarding hydraulic gradients and hydraulic conductivity were unavailable, and developing an adequate understanding of the physical hydrogeologic system was not possible. In addition, groundwater samples had not been collected near the leading edge of the plume, where aerobic biodegradation reactions would be most likely to occur.

The current study was initiated to more completely delineate the plume of process-affected water, incorporating physical hydrogeologic data (i.e., hydraulic conductivity and water level measurements), and a more complete assessment of biogeochemical conditions. The primary objective was to clarify the potential for anaerobic biodegradation of NAs as suggested by Gervais and Barker (2004).

As a secondary objective, this study evaluates the potential for trace metal mobilization by migration of moderately reduced, process-affected water into aquifers adjacent to oil sands tailings impoundments. Specifically, the potential for As mobilization has been evaluated in this publication. Such adverse secondary effects of reducing conditions have been noted previously. For example, reductive dissolution of Fe-(oxy)hydroxides has been suggested as a cause of elevated As concentrations in groundwater of Bangladesh (e.g. Harvey et al. 2002). Keimowitz et al. (2005) and deLemos et al. (2006) also attributed elevated dissolved As concentrations in landfill leachate plumes to reductive dissolution reactions. In laboratory batch studies, the release of As has been noted upon the addition of an organic carbon source to sediments containing Fe (oxy)hydroxides (e.g. Bennett and Dudas, 2002). Furthermore As desorption may be favoured due to the elevated bicarbonate concentrations characteristic of the process waters (Smedley et al., 2005; Appelo et al., 2002).

To improve the understanding of the geochemical processes which may affect NA and As behaviour, the redox state, potential electron acceptors, general aqueous organic geochemistry, and general inorganic and metal geochemistry of the aqueous and solid phases were examined. This included selective extractions designed to characterize metal availability and distribution within the solid phase. These data allow us to assess the potential for metal release by desorption or dissolution.

2. Methods

2.1. Drilling and coring

Six locations were selected, and at each location, groundwater was sampled from various depths (Figs. 1 and 2).