

## The roles of water in subsurface petroleum biodegradation-Part 1 The role of water radiolysis.

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### Abstract

Water plays many roles in subsurface petroleum biodegradation including that of reactant and nutrient carrier. Water may also play a more subtle role and in this paper we review the possible role of water as a source of radiolytic oxygen species. We review studies of biodegradation rates in severely biodegraded oil reservoirs in China and Alberta showing that at PM 5-8 levels of severe biodegradation seen in parts of the oil sands, net biodegradation fluxes drop by an order magnitude or more compared to biodegradation fluxes in light oil reservoirs (PM 1-3). In an Albertan oil sands reservoir, the oil column exhibits systematic gradients in oil physical properties and hydrocarbon composition, and showed variations in biodegradation level throughout the reservoir consistent with the notion that the biodegradation of oil is focussed in a bioreactor zone at the base of the oil column.

The highest bacterial abundance and geochemical gradients in the reservoir define a zone near the oil water contact as likely the most active in terms of biodegradation. This is consistent with abundant water being a necessary component for an actively biodegrading petroleum column and we review the roles water, in the oil leg and transition zone, plays in these reservoirs as reactant, nutrient carrier, waste product remover and even as a source of reactive oxygenic species. We examine the extent of possible radiolytic oxygen species generation from water in heavy oil reservoirs, using literature, models and experiments and conclude that plausible radiolytic oxygen generation rates in reservoirs could not account for any significant fraction of subsurface oil biodegradation rates (<1% of biodegradation), even with very degraded oils biodegrading at the low net rates found in the Canadian oil sands. Radiolytic derivitisation of hydrocarbons (addition of oxygen), to make functionalised species may however occur and we discuss how significant that may be. Overall we would not expect under typical conditions, radiolytic processes to be a major factor in subsurface biodegradation. However, because of the much larger growth yields of aerobic hydrocarbon degraders compared to anaerobic hydrocarbon degraders even small amounts of endogenously generated oxygen could have an impact on the composition of microbial communities in biodegraded/biodegrading petroleum reservoirs.

### Introduction

The relationship between heterogeneous petroleum composition in heavy oilfields and petroleum biodegradation caused by biological action in reservoirs, has been qualitatively well known for many decades. The details of the organisms, the spatial relationships between the biological, physical and chemical processes involved and the timescales of in reservoir petroleum biodegradation have however, remained mysterious until the last decade or so. Perhaps the most important discovery in heavy oil petroleum geology was the observation by Zengler et al (1999), that alkanes can be directly biodegraded anaerobically, using water as a co-reactant. Similar anaerobic processes have now been established as active in many heavy oilfields and oil sands reservoirs (Jones et al, 2008). Observations of the resulting systematic vertical and lateral compositional and fluid property gradients in

biodegrading oilfields are now well described as are their impacts on fluid properties such as oil viscosity (Larter et al, 2006; 2008). Such in-reservoir chemical gradients were used to establish the timescales and average rates of biodegradation and suggest that the gradients indicate biodegradation takes place over long geological timescales with the process taking millions, to tens of millions of years to degrade up to 50% or more of a light oil accumulation (Head et al, 2003). With the rates of biodegradation decreasing through time, as oils become more degraded and more reactive fractions are lost, much of the biodegradation of Albertan heavy oil and oil sands reservoirs occurred at depths much greater than today where surface driven water movements were much more restricted.

Water is a reactant in the methanogenic biodegradation process occurring in many heavy oilfields (MADCOR-Jones et al, 2008), and also carries nutrients needed for life. Water may also be important in removing inhibitors to biological processes and thus may play secondary roles in controlling life in petroleum reservoirs. While water is present both within and below the oil leg of a typical oil accumulation, the geochemical gradients commonly seen and numerical models of oil degradation (Larter et al, 2006; Adams et al, 2012), suggest that petroleum biodegradation takes place predominantly at oil water contacts or in transition zones rather than within the oil leg itself even though water (even mobile water!), is present in the oil leg itself. Recent investigations of the location of microorganisms within heavy oil reservoirs confirms that microorganisms are located predominantly near the oil water contacts (Bennett et al, 2013). Here, we describe these new results, plus we expand on the nature of the petroleum reservoir biome and the role of water in petroleum reservoir processes, reviewing recent advances understanding the extent and role of radiolytic oxygen species generation in supporting the petroleum reservoir biome.

## Results and Discussion

We summarise a recent unique, combined geochemical, geological and microbiological analysis of an actively biodegrading Albertan heavy oil reservoir (Bennett et al, 2013). The reservoir properties associated with the cored vertical well are characterised by a 15.75 m thick oil column and a 8.75 m zone of steadily decreasing oil saturation below the oil column, referred to as the oil-water transition zone (OWTZ), grading down into a thin water leg. The oil column exhibits systematic gradients in oil physical properties and hydrocarbon composition, and shows variations in biodegradation level throughout the reservoir consistent with the notion that the biodegradation of oil is focussed in a bioreactor zone at the base of the oil column. Different compound classes decreased to levels below their detection limit at different depths within the OWTZ, defining a likely bioreactor extent of over 5 meters in depth with, for example, *n*-alkanes being reduced to their detection limit concentration at the bottom of the oil column/top of the OWTZ, while branched isoprenoid alkanes were not completely degraded until well into the OWTZ.

The highest bacterial abundance and geochemical gradients of, for example, methylphenanthrene biodegradation define a zone near the oil water contact as likely the most active in terms of biodegradation. This is consistent with abundant water being a necessary component for an actively biodegrading petroleum column and we review the roles water in the oil leg and transition zone plays in these reservoirs. One of the most surprising features of the reservoir biome is that the most biologically active zone in the reservoir contains abundant organisms related to *Pseudomonas* spp, organisms known for their metabolic versatility which are known to degrade a wide range of aliphatic and aromatic hydrocarbons and xenobiotics but which often function as aerobes or use nitrate as an electron acceptor. Head et al (2012) however, suggest that these organisms may be functioning anaerobically and anaerobic activity by *Pseudomonas* spp has been reported by Budwill (2011) in anaerobic methanogenic coal biodegradation microcosms. In this context then, we examine the geochemical constraints of biological models of oil biodegradation and in particular look at the possible role of water radiolysis as an oxygen source for the reservoir biome.

The bulk, molecular and gas geochemistry (very dominant methane and minor CO<sub>2</sub> in produced gases), of the Albertan heavy oil fields (Adams, 2008), shows the carbon isotopic signatures of associated carbon dioxide in equivalent reservoirs are much heavier ( $\delta^{13}\text{C}$  CO<sub>2</sub> of -10 to +20 per mil typically- Jones et al, 2008) than that expected by direct aerobic oxidation of source crude oils for the oil sands. Thus, Exshaw and Gordondale Fm., sourced oils have whole oil  $\delta^{13}\text{C}$  signatures of around -30 to -31 per mil (Adams et al, 2012), and would be expected to produce CO<sub>2</sub> in dominant abundance, with a similar carbon isotopic signature to the source oils if the oil sands were dominantly produced by aerobic biodegradation. Thus the gas geochemistry of the heavy oils and oil sands is not consistent with aerobic biodegradation being overall a very significant formative process. The dominant methane, subordinate CO<sub>2</sub> and often very heavy carbon isotopic signatures of the CO<sub>2</sub> observed in heavy oils and oil sands reservoirs, is consistent with anaerobic and specifically methanogenic processes. Low levels of oxygen may however be produced insitu by natural gamma ray radiolysis of formation waters and we examine to what extent this process may be important in initial derivitisation of crude oil molecules to possibly aid in subsequent anaerobic biodegradation.

The occurrence of a “cryptic” subordinate aerobic community, which uses in situ generated oxygen, is theoretically possible and because microorganism growth yields on oxygen are about an order of magnitude higher than growth yields from methanogenesis, even a small amount of in situ generated oxygen could lead to significant “aerobic populations” in sampled biomes even if anaerobic processes were quantitatively more important for the overall geochemical processes. If this were the case then one must explain how oxygen could be produced at low levels in situ. While very low levels of molecular oxygen ingress with formation waters is not impossible, one possibility is radiolysis of water and even if the amount of oxygen potentially generated cannot account for degradation of a large mass of oil, this could support a cryptic aerobic, microbial population.

Hydrogen from radiolytic splitting of water is likely an important energy source in the deep biosphere (Lin et al., 2005a) and one important, but overlooked, aspect of radiolysis of water is that it not only generates hydrogen but also oxidizing species such as hydrogen peroxide and even oxygen (Bjergbakke et al., 1989) and the quantities of oxygen produced may be comparable to the amounts of hydrogen generated (Draganic, 1991). Abiotic oxidation of organic matter under radiolytic conditions may also be a factor in derivitisation (ie oxygen species addition) of hydrocarbons that would facilitate subsequent biological degradation. Bharati et al (1995) examined the highly uraniferous Late Cambrian Alum shale of Norway and Sweden, showing anomalous oxygen functionality and abundance on organic matter in that unit. This, we speculate, is likely due to radiolytic water mediated oxidation of the organic matter in the shales.

Using petroleum geochemical analyses of oilfields and numerical simulations, we review our studies of biodegradation rates in severely biodegraded oil reservoirs in China and Alberta showing that at PM 5-8 levels of biodegradation, net biodegradation fluxes drop by an order magnitude or more compared to biodegradation fluxes in light oil reservoirs which might thus favour a role of radiolytic oxygen species as a factor in in-reservoir biodegradation. We examine the extent of possible radiolytic oxygen species generation in heavy oil reservoirs using literature, models and experiments and conclude that plausible radiolytic oxygen generation rates in reservoirs could not account for any significant fraction of subsurface oil biodegradation rates (<1% of net oil biodegradation), even with very degraded oils biodegrading at low net rates, such as found in the Canadian oil sands. Radiolytic derivitisation of hydrocarbons (addition of oxygen), to make functionalised species may however occur and we discuss how significant that may be for in- reservoir processes. Overall we would not expect, under typical conditions, radiolytic processes to be a major factor in subsurface oil biodegradation even though radiolytic hydrogen may be important for deep biosphere sustenance in other deep geological settings (Lin et al, 2005).

## Conclusions

In an Albertan oil sands reservoir, the oil column exhibits systematic gradients in oil physical properties and hydrocarbon composition, and showed variations in biodegradation level throughout the reservoir consistent with the notion that the biodegradation of oil is focussed in a bioreactor zone at the base of the oil column, the bioreactor extent being over 5 meters in depth. The highest bacterial abundance and geochemical gradients define a zone near the oil water contact as likely the most active in terms of biodegradation. This is consistent with abundant water being a necessary component for an actively biodegrading petroleum column. We review the roles water, in the oil leg and transition zone plays in these reservoirs as reactant, nutrient and electron acceptor carrier and even as a source of reactive oxygenic species. Overall we would not expect under typical conditions, that in-reservoir radiolytic processes would be a major factor in subsurface biodegradation.

## Acknowledgements

We thank the BACCHUS 3 biodegradation consortium (Anadarko, Petrobras, BG-Group, ConocoPhillips, Shell, and Total) for support and discussions. The industrial sponsors of Bacchus 1 and 2 are also thanked for sustained support. We acknowledge support from the Canada Research Chairs, CFI, NSERC, Carbon Management Canada, Canada Genome and NERC. Gerrit Voordouw is thanked for many stimulating discussions.

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