

# An Initial Evaluation of Some Biogeochemical-engineering Routes to Carbon Management

Steve Larter, Ian Gates, Jennifer Adams<sup>1</sup>. Dept of Geosciences, University of Calgary, Canada [slarter@ucalgary.ca](mailto:slarter@ucalgary.ca) <sup>1</sup>-present address. ConocoPhillips, 600 N Dairy Ashford, Houston, TX. and Ian Head, Newcastle University, Newcastle upon Tyne, , UK

## Summary

Popular carbon management strategies focus in part, on removal of CO<sub>2</sub> from flue gas streams or even from the atmosphere to subsurface storage. Alternative approaches to climate change mitigation, which effectively convert degradable biomass to inert carbon, radiate the sun's energy back into space or sequester CO<sub>2</sub> into solid form, may also have merit. In this paper we present initial scoping studies for three possible alternative biogeochemical-engineering carbon management schemes suggested by observations from our studies of petroleum systems and fossil fuel energy recovery systems. We evaluate the feasibility of recovering hydrogen, instead of oil, directly from oilfields undergoing natural biodegradation processes and we also examine the feasibility of using a related process, biologically assisted carbon capture and conversion of CO<sub>2</sub> to methane, via H<sub>2</sub> + CO<sub>2</sub> methanogenesis in the hydrogen-rich environments of weathering subsurface ultrabasic rocks, as a route to recycle carbon dioxide in flue gases as methane. We also cautiously examine the use of restricted portions of forests to produce, at very large scale, functionalized, biologically refractory water soluble carbon compounds, similar to oceanic dissolved organic matter, that would survive as stable inert carbon sequestration materials. We look at some of the engineering, energy and geochemical barriers to the feasibility of these possible technology routes. While rapid, substantial carbon emissions reductions are by far the desired course of action, we feel prudent scoping of potential alternative routes, some of which will inevitably be risky is however desirable.

## Introduction

Low carbon emission energy sources are urgently needed to support and develop society in a sustainable manner. The timescales of new C-neutral technology deployment, however, dictate that fossil fuel carbon will be burnt for decades as energy requirements of the global population continue to rise. Against this scenario play the conflicting demands of rapidly mitigating human impacted climate change and Homo sapiens penchant for business as usual, despite evident dangers! Currently our response to the challenge of decarbonizing the atmosphere has been limited, thus some have suggested that in addition to renewable energy alternatives and immediately pursuing strategies such as carbon capture and storage(CCS) and carbon efficient energy recovery and processing(CERP), large scale management of atmospheric carbon budgets or incident solar radiation via geoengineering should be cautiously researched as a precaution (Shepherd et al., 2009 for a review). Carbon management geoengineering has focused, among other areas, on large scale air capture systems (Keith et al., 2005) or accelerated mineral carbonation processes (Lackner et al., 1997). These both require large scale air capture facilities or large scale mining activities.

Shepherd et al(2009) subdivides geoengineering methods into two categories, emphasizing the uncertain nature of the technologies, their risks and effects as below:

1. Carbon Dioxide Removal (CDR) techniques remove CO<sub>2</sub> from the atmosphere, addressing the root cause of climate change and have comparatively low uncertainties and risks. However, these techniques work slowly to reduce global temperatures and must be deployed on a very large, global scale to make a sufficient impact.
2. Solar Radiation Management (SRM) techniques address rising global temperatures by reflecting a small percentage of the sun's light and heat that enters the Earth's atmosphere back into space. These methods could be effective on short time scales in lowering global

temperatures quickly in the event of a catastrophic climate change event but do not address other factors related to rising CO<sub>2</sub> levels (oceanic pH changes etc). Shepherd et al (2009) suggest that CDR approaches are preferred as a solution if sensible, available carbon management strategies are not quickly implemented to curb increasing CO<sub>2</sub> concentrations.

Much research has focused on converting CO<sub>2</sub> capturing biomass (plants) to an inert storable carbon form (e.g., biochar) or storing CO<sub>2</sub> or other form in the subsurface (e.g., CCS) to reduce atmospheric CO<sub>2</sub> content. One proposed route that reduces release of CO<sub>2</sub> into the atmosphere is recycling captured carbon dioxide through a process that reduces it to back to a fuel such as methane or other hydrocarbons using carbon neutral hydrogen as suggested by Zeman and Keith (2008) and Larter et al. (2007). Here, we discuss the feasibility of three unproven processes suggested by our studies of biodegrading oils that might limit growth of atmospheric CO<sub>2</sub>: i) acceleration of hydrocarbon biodegradation to recover hydrogen rather than hydrocarbons, ii) subsurface injection of CO<sub>2</sub> into naturally hydrogen-rich reservoirs and iii) conversion of biomass into storable, inert, functionalized water soluble organic compounds.

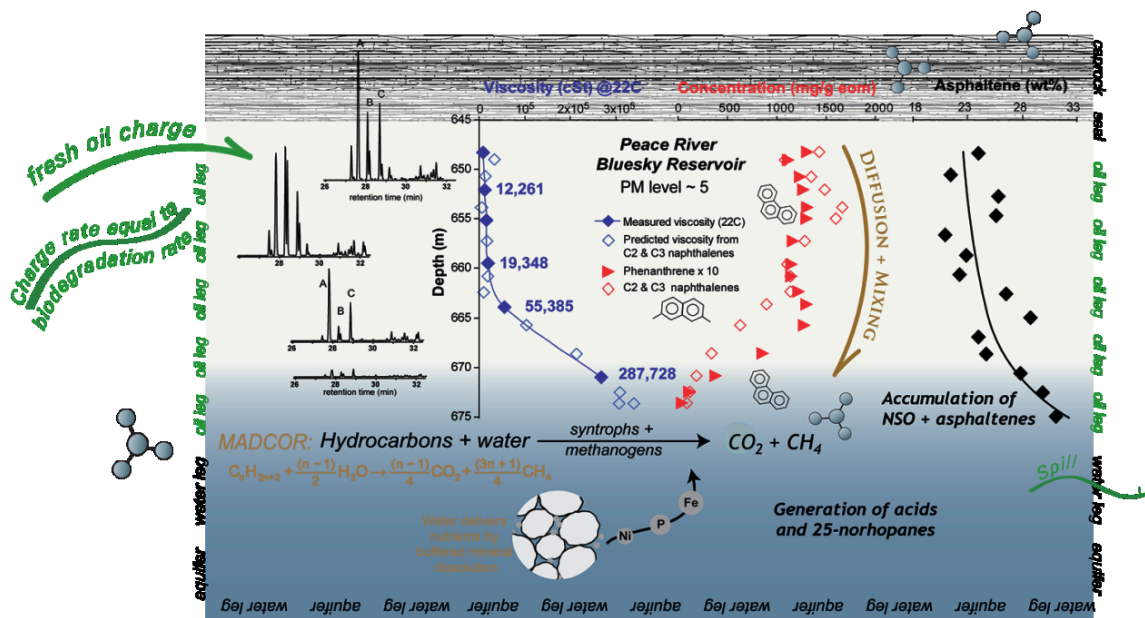


Figure 1. Carbon cycling processes in biodegrading deep subsurface petroleum reservoirs

## Methods: Recovery Processes

### i) acceleration of natural biodegradation of hydrocarbons to recover intermediate hydrogen:

Recent research into subsurface microbial ecology has shown that CO<sub>2</sub> utilizing methanogens, which convert CO<sub>2</sub> with hydrogen to methane, are found in significant proportions throughout the subsurface (Head et al, 2003). For instance, anaerobic biological conversion of liquid petroleum hydrocarbons to methane in oil reservoirs (methanogenesis), on geological timescales, occurs through biological action by syntrophic bacteria and methanogenic archaea at temperatures as low as 12°C, albeit at slow rates naturally (Head et al., 2003; Jones et al., 2008). Most of the hydrogen from the degrading hydrocarbons and water pass, through a molecular hydrogen intermediate and this is manifested in petroleum reservoirs as the Methanogenic Alkane Degradation Dominated by CO<sub>2</sub> Reduction (MADCOR) process (Figure 1). If the process could be significantly accelerated, with hydrogen recovered and CO<sub>2</sub> remaining dissolved or precipitated in situ, this greener recovery process may generate hydrogen or methane as a significant energy recovery vector. This process could be quickly implemented by using existing oil and gas industry infrastructure. Unfortunately, it has been shown that the thermodynamic window in which active hydrogen generation occurs limits it to conditions of low hydrogen partial pressure (Dolfing et al., 2008), so dynamic material circulation

is required for effective hydrogen recovery. We conclude this will be very difficult to achieve. As all produced hydrogen is consumed during methanogenesis, injection of additional CO<sub>2</sub> into oilfields doesn't result in additional methane production and CO<sub>2</sub> consumption.

*ii) subsurface injection of CO<sub>2</sub> into naturally hydrogen-rich ultrabasic rocks:* If natural hydrogen-rich reservoirs that host methanogens could be found, then, injection of CO<sub>2</sub> from an industrial process or from air capture would result in conversion to methane which could then be recovered for fuel use (Larter et al., 2007). Excess hydrogen at low concentration is commonly found in weathering basic and ultrabasic rocks, being produced in the subsurface by reactions of Fe II bearing minerals with water (Sherwood Lollar et al., 2007). In some rare natural accumulations of produced gas associated with such bodies, significant quantities of isotopically depleted hydrogen are found (Coveny et al., 1987). We discuss the concepts and show simulations from a dual-permeability system i.e. a reservoir with low matrix permeability and significant fracture permeability. We examine the geochemical and engineering feasibility of injecting carbon dioxide into microbially active hydrogen enriched hard rock environments and recovery of produced methane as a potential carbon recycling strategy and conclude that it would be very difficult to do on any large scale but may have local value.

*iii) conversion of degradable biomass into biogeochemically inert polycyclic heteroatomic hydrocarbons soluble in water:* Storage of carbon dioxide in the subsurface via CCS is a major planned component, typically 1/3<sup>rd</sup>, of most countries carbon management strategies at 2050 yet the rise of CCS NIMBYism in N.America and Europe may yet slow progress even if technical issues are overcome. Alternate, non CO<sub>2</sub> carbon storage vectors are possible, if energetically more difficult to manufacture and offshore disposal reservoirs may need to be very cautiously relooked at too. Our studies of biodegraded crude oils show that severely biodegraded crude oil becomes more enriched in non-hydrocarbons of high molecular weight with a dominance of polycyclic heteroatomic species present. Surface seeped crude oils, either to the seafloor or onshore, are degraded subaerially or in marine environments and the compounds that are most resistant to degradation may persist in the ocean as representatives of severely biodegraded oils such as might occur during long term degradation of seeped oil. Recent advances in Fourier Transform Mass Spectrometry (FTMS) suggest that functionalized polycyclic aromatic species may dominate these severely degraded oils and Dittmar et al. (2009), suggest that these thermogenically derived oil compounds are found as dissolved organic matter (DOM) in the oceans and may represent 1.5-2 wt% of total marine dissolved organic carbon. The global amount of thermogenic DOM in the deep ocean is approximately one Petamole carbon and there may be more capacity for such compounds in the ocean. They also suggest homogenous distributions of thermogenic DOM in the abyssal ocean indicate that polycyclic functionalised DOM behaves as virtually inert material in the abyssal environment. If confirmed this may offer an alternate, if risky route to a large scale high injectivity carbon store.

Accelerated conversion of biodegradable organic material, like sustainable forest and forest floor material, to inert water soluble carbon compounds is at least a conceptual route to sequestration of inert C from the atmosphere. Northern forests, such as the Canadian Boreal Forest are extremely large carbon sinks, storing several hundred billion tons of carbon in forest and peatland ecosystems. Goodale et al., (2002) suggests northern forests and woodlands in the boreal regions provided a total sink for 0.6-0.7 Pg of C per year (during the early 1990s). So, if the not insubstantial risks and uncertain energy balances could be evaluated and mitigated, harvesting half a gigatonne of carbon per year (circa projected Canadian emissions by 2050) for soil or ocean disposal from Canadian forests might be conceptually viable, if very risky and difficult! We quantitatively examine the various process steps necessary to evaluate such a scheme for mitigating atmospheric carbon dioxide content by using forest air capture of CO<sub>2</sub> and large scale conversion of biomass to biogeochemically inert water soluble FRACCC (functionalised, refractory, aqueous compatible carbon compounds), for soil, ocean or subsurface disposal.

## Conclusions and Discussion

Disposal of carbon to the soil and oceans has been considered before and as with land burial of biochar, energy consumption during processing, transport and burial would be large (Shepherd et al., 2009). Mineralization of any biomass derived carbon in the ocean releasing nutrients would potentially cause eutrophication thus inert carbon forms are needed. Land based biomass burial as biochar has been widely discussed and Lehmann *et al.* (2006) quote a potential carbon sink of up to 9.5 Gt C/yr by 2100. Shepherd et al. (2009) suggest that such fluxes assume unrealistic growth in resources devoted to biofuels production, with a large fraction of this carbon being converted to biochar and they suggest this would likely conflict with the use of agricultural land for the production of food and thus this is unlikely to happen.

One hesitates to disturb forests or oceans given their crucial role in planetary ecology but it is prudent, given our situation, to do some basic scoping of whether such systems are feasible or sensible even in an emergency. We therefore, on this very preliminary basis, examine the feasibility and steps needed to convert, in a sustainable manner, forest material to inert water soluble disposable organic material similar to oceanic DOM components. As recommended by Shepherd et al(2009), even small field deployments or large scale testing of any geoengineering technology would of course require prior international regulation and agreements. Of course such drastic strategies would prove unnecessary if sensible quick prudent action to reduce carbon emissions is taken.

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