

Characterisation of Organic Compounds That Could Potentially Leach From Coal under Field-Simulated Conditions during CSG Development

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Abstract

Coal Seam Gas (CSG) is currently being produced from wells in both the Surat and Bowen basins in QLD. In order to desorb target coal seams and extract CSG, significant quantities of coal seam water are being pumped to the surface. CSG operators consistently monitor both the quantity and quality of coal seam water, which is known to have a somewhat consistent geochemical signature (high bicarbonate, high sodium, moderate chloride, low calcium, low magnesium, and very low sulphate concentrations) (Van Voast, 2003). However, individual organic compounds are rarely measured in coal seam water during depressurisation operations, which has made it difficult to fully identify these compounds. Previous studies in the US (Orem et al., 2014; Orem et al., 2007) have identified low concentrations of various organic compounds in coal seam water samples from various US basins, while QLD studies by Stearman et al (2014) and Tang et al (2014) have reported similar results. However, little is known about the origin of these compounds. It is widely accepted that coal contains a number of organic compounds including PAHs, heterocyclic compounds, and aromatic amines (Orem et al., 2007). Therefore, it is hypothesized that groundwater in contact with coal could potentially leach organic compounds from coal units. In 2013, Queensland University of Technology (QUT) carried out a study aiming to test the hypothesis of coal acting as a natural source of organic compounds in coal seams targeted for CSG development. An additional aim of this study was to test whether the coal material itself could act as a sink for organic compounds (e.g. benzene absorption) and determining whether the use of sodium hypochlorite (as a biocide) would induce Trihalomethane (THM) formation.

On a previous study carried out by the USGS (Orem et al., 1999), Balkan coal samples were analysed using Nuclear Magnetic Resonance (NMR) to assess their organic character. In addition, to assess whether these coal samples could release organic compounds, these samples were leached with deionised water (to simulate groundwater leaching). The leachate was analysed using GCMS techniques. A similar study by Stearman et al (2014) has used similar techniques to characterise organic compounds that could potentially leach from Australian coals. The idea behind these experiments is to simulate the water-coal interaction to assess the character of leachable organic compounds from coal. Consequently, the analysis techniques used in the present study focus on coal characterisation (to assess the nature of organic compounds contained in the coal samples) and leachate characterisation (to identify specific organic compounds and their concentrations in aqueous form). Coal samples from exploratory drilled holes were taken from coal cores, supplied by a CSG operator, from well fields in the Surat and the Bowen basins in QLD. These samples ranged from dull brown coal (e.g. lignite A) to brighter bituminous coals (e.g. low volatile bituminous). Traditional coal characterisation techniques (proximate analyses, vitrinite reflectance) in combination with solid Nuclear Magnetic Resonance (NMR) were used to characterise these coal samples. Samples were leached using an adaptation of the Toxicity Characteristic Leaching Procedure (TCLP) in order to characterise the compounds that could leach from coal during water-rock interactions. The leachates were analysed using liquid NMR (for its ability to identify organic compounds) as well as GCMS (for its ability to measure actual concentrations). In addition, Triaxial testing was used to simulate leaching under different pressure and temperature conditions; laboratory batch tests were carried

out with sodium hypochlorite and benzene, to test THM formation and benzene adsorption respectively. The organic analytes of interest were polyaromatic hydrocarbons (PAH), phenolic compounds, total petroleum hydrocarbons (TPH), total recoverable hydrocarbons (THM), monocyclic aromatic hydrocarbons (MAH), and trihalomethanes (THM).

The structural characteristics of Bowen Basin coal samples were analysed using both solid and liquid state (NMR). Results of the Bowen Basin Solid State NMR analysis revealed a strong aromatic peak at about 102 ppm and a less pronounced aliphatic peak at about -0.7 ppm. Consequently, the coal material itself has both aliphatic and aromatic compounds. For the solution state NMR, samples were prepared by suspending the crushed coal in deuterated water (D₂O) at a 1:10 (coal: D₂O) ratio (leached for 16 hours at a constant temperature of 20°C). Solution NMR results (Figure 1) revealed a strong water signal (4.7ppm), which is consistent with water absorbed from the atmosphere by the D₂O used as the leaching medium. The major peaks presented in Figure 1 indicate a strong aliphatic signature (0.5-5.0 ppm) with only one strong aromatic peak at 8.25 ppm. This suggests that, although coal is conformed mainly of aromatic substances, the leaching was only able to extract aliphatic compounds from the coal matrix. Consequently, rather than characterising the coal itself, this technique provides insight into the nature and relative proportions of the potential organic compounds that could leach from the coal material at ambient temperature condition. Figure 1 also shows that lower molecular weight aliphatics are more likely to be extracted from coal using deuterated water as most peaks occur at the lower end of the ppm scale. These results indicate high CH₃ concentrations, which is consistent with various organic compounds having short open chain configurations or organic compounds with several branches. In either case, these organic compounds would have lower molecular weights and higher solubilities than longer chained compounds. In addition, the lack of broad baseline peaks (humps) suggests that there are low concentrations of large molecular compounds in the coaly D₂O extract.

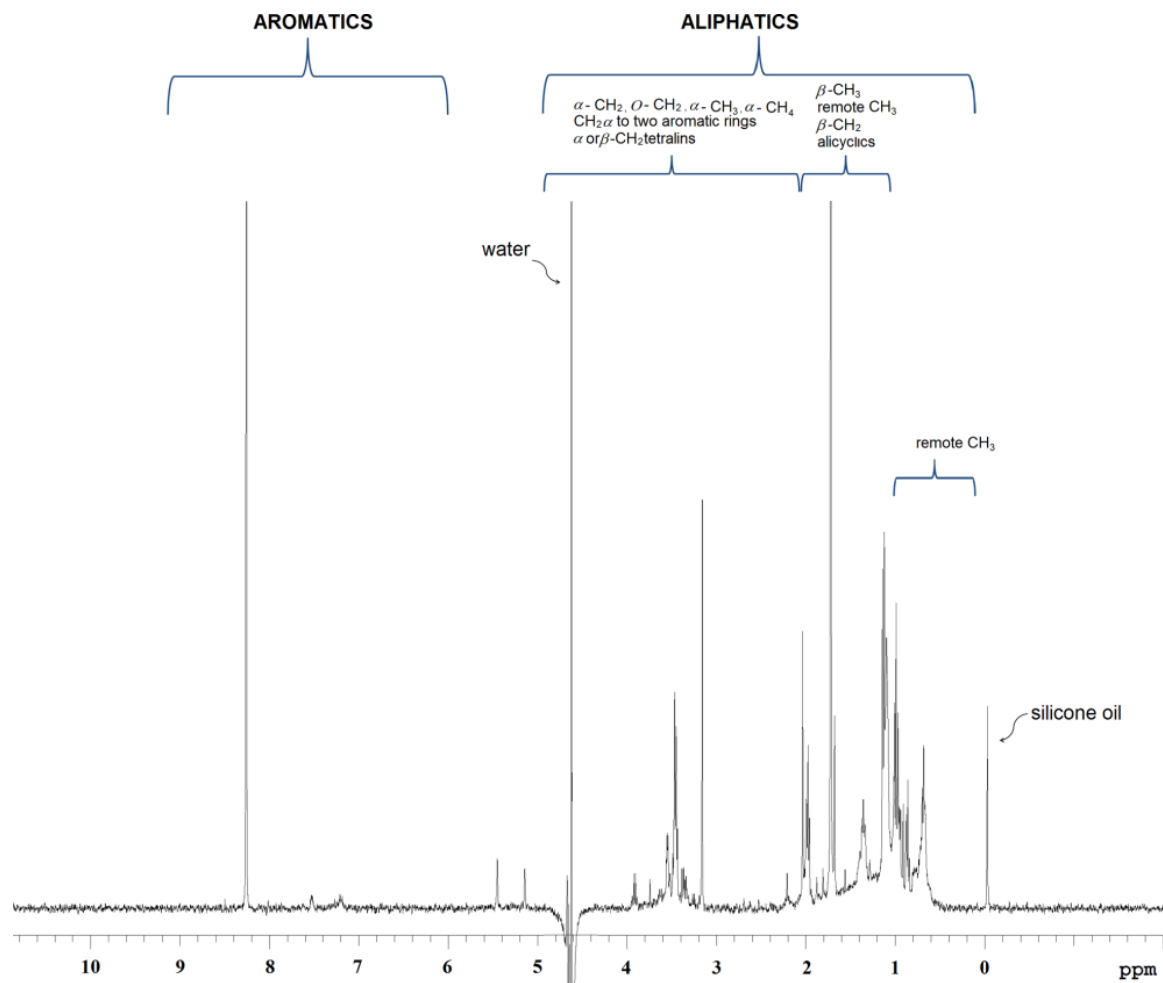


Figure 1. ¹H NMR analysis of Bowen Basin sample leached with deuterated water (T=20°C).

TCLP leaching tests were carried out using crushed coal samples and synthetic coal seam water as the leaching medium. After each test, leachates were filtered and analysed in a certified laboratory. Test results indicate that both MAHs and PAHs occurred at very low concentrations in solutions leached from coal samples at 20°C. Likewise, the Surat coal samples leached benzene at very low concentrations, while one of the Bowen Basin samples leached benzene at a higher concentration. No detections of TPH or TRH occurred with this leaching procedure.

The most commonly detected PAH in this study was naphthalene (leached in 47% of tests) followed by phenanthrene (leached in 28% of tests). Both naphthalene and phenanthrene are PAHs of low molecular weight; conversely, these particular PAHs exhibit some of the highest water solubilities. Higher ringed PAHs were only detected in 2 Bowen Basin samples: one sample leached 4-5 ring PAHs to deionised water at 20 °C and a second sample leached ultra-trace amounts of 4-5 ring PAHs to synthetic coal seam water at 75 °C. These 4-5 ring PAH compounds included fluoranthene and pyrene, chrysene, benzo(b)fluoranthene, and benzo(a)pyrene. As the concentrations of PAHs leached from the coals were low, little trending became apparent other than the number of instances in which the (more soluble) 2-3 ring PAHs were detected over the (less soluble) 4-6 ring PAHs. As a general trend, the solubilities of PAHs will decrease with the addition of aromatic (benzene) rings to the PAH structure, which in turn results in higher molecular weight (Figure 2). Therefore, higher molecular weight PAHs (e.g. benzo[a]pyrene) will be less likely to dissolve in water than the lower molecular weight PAHs (e.g. naphthalene). In general, the 4-6 ring PAHs have very low solubilities but a higher sorption potential (e.g. higher distribution coefficients due to higher K_{ow}) (Figure 2). These properties limit, but do not exclude, concentrations of other PAH compounds in the coal leachates.

Triaxial testing of both intact and reconstituted coal core was carried out at a lithostatic pressure equivalent to 800m, a simulated reservoir temperature of 60°C, and using synthetic coal seam water. Results from these tests revealed low concentrations of benzene and xylenes in the resulting leachate product. These detections occurred in the leachate that had percolated through the reconstituted samples; no detections occurred with the recorded coal samples.

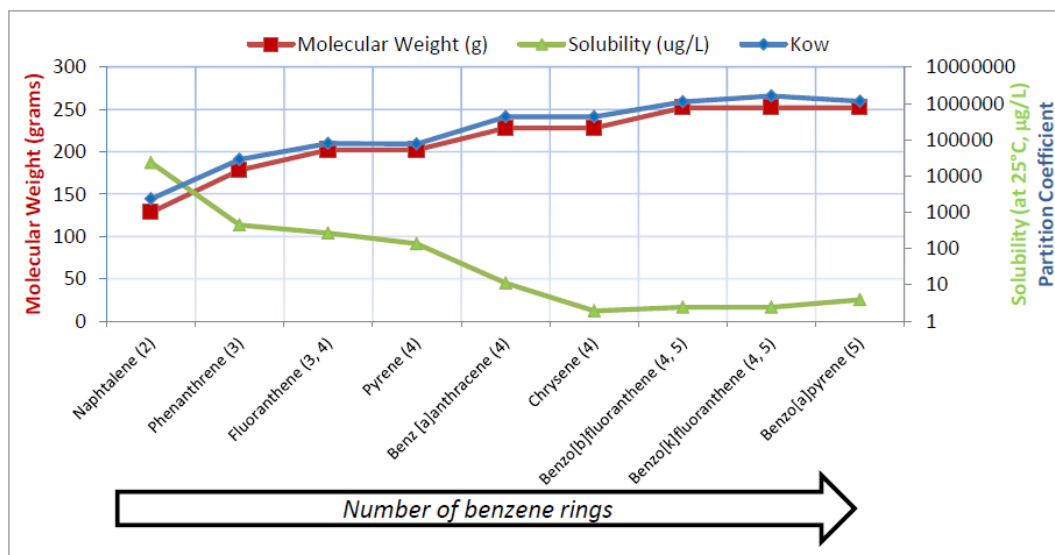


Figure 2. Polycyclic aromatic hydrocarbons (PAHs) detected in leaching experiments presented along their physico-chemical properties. Bracketed numbers next to compound names indicate PAHs with an additional, but not truly aromatic, ring-like structure. The K_{ow} value refers to the octanol/water Partition Coefficient (a measure of the tendency of these chemicals to become absorbed in organic matter).

THMs are common disinfection by-products (e.g. produced in water treatment plants) resulting from the reaction between chlorine and organic matter in solution. Therefore, as it was originally theorised, leaching of coal samples with sodium hypochlorite induced the formation of THM compounds. This suggests that the use of biocides containing sodium hypochlorite (during drilling or hydraulic fracturing operations) may be a potential source of THM formation. However, dilution effects would result in lower THM concentrations because the majority of these THM compounds would be pumped to the surface as flowback water, along with formation water that has not been in contact with the biocides. In addition, the normal procedure for managing flowback water at the surface is to contain it in specially designed containers or reservoirs, and to transport the flowback water to a wastewater treatment facility.

The benzene absorption experiment showed that sub bituminous coal from the Surat Basin has the capacity to absorb benzene from aqueous solutions. This experiment showed that 100 g of coal would absorb 8.82 µg of benzene from a stock solution having an original concentration of 68.45 µg/L of benzene. This stock solution had elevated benzene concentrations that in no way reflect actual concentrations found in either flowback or coal seam water. The sole purpose of using this concentrated solution was to test the absorption potential of coal, which turned out to be significant (99% absorption at these concentrations). However, the actual absorption of benzene by coal would be less substantial if volatilisation, which took place during this experiment, is taken into account. In addition, benzene absorption would decrease if a stock solution with a lower benzene concentration is used, as absorption is favoured when higher concentrations are present.

Results from these experiments are similar to results from previous studies (Orem et al., 2014; Orem et al., 1999; Stearman et al., 2014) which have aimed to characterise organic compounds that could potentially leach from coal. In general, these experimental results add support to the hypothesis that coal could be a potential source of organic compounds in coal seam water, but this tends to occur at very low concentrations in low temperature environments ($T < 30^{\circ}\text{C}$) as shown by this experimental work. Consequently, these results suggest that the presence of organic compounds in coal seam water could be the result of a natural process involving the interaction between groundwater and in situ coal seams, without anthropogenic interference.

Liquid state HNMR analysis of Bowen Basin coal samples revealed the presence of aliphatic compounds in sample leachates, while actual solid-state sample analysis using CNMR showed aromatic compounds as major spectrum peak contributions in the structural framework of the coal material itself. This suggests that, despite their abundance in the coal material itself, high-molecular weight aromatic compounds are less likely to leach from coal than lower-molecular weight aliphatic compounds. Consequently, it is recommended that environmental practitioners wanting to sample coal seam waters concentrate their efforts sampling for Monocyclic Aromatic Hydrocarbons (MAHs) and low-molecular weight PAHs. The effect of reservoir pressure and lithostatic pressure, as measured with the Triaxial leaching experiment, was not significant but it was noted that formation water would flow through the coal pores and cleats at very low flow rates and not all surface coal area would get directly exposed to flowing water.

In general, the maximum magnitude of benzene detected in this study (e.g. leaching with synthetic coal seam water at $T > 60^{\circ}\text{C}$) is of similar magnitude than the maximum benzene concentration detected in samples from the Bowen Basin. On the other hand, the benzene absorption experiment showed that sub bituminous coal from the Surat Basin has the capacity to absorb benzene from aqueous solutions. This suggests that, at high concentrations, the coal material itself would act as a sink of benzene and other organic compounds. As expected, leaching with

sodium hypochlorite induced the formation of THM compounds; this is not surprising as this is a common formation process (e.g., similar processes have been observed at wastewater treatment plants using chlorine as a disinfection agent). In general, more aggressive leaching methods that are not representative of in situ reservoir conditions were required to leach more elevated concentrations of organic compounds from coal. Therefore, these experiments could represent a worst-case synthetic-scenario as per the leaching of organic compounds from coal. Further work is required to assess the organic compound concentrations of actual coal seam water samples in the areas from which these coal samples were collected. However, the general low coal seam water concentration trends reported in previous studies (Orem et al., 2014; Stearman et al., 2014; Tang et al., 2014), suggest that the concentrations of organic compounds detected in this synthetic study are generally higher than concentrations of actual samples collected in the field. In addition, the likelihood of measurable impacts from benzene sourced from the coal matrix, appear low given the aggressive leaching needed to achieve measurable benzene concentrations, and therefore may form a low risk to the environment.

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