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Occurrence and fate of natural hydrocarbons and other organic compounds in groundwater from coal-bearing basins in Queensland, Australia

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Executive summary

The harnessing of unconventional petroleum sources has elicited intense public concerns about potential impacts to groundwater quality. Specific contamination sources and pathways of public concern have been identified but the temporal and spatial extent to which hydrocarbons can contaminate groundwater remains ambiguous. A large majority of environmental studies have thus far focused on gaseous hydrocarbons (mainly methane) and more work is needed to better understand *naturally occurring* higher molecular weight counterparts including BTEX (benzene, toluene, ethylbenzene and xylene), polyaromatic hydrocarbons, total petroleum hydrocarbons, and organic compounds such as phenols. These compounds can occur naturally in coal and crude oils as well as in manufactured products such as gasoline and engine oil. Many petroleum-derived products commonly used in industrial processes may contain BTEX such as grease, lubricants and fuels. Historically, some hydraulic fracturing fluids have had additives that contained BTEX components, however in most jurisdictions modern fraccing fluids no longer contain such compounds. Drilling rigs in general (both water well drilling rigs and gas industry drilling rigs), will have components that require grease or various types of lubrication. The potential occurrence of BTEX in groundwater (whether naturally occurring or introduced by human activity) has prompted public debate due their potential to cause adverse health effects.

The study presented herein aims to provide the first steps into understanding the composition, distribution and attenuation of naturally occurring hydrocarbons and other organic compounds in the Bowen and Surat basins, Queensland, Australia. These basins form some of the largest sources of CSG in the world, actively producing commercial quantities of methane since 1996 as well as conventional oil and gas since the late 1960s. Currently, only limited integrated studies are available that take organic chemistry information (e.g. solubility, reactivity etc) and combines it with the geology (e.g. coal rank) and microbiology (biodegradation of these compounds). Such an interdisciplinary study will provide us with a more comprehensive and integrated view of the fate of hydrocarbons in groundwater. Furthermore, this study allows the identification of potential indicator compounds which could be used to identify natural pathways by which hydrocarbons and other organic compounds can enter groundwater systems. It also provides important information against which potential, human-induced contamination could be assessed in future studies.

In particular, we 1) reviewed existing geological, physico-chemistry, and biological literature to better define and understand the properties of the various hydrocarbons and other organic compounds that might occur in groundwater; 2) build a dataset derived from publically available borehole logs; 3) identified indicator compounds which could be used to identify natural pathways by which hydrocarbons and other organic compounds can enter groundwater systems; 4) constructed a conceptual model of natural pathways for the generation and distribution of hydrocarbons and other organic compounds in groundwater; and 5) used an archive of geochemical groundwater data (University of Queensland Centre for Coal Seam Gas, Queensland Water Atlas) collected during active coal seam gas (CSG) development from 2009 to 2014 to determine the occurrences of various non-gaseous hydrocarbons and other organic compounds from the Bowen and Surat basins in Queensland, Australia.

Natural sources of organic compounds in groundwater in the Bowen and Surat basins are many and varied. Modelling the fate of hydrocarbons and other organic compounds in groundwater in

Queensland's coal-bearing sedimentary basins is a complex task that involves the interaction of numerous sedimentary/mineral assemblages, aqueous and gas phases as well as the biosphere. Such systems are characterized by complexity seldom encountered in the laboratory. Both migrated petroleum as well as coal layers could, in principle, be major suppliers of natural hydrocarbons and other organic compounds in these basins. Provided a transport mechanism is available (e.g., flowing water), hydrocarbons and other organic compounds will spread within the soil-rock-groundwater system. However, these compounds will also be affected by geological, physico-chemical and biological influences. These processes rarely act in isolation but rather are related to each other through complex interactions. While some of these processes may attenuate hydrocarbons and other organic compounds, others will have the opposite effect.

In this study, relatively few hydrocarbons and other organic compounds were found to have concentrations above the limit of reporting in the Surat CMA. Based on these results, it appears that the occurrences of hydrocarbons and other organic compounds in the CMA groundwater is limited both in frequency of occurrence and in concentration. These results also compare with a previous literary survey of hydrocarbon and other compounds in groundwater from coal-bearing Australian basins in Queensland and New South Wales (Schinteie et al., 2015). In conclusion, while sources for these detected hydrocarbons in the Surat CMA can be hypothesized, concrete evidence is lacking. Furthermore, due to the lack of any supporting data and no quantitative information in regards to hydrocarbon occurrences in over a longer period of time, any interpretations on the sources of these hydrocarbons need to be treated with caution. Groundwater chemistry data presented here show relatively low concentrations of various hydrocarbons in the Surat CMA. Concentration levels of detected compounds were ≤9.64 ppb for TPH compounds and ≤203 ppb BTEX compounds (mostly toluene). Such values were well below drinking water guidelines for BTEX compounds developed by various government agencies.

Finally, we investigated the applicability of historical mud log data to estimate hydrocarbon gas concentrations and their distributions in the Bowen and Surat basins - two economically important coal-bearing basins. The resulting data set, consisting of recorded hydrocarbon gases (methane, ethane, propane, butane) and higher *n*-alkane homologues (pentane and hexane) in parts per million (ppm), was allocated to stratigraphic horizons and mapped. While mud log gas data suffers from a range of limitations, broad distribution and concentration trends were discernible. These trends were in agreement with previous geochemical and isotopic work in the Bowen and Surat basins on the occurrences of hydrocarbon gases. In particular, the distribution of wet gases in the thermally less mature WCM indicate significant upward migration of thermogenic gases. The approach and results presented in this study can have multiple applications, such as serve as a low cost exploration tool in the search for economic hydrocarbon gas reserves in frontier basins. Provided mud logs are publically available for such basins, their digitization and interpretation can provide useful information on the composition, relative quantity and distribution of potentially exploitable methane and wet gases.

Proposed scope of work for CSIRO to undertake as part of the Collaboration Project with the University of Queensland, Centre for Coal Seam Gas, for the GISERA project "Hydrocarbons in Groundwater"

Continuous global demand for natural gas combined with declining conventional petroleum sources has made coal seam gas (CSG) an economically viable energy resource (e.g. Flores, 2014). The production of this unconventional resource relies on the extraction of water from coal seams to depressurize the areas of interest and allow natural gas to desorb and flow from the coal matrix (e.g. Moore, 2012; Flores, 2014). To a limited extent, hydraulic fracturing is also employed in low permeability coal seam reservoirs to enhance the production efficiency of CSG by creating new and enlarging existing fractures in coal (e.g. Holditch et al., 1988; Holditch 1993; Ren et al., 2014; Kang et al., 2016). The increased exploitation of this natural gas resource has elicited significant concerns over the possible presence of dissolved hydrocarbons and other organic compounds into produced groundwater, as well as the release of these compounds into groundwater systems hosting coal formations. The occurrence of such contaminants has prompted significant worldwide public debate due their potential to cause adverse human health effects (e.g. Stearman et al., 2014). However, the overall extent, rates and pathways of groundwater contamination resulting from drilling and production operations remain controversial due to a paucity of open-access data of sufficient regional extent over a significant period of time. Furthermore, while significant research and debate has focused on whether subsurface CSG developments increase the methane flux in these areas or induced additional migratory pathways (e.g. Sherwood et al., 2016; Iverach et al., 2017; Lafleur and Sandiford, 2017), very few studies have payed attention to natural occurrences non-gaseous counterparts, including BTEX (benzene, toluene, ethylbenzene and xylene), polyaromatic hydrocarbons, total petroleum hydrocarbons, and organic compounds such as phenols. In most cases, studies of non-gaseous compounds have focused on their relationships with hydraulic fracturing fluids and flowback water (Steliga et al., 2015; Elliott et al., 2017) and surface spills (DiGiulio et al., 2011; Gross et al., 2013) at shale gas extraction sites. However, hydraulic fracturing for CSG is relatively minimal and some countries, such as Australia, have banned the addition of BTEX and other hydrocarbons into fracturing fluids. Nevertheless, the potential input of hydrocarbon and organic compounds into groundwater from large coal-bearing formations cannot be discounted and significant research is still required to investigate and distinguish contributions from both natural and artificial sources.

The Bowen and Surat basins in south-eastern Queensland, Australia, cover an area of intense CSG development with commercial production starting in 1996 and significant ramp up occurring since 2001 (Day, 2009; Moore, 2012). These basins have long and complex petroleum generating histories, involving both thermogenic and biogenic hydrocarbon gas formation as well as the formation of crude oil (Boreham et al., 1996; Carmichael and Boreham, 1997; Underschultz et al., 2016). Almost all Australian CSG activity occurs in these basins with only relatively minor production taking place in the state of New South Wales (Moore, 2012). Hydraulic fracturing in Queensland is

rarely employed and gas production is stimulated in only a small percentage of wells (APPEA, 2018). A key issue in Queensland is related to hydrocarbon occurrences in bores and water bodies and the potential impairment of aquifers that form part of the Great Artesian Basin (GAB), one of the largest freshwater artesian basins in the world (e.g. Habermehl, 1980). On rare occasions, CSG companies as well as governmental organizations have reported the detection of various non-gaseous hydrocarbons in groundwater bores, leading to temporary closures of CSG operations (Schinteie et al., 2015). However, such reports of non-gaseous compounds are usually only reported as isolated well-site incidences and do not provide insights into potential groundwater occurrences over a large regional extent and over a significant period of time.

The collaboration between the Commonwealth Industrial and Scientific Research Organisation (CSIRO; Energy Business Unit) and the University of Queensland (UQ) will look to share and further enhance certain datasets and data analyses already developed as part of the UQ "Water Geochemistry Atlas" project and the "Surat and Bowen Basin Hydrocarbon Systems" project. Herein, we present a modified scope of a pre-existing contract between CSIRO and UQ. The modified scope pertains to the work CSIRO will undertake as part of this collaborative project. The purpose of this project is for CSIRO researchers (Dr. Richard Schinteie, Dr. Kaydy Pinetown, Dr. David Midgley and other appointed staff) undertaking CSIRO project W5, to access organic chemistry data as part of the groundwater database held by UQ (under various agreements) and organic geochemistry data from the University of Queensland Centre for Coal Seam Gas (UQ CCSG) Hydrocarbon Systems project to conduct the following scope of work:

Project objective

Characterising the distribution and fate of naturally occurring hydrocarbons in groundwater of the Surat Basin.

Currently, no integrated study is available that takes organic chemistry information (e.g. solubility, reactivity etc) and combines it with the geology (e.g. geothermal gradient, coal rank etc) and microbiology (biodegradation of these compounds). Such an interdisciplinary study will provide us with a more comprehensive and integrated view of the fate of hydrocarbons in groundwater. Furthermore, the study may allow us to identify indicator compounds (if any) which could be used to identify natural pathways by which hydrocarbons and other organic compounds can enter groundwater systems. It also forms an important "baseline type" study on which human-induced contamination could be assessed in future studies.

Methods and revised scope

Essentially, we will focus on the <u>natural</u> occurrences of hydrocarbons in groundwater. Importantly, we wish to better understand the chemistry of these hydrocarbons by:

1. Review existing chemistry literature to better define and understand chemical properties of the various organic compounds of interest. Collect data such as solubility states at different temperatures, reactivity, adsorption states and other previously derived chemical models. Also review the literature and previous geological work germane to natural release of organic compounds into groundwater. Examples include collecting data on the susceptibility of different coal types of different ranks in releasing hydrocarbons and consideration of

porosity and permeability effects. Consideration will also be given to the potential for microbial degradation of the compounds of interest. The work will lead to some understanding of hydrocarbon compounds in groundwater pre-CSG production. Review the solubility and reactivity of these various hydrocarbon compounds at various environmental conditions typical of Great Artesian Basin aquifers.

2. Building a dataset derived from publically available borehole logs (e.g. mud log gas analyses) and the existing organic geochemistry dataset from the UQ CCSG Hydrocarbon Systems project, providing a student can be recruited to undertake such task.

3. Identifying indicator compounds (if any) which could be used to identify natural pathways by which hydrocarbons and other organic compounds can enter groundwater systems and migrate.

4. Construct a conceptual model of natural pathways for the generation and distribution of hydrocarbons and other organic compounds in groundwater.

5. Working with UQ CCSG, ground truth the collected data from the literature (CSIRO scope, step 2) and the indicator analysis (CSIRO scope, step 4) by comparing it with the UQ CCSG Water Atlas organic geochemistry database across agreed geographic areas in point 6 below. This will also include QA/QC of all hydrocarbon and organic chemistry data particularly in relation to analytical methodology (eg silica gel clean up). The study will encompass the coal seams as well as other lithologic units (e.g. sandstones and shale).

6. Working with UQ CCSG, undertake a validation step i.e. a case study of two complementary key cross sections of the Surat and Bowen basins. This validation step may also require use of such data as water and gas (CH_4) stable isotopes to aid interpretation.

Data sources

Hydrocarbon and organic compound concentration data will be provided by OGIA as part of the existing arrangement for data acquisition for the UQ CCSG Water Atlas as agreed by Arrow Energy, QGC/Shell, and Santos. APLNG will supply data separately.

Other data required:

1. Details regarding the completed intervals on CSG wells and screened intervals of bores. This includes single seam and multiple seam names and depths.

2. Information on analytical methods used for hydrocarbon analyses in each sample and any changes over time.

3. For a subset of wells and bores to be decided after QA/QC of the water analyses, data including geothermal gradient and coal rank.

4. For a subset of wells and bore data for gas (CH_4) and water stable isotopes.

Note

In this study, we focus mostly on non-gaseous (i.e. >C4) hydrocarbons and other organic compounds. An exception is made in section 5 (Part II), where we tested applicability of using historical mud log data as a first step to in establishing historical hydrocarbon gas fluxes in the Bowen and Surat basins. We also placed most of our attention to coal seams as the source of naturally occurring hydrocarbons and other organic compounds. Only limited attention was placed on crude oil.

Milestone achievements

The list of six tasks outlined above in 'Methods and revised scope' acted as milestone targets before the commencement of this project. While we adhered strictly to these milestone, the nature of the project caused some slight modifications. These are listed for each task below.

1. This task was mostly achieved as was set out at the onset of the project. However, due to the overwhelming number of hydrocarbons and other organic compounds present in naturally occurring sources, we focused on broad groups of compounds.

2. With the help of a research assistant, we managed to build a dataset derived from publically available borehole logs (e.g. mud log gas analyses) and combined it with the existing organic geochemistry dataset from the UQ CCSG Hydrocarbon Systems project. The resulting dataset was graphed and mapped using a geographic information system.

3. A broad range of indicator compounds were identified. However, due to the large number of hydrocarbons and other organic compounds present in naturally occurring sources, we focused on broad groups of compounds only.

4. Constructed a conceptual model of natural pathways for the generation and distribution of hydrocarbons and other organic compounds in groundwater.

5. Working with UQ, we ground truthed the collected data from the literature and the indicator analysis by comparing it with the UQ CCSG Water Atlas organic geochemistry database across agreed geographic areas (Surat Cumulative Management Area). However, a sparsity of measured hydrocarbons and other organic compounds above the detection limit limited this investigation.

6. Due to the sparsity of measured hydrocarbons and other organic compounds in the groundwater dataset, we could not undertake a validation step.

Part I   Review on the chemistry and natural release of hydrocarbons and other organic compounds into groundwater

1 Overview of the Geological Setting of the Bowen and Surat basins: main emphasis on the coal layers and hydrogeology

1.1 Tectonic history of the Bowen and Surat basins

The Bowen Basin forms part of the larger Permo-Triassic Sydney-Gunnedah-Bowen Basin system which is a composite structural basin covering ~1700km from southern NSW to central Queensland (Scheibner, 1999). The basin was formed in a back-arc setting (Korsch et al., 2009), with formation beginning during the Late Carboniferous and Early Permian, when tectonic extension and extensional subsidence was followed by the deposition of the earliest known sedimentary sequences of the basin (Cadman et al., 1998). Subsidence continued until the Early Triassic with varying thermal subsidence rates (Korsch and Totterdell, 2009) giving rise to many of the structures within the basin. Deposition ceased during the Late Triassic with a 30 Ma-year period of erosion forming a regional unconformity and marking the divide between Bowen and Surat basins (Cadman et al., 1998). The overlying Jurassic-Cretaceous Surat Basin formed as a result of tectonic subsidence caused by dynamically induced platform tilting (Korsch and Totterdell, 2009). Basin formation ceased at about 95 Ma once uplift began (Yago, 1996). The Cenozoic is characterised by volcanic activity which resulted in localised compression and some folding (Fielding et al., 1993; Yago, 1996), followed by uplift, erosion and more volcanic activity (Cadman et al., 1998). Throughout the Late Oligocene and Early Miocene tectonic compression resulted in reverse faulting and the formation of intrusive and extrusive igneous rocks (Cadman et al., 1998). Contractional deformation is more apparent on the eastern side of the basins whereas the western side was not physically affected by the retrothrust belt (Korsch et al., 2009).

In the Bowen Basin, volcanic activity during the Early Permian led to the formation of the Combarngo Volcanics to the east of the Roma Shelf and the Camboon Volcanics near the Auburn Arch (Cadman et al., 1998). Exon (1976) notes that Jurassic volcanism contributed significant amounts of lithic detritus to the sedimentary record of the Surat Basin. During the Middle and Late Jurassic, material for the formation of the Springbok Sandstone, the Orallo Formation and the Westbourne Formation of the Surat Basin was contributed by andesitic volcanism (Exon, 1976). As mentioned above, Late Oligocene to Early Miocene tectonic activity resulted in the formation of numerous intrusive and extrusive igneous rocks throughout the basin, examples of which are the Mount Warning volcanic complex and the Main Range and Lamington volcanic flows (Cadman et al., 1998).

Peak subsurface paleotemperatures in the Bowen Basin were reached through increased depth of burial during the Early Cretaceous, with values becoming 28-58°C higher than at present (Raza et al., 2009). During the mid-Cretaceous the greatest amount of cooling occurred, with paleogeothermal gradients generally in the range of 21-35°C/km, similar to present-day geothermal gradients (Raza et al., 2009). According to Uysal et al. (2000) the high palaeogeothermal gradients estimated in the northern Bowen Basin are due to convective heat transfer during a hydrothermal event. Locally fracture-enhanced permeable zones acting as hot reservoirs in the deeper part of the basin may have been responsible for some significant local thermal anomalies (Uysal et al., 2000).

Similarly, in the southern Bowen Basin high heat flow in the lower sections of the stratigraphy reflect a rock dominated semi-closed system with low water/rock ratio, where rocks are impervious to circulating fluids encouraging heat transfer by conduction (Uysal et al., 2000).

1.2 Structure of the Bowen and Surat basins

The Bowen Basin is an elongate north-south trending asymmetrical basin that covers an area of approximate 200,000km^2 (Cadman et al., 1998; Figure 1). The basin is bound in the southeast by north-south orientated Triassic thrust faults, the Moonie-Goondiwindi Fault System and the Leichardt-Burunga Fault System; the Moonie-Goondiwindi and Leichardt-Burunga fault systems extend upwards through the strata of the Surat Basin from the underlying Bowen Basin (Exon, 1976; Cook and Draper, 2013). The Taroom and Denison troughs, which are the major depocentres of the basin, are separated by the Comet Ridge in the northwest, with half-grabens in both troughs present as evidence of Late Carboniferous and Early Permian tectonic extension. In the west, the Hutton-Wallumbilla Fault System, a major lower basement structure, forms the boundary between the Comet Ridge and the Roma Shelf. This structure is not strongly developed in the Surat Basin (Draper, 2013). The Merrivale Fault System forms the western limit of the Roma Shelf (Cadman et al., 1998). The Bowen Basin margins are less defined in the central west and southwest, as sediments deposited on the St George-Bollon Slope are thinning and inter-fingering with sediments of the Galilee Basin (Cadman et al., 1998). According to Draper (2013) the Springsure Shelf is a half-graben that marks the western boundary of the basin. Tadros (1993) considers the southern boundary generally drawn across the basement high near Moree.

The Mimosa Syncline, which is the main depositional centre of the Surat Basin (Fielding et al., 1993; Yago, 1996), is a reflection of the Taroom Trough in the underlying Bowen Basin (Fielding et al., 1993). During the Middle Jurassic, deposition slowed and centred on the Dirranbandi Syncline, which was once thought to be part of the Mimosa Syncline (Exon, 1976). The Nebine Ridge is a north-north-east trending basement high that separates the Surat and Eromanga basins (Cook and Draper, 2013). It is a fragment of Precambrian cratonic crust that has been altered significantly by tectonism during the Carboniferous and Middle Jurassic (Exon, 1976). Towards the east the Kumbarilla Ridge is structural basement high that separate the sedimentary rocks of the Surat and Clarence-Moreton basins (Cook and Draper, 2013).
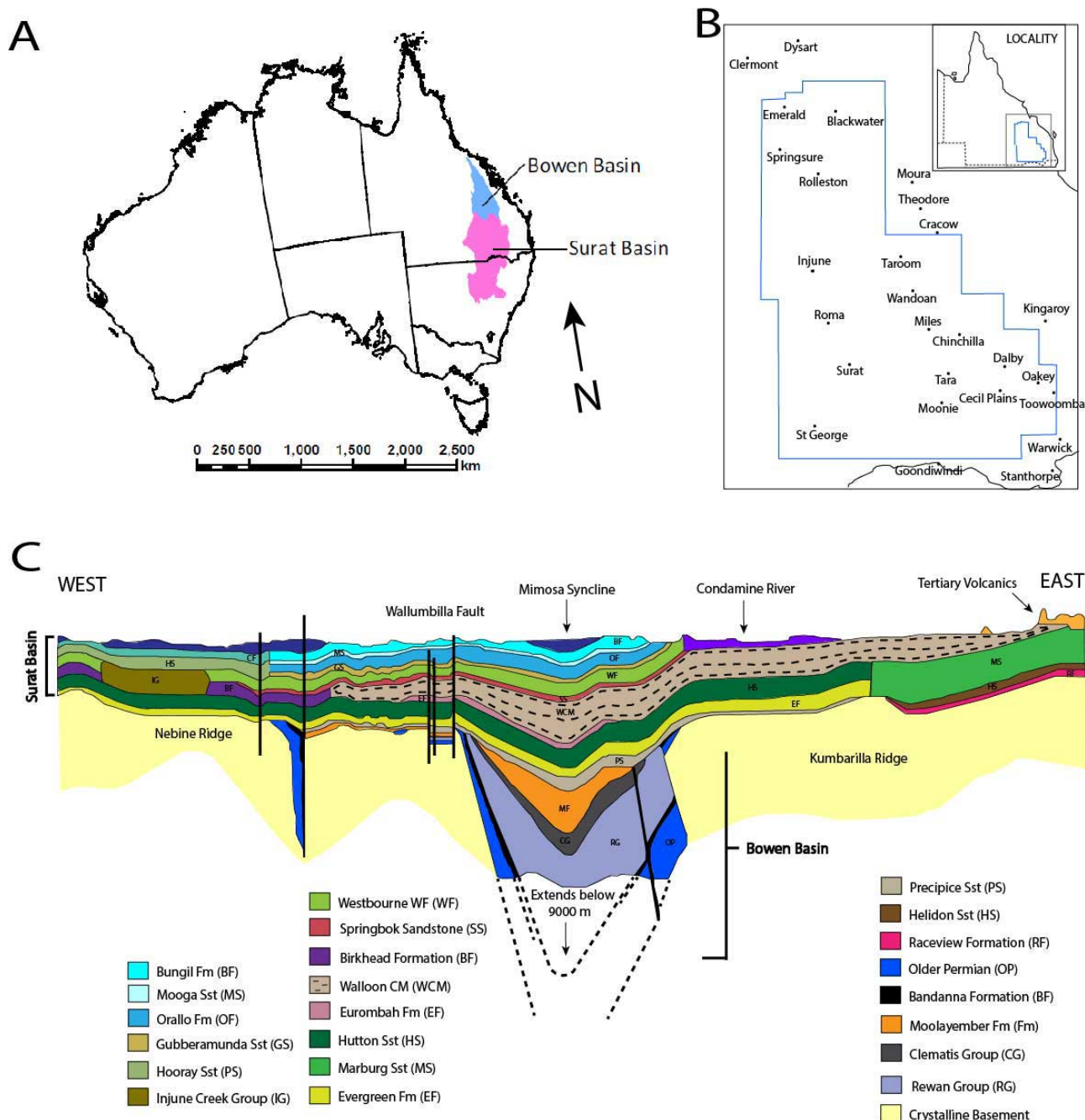
Figure 1 A) Location of the Bowen and Surat basins (data source: Geoscience Australia). B) The extent of the Surat Cumulative Management Area in Queensland (adapted with modifications from DNRM, 2016). C) Cross-section of the Bowen and Surat basins (adapted with modifications from Hodgkinson et al., 2009).

1.3 Stratigraphy and rock type

1.3.1 Bowen Basin

The Taroom Trough is known to contain the thickness stratigraphic sequence of the Bowen Basin of ~ 9 km (Cadman et al., 1998), and recently Korsch and Totterdell (2009) estimated maximum sedimentation of up to 10km thick in a repeated sequence of marine and terrestrial deposition. Rocks within the Bowen Basin are predominantly sandstones, shales, claystones and coal

intermingled with extrusive volcanics and the intrusion of plutons (Danis et al., 2012). A detailed stratigraphic column is presented in Figure 2.

Brakel et al. (2009) identified the basin-filling episodes and nine depositional supersequences for the Bowen Basin through a regional seismic study of the basin. An Early Permian extensional phase is characterised by thick volcanics and fluvio-lacustrine sediments marking the first supersequence of the basin. This was followed by the thermal subsidence phase during which four marine supersequences were generated. During the Late Permian, foreland loading first affected the entire basin and lasted until the end of Triassic deposition, where another four supersequences, some parts of which consists almost wholly of non-marine coal measures, have been identified (Brakel et al., 2009).

Based on the compilation by Danis et al. (2012; Figure 2) the Permian and Triassic strata of the Bowen Basin includes the Early Permian Reids Dome Beds, Lizzie Creek Volcanics and Camboon Volcanics, followed by the deposition of the Back Creek, Black Water, Rewan and Mimosa groups. The subdivisions within each group varies from the western to eastern margins of the basin and a general overview of the stratigraphy within each group is provided in this report.

Reids Dome Beds, Lizzie Creek Volcanics and Camboon Volcanics

The Reids Dome Beds are a non-marine sequence filling the Denison Trough containing widespread coal seams, usually covered by significant thicknesses of marine sediment. The coal seams are associated with lacustrine, fluvial and alluvial deposits (Mallett et al., 1995). The Lizzie Creek Volcanics occur in the north and the Camboon Volcanics are found in the southeast. The Lizzie Creek Volcanics comprise basaltic to andesitic lava and volcaniclastic rocks with local siltstone, shale and conglomerate. Similarly, the Camboon Volcanics comprise basaltic to andesitic lava and equivalent volcaniclastic rocks with subordinate felsic ignimbrite and is commonly deformed (Mallett et al., 1995). Coals of the Reids Dome Beds and those interbedded with the volcanics in the north are considered part of the Group I Coal Measures according to Mallett et al. (1995).

Back Creek Group

The Back Creek Group hosts predominantly Group II Coal Measures of the Bowen Basin (Mallett et al., 1995). In the Capella area the Aldebaran Sandstone is a pebbly quartz sandstone with conglomerate, minor shale, siltstone and coal, which unconformably overlies the Reids Dome Beds. The Freitag Formation is a thinly interbedded sandstone with siltstone, mudstone and minor coal seams. It includes thin and often split paralic coals which are locally developed in the Denison Trough (Mallett et al., 1995). The Collinsville Coal Measures in the north of the basin contains nine persistent coal seams, and comprises quartzose sandstone, siltstone, mudstone, carbonaceous shale, conglomerate and coal that accumulated in marginal environments (Mallett et al., 1995).

The Catherine Sandstone found in the Denison Trough is a quartzose to sublabile sandstone with siltstone and mudstone, and is equivalent to the German Creek Formation in the Comet Ridge/Collinsville Shelf region. The German Creek Formation (previously known as the German Creek Coal Measures) contains quartzose and sublabile sandstone, lithic and feldspathic labile sandstone, calcareous sandstone, siltstone, mudstone, carbonaceous mudstone, coal and conglomerate (Mallett et al., 1995). Around the Roma Shelf region the Muggleton Formation is a shale, siltstone and sandstone unit with minor coal and tuff layers. It hosts the Lorelle Sandstone Member which is composed largely of sandstone with minor shale, siltstone, coal and tuff (Green et

al., 1997). The Arbroath beds is known only from the Roma Shelf region. It formed during Early Permian deposition and consists of shale and siltstone with some sandstone, conglomerate and coal. It can be correlated with the more widely distributed Reids Dome beds (Green et al., 1997).

Black Water Group

The Black Water Group hosts the Group III Coal Measures which are best developed in the Comet Ridge/Collinsville Shelf region, and are overlain by the Group IIIA Coal Measures which are distinguished by the presence of numerous tuff beds (Mallett et al., 1995). It also hosts the Group IV Coal Measures which includes the Rangal Coal Measures in the north and central areas, and the Baralaba Coal Measures in the southeast of the basin (Mallett et al., 1995).

The Peawaddy Formation in the Denison Trough region is a carbonaceous mudstone with siltstone and lithic sandstone. The Late Permian Moranbah Coal Measures are developed throughout the northern and central Bowen Basin where it forms the basal formation of the Blackwater Group. The thickness of the Moranbah Coal Measures on the western margin of the basin is relatively uniform and it increases eastwards to a maximum development of 760m (Mallett et al., 1995).

Around the Roma Shelf region the Early Permian Tinowon Formation is a fluvio-deltaic and brackish marine unit consisting of shale, siltstone, sandstone and significant amounts of coal. The Wallabella Coal Measures which is hosted within the Tinowon Formation occurs in relatively thick and continuous sections, and is a swamp coal deposit interbedded with shale, siltstone, tuff and minor sandstone (Green et al., 1997). The Flat Top Formation comprises siltstone, sandstone, mudstone, conglomerate, coal and tuff that was formed in a delta fan to shallow marine setting (Draper, 2013).

Late Permian deposits of the Black Water Group includes the Black Alley Shale/Winnathoola Coal Measures and Bandanna Formation which are developed in the Denison Trough and Roma Shelf regions, the Fort Copper and Rangal coal measures in the Comet Ridge/Collinsville Shelf region, and the Baralaba Coal Measures around the Taroom Trough. The Black Alley Shale is shale-rich unit with beds of tuff, coal and sandstone. It was formed in brackish marine conditions during a Late Permian transgression and was followed by a change to freshwater lake sedimentation. The Winnathoola Coal Measures, comprising a thin bed of coal and sandstone formed in a deltaic setting, is hosted within the Black Alley Shale (Green et al., 1997).

In the north of the Bowen Basin the Fort Copper Coal Measures has a thickness of up to 500m consisting of lithic sandstone, conglomerate, mudstone, carbonaceous shale, coal, tuff and tuffaceous mudstone (Mallett et al., 1995). The Rangal Coal Measures comprises calcareous sandstone, calcareous shale, mudstone, coal and concretionary limestone resting conformably on the Fort Copper Coal Measures. At the base of the Rangal Coal Measures the appearance of clean coals is widespread, and at the top the sandstones and siltstones change from grey to green indicating distinct depositional and diagenetic changes (Mallett et al., 1995)

The Bandanna Formation is composed of mudstone, siltstone, sandstone and coal, and also includes laminated to massively bedded labile sandstone, interbedded with mudstones and siltstones, formed as infill sediments within a large lake or inland sea by deltaic input. It is one of the main geological units mined for coal in the Bowen Basin (Green et al., 1997; Draper, 2013). The Baralaba Coal Measures is a marine and fluvial unit comprising feldspatholithic sandstone, siltstone, calcareous mudstone and shale, coal and tuff. The Kaloola Member is the basal sub-unit of the

Baralaba Coal Measures and consists of blue-grey to white, silicified mudstone, siltstone, feldspathic and lithic sandstone, tuff, conglomerate and minor coal layers (Green et al., 1997).

Rewan Group, Clematis Group and Moolayember Formation

Rocks of the Rewan Group include lithic sandstone, pebbly lithic sandstone, green to reddish brown mudstone and minor volcanilithic pebble conglomerate. The sequence is made up of a conglomeratic unit at the base, a unit with predominantly lithic arenites in the middle, and a unit dominated by sub-lithic arenites at the top (Bashari, 1998). The rocks were deposited in a fluvial-lacustrine environment. The lithic arenites of the Rewan Group, which contain high proportions of volcanic rock fragments, are cemented by abundant authigenic quartz, carbonates and clay minerals (Bashari, 1998). The Clematis Group contains medium to coarse-grained sandstone, siltstone, mudstone and conglomerate. The Moolayember Formation comprises predominantly micaceous lithic sandstone and micaceous siltstone, and hosts the Snake Creek Mudstone Member, which is a dark grey to black mudstone with minor laminae and thin beds of very fine-grained sandstone.

1.3.2 Surat Basin

The infill sequence of the Surat Basin is approximately 2.5km (Exon, 1976) with up to 1800m of undeformed, quartz-rich continental Jurassic-aged sediments, overlain by ~900m of mainly paralic fine grained sediments of Early Cretaceous age (Goscombe and Coxhead, 1995).

Precipice Sandstone

The Precipice Sandstone consists mainly of quartzose sandstone deposited fluviatile transgressive environment, becoming finer upwards (Goscombe and Coxhead, 1995). It also contains common siltstone, shale and coal laminae in the upper part of the formation, with a thickness of up to 150m (Exon, 1976). The unit was formed as part of supersequence, together with the overlying Evergreen Formation, that was deposited over a period of 24Ma and its formation is consistent with the non-marine sequence-stratigraphic model of a lowstand systems tract (Hoffmann et al., 2009).

Evergreen Formation

The Precipice Sandstone grades upwards into the Evergreen Formation which consists of mainly of carbonaceous siltstone with horizons of shale, carbonaceous mudstone, oolitic ironstone, sandstone and coal deposited in a fluvial setting on a coastal plain, with possible deltaic influence (Exon, 1976; Green et al., 1997). The formation is up to 300 m thick and more widespread than the Precipice Sandstone. It hosts the Boxvale Sandstone Member and the Westgrove Ironstone Member. The Boxvale Sandstone Member, is confined mainly to the northern region of the basin and is composed of fine- to coarse-grained quartzose sandstone which was deposited during a brief marine transgression. The Westgrove Ironstone Member consists of fine lithic sandstone, siltstone, mudstone and concretionary ironstone (Exon, 1976). Current work on the sequence stratigraphic delineation of the Surat Basin (La Croix et al., 2018) would reference the transition zone between the top of the Blocky Braided Fluvial Precipice Sandstone and the Westgrove Ironstone as being the Upper Precipice Sandstone, with the Evergreen Formation occurring above this.

Hutton Sandstone

At its base the Hutton Sandstone consists of poorly sorted, coarse to medium-grained, feldspathic sandstone becoming a well-sorted and fine-grained quartzose sandstone at the top. It also contains minor carbonaceous siltstone, mudstone, coal and rare pebble conglomerates bands. The unit is very porous and permeable and has a maximum preserved thickness of 250m in the Mimosa Syncline (Goscombe and Coxhead, 1995). The sandstone was derived from varied, but generally quartz-rich, terrains to the northeast, southeast, and southwest and varies considerably in composition (Exon, 1976).

Walloon Coal Measures

The Walloon Coal Measures contain the most significant coal resources in the Surat Basin. Its composition is highly varied comprising thinly bedded claystone, shale, siltstone, sandstone (lithic and sublithic to feldspathic arenite), coal seams and minor limestone, with a muddy pebble conglomerate also occurs in several locations (Exon, 1976). According to Exon (1976) most of the sequence was deposited in coal swamps, with the lower part consisting mainly of stream, and especially overbank, deposits. The coal measure sequence is subdivided into four sub-units: the Durabilla Formation, Taroom Coal Measures, Tangalooma Sandstone and the Juandah Coal Measures (Exon, 1976; Goscombe and Coxhead, 1995). The Taroom Coal Measures is a 50 to 200m thick unit of mixed sandstone, siltstone, mudstone and carbonaceous shale with abundant coal and carbonaceous mudstone interbeds. It also includes impure limestone and ironstone lenses (Goscombe and Coxhead, 1995). The Tangalooma Sandstone comprises a mixed assemblage of sandstone, siltstone, mudstone, claystone, tuff and thin coal to carbonaceous mud seams (Exon, 1976), which is up to 200m thick (Goscombe and Coxhead, 1995). The feldspathic labile sandstone commonly contains a carbonate cement. The Juandah Coal Measures are similar to the Taroom Coal Measures in composition and coal volume, although the former has thicker coal seams towards the top of the formation (Goscombe and Coxhead, 1995). In a study aiming to provide a regionally consistent stratigraphic framework model for the Walloon coal seam gas (CSG) play in the eastern Surat Basin, Esterle et al. (2013) and Hamilton et al. (2014a) found that lithofacies in the Walloon Subgroup show systematic changes that enable regional correlation at unit level, but that the main subunits of the eastern Surat Basin (Durabilla Formation; Taroom Coal Measures; Tangalooma Sandstone; Juandah Coal Measures) do not correlate along the entire CSG play area. The overlying Springbok Sandstone has incised to the lower Juandah Coal Measures in some cases and to the south the Walloon Subgroup thins through a combination of depositional thinning and truncation. (Esterle et al., 2013; Hamilton et al., 2014a).

Westbourne Formation and Springbok Sandstone

The Late Jurassic Westbourne Formation consists of fluvial-lacustrine rocks such as fine-grained sandstone interbedded with siltstone, mudstone with lenticular bentonite beds and thin coal seams (Exon, 1976; Goscombe and Coxhead, 1995). The formation ranges from 80 to 100m in thickness and can be up to 200m in the Mimosa Syncline. The Springbok Sandstone, which has equivalents in the Adori Sandstone in the Nebine Ridge and the Pilliga Sandstone towards the south of the basin, is a clayey lithic to very lithic sandstone interbedded with carbonaceous mudstone and siltstone. The unit can is generally <50m but can be up to 150m (Goscombe and Coxhead, 1995).

Orallo Formation and Gubberamunda Sandstone

The Early Cretaceous to Late Jurassic Orallo Formation was deposited in fluvial channels and composed of thin beds of siltstone and mudstone with some sandstone and minor conglomerate and coal in the (Exon, 1976). The Gubberamunda Sandstone is a medium- to coarse-grained, largely quartzose, poorly sorted sandstone with minor conglomerates and siltstones, deposited in high energy braided streams to low energy meandering rivers (Goscombe and Coxhead, 1995).

Mooga Sandstone, Bungil Formation and Wallumbilla Formation

The Mooga Sandstone is sandstone-dominated unit that with interbeds of siltstone and mudstone at the top, ranging from 50 to 150m in thickness (Goscombe and Coxhead, 1995). Minor conglomerate and coal bands are present throughout and more common in the upper section (Exon, 1976). The paralic Bungil Formation is a sequence of labile sandstone, siltstone, mudstone with subordinate coarse-grained quartzose sandstone and minor thin coal seams deposited in environments ranging from paludal to neritic (Goscombe and Coxhead, 1995). The Cretaceous Wallumbilla Formation contains 100 to 200m of marine, grey carbonaceous mudstone and siltstone with minor interbeds of fine-grained glauconitic and calcareous sandstone (Doncaster Member), as well as 50 to 200m of paralic sediments comprising interbedded mudstone, siltstone and lithic sandstone which is commonly glauconitic (Coreena Member; Exon, 1976; Goscombe and Coxhead, 1995).

Figure 2 Simplified stratigraphy of the Bowen and Surat basins. Modified from Danis et al. (2012)

AGE		GROUP	WEST	Denision Trough	Comet Ridge	Collinsville Shelf	Roma Shelf	Taroom Trough	EAST
CRETACEOUS	EARLY	Rolling Downs GP / Blythesdale GP	Wallumbilla FM; Bungil FM; Mooga SS; Orallo FM; Gubbermunda SS					Wallumbilla FM; Bungil FM; Mooga SS; Orallo FM; Gubbermunda SS	Bungil FM; Mooga SS; Orallo FM; Gubbermunda SS
JURASSIC	LATE	Injune Creek GP/ Walloon FM	Westbourn FM; Springbok SS; Walloon CM	Westbourn FM; Springbok SS; Walloon CM				Westbourn FM; Springbok SS; Walloon CM	
JURASSIC	MIDDLE	Bundamba GP	Hutton SS; Evergreen FM; Precipice SS	Hutton SS; Evergreen FM; Precipice SS				Hutton SS; Evergreen FM; Precipice SS	
JURASSIC	EARLY								
TRIASSIC	LATE	Mimosa GP							
TRIASSIC	MIDDLE		Moolayember FM; Clematis FM	Moolayember FM; Clematis FM		Moolayember FM	Moolayember FM; Clematis FM	Moolayember FM/ Wandoan SS	Wandoan SS; Cabawin FM
TRIASSIC	EARLY	Rewan GP			Rewan FM	Rewan FM			Cabawin FM
PERMIAN	LATE	Black Water GP		Bandanna FM; Black Alley Shale/ Winnathoola CM; Peawaddy FM; Catherine SS/ Ingelara FM; Freitag FM; Aldebaran SS; Cattle Creek FM; Reid Dome beds	Rangal CM; Fort Cooper CM; Moranbah CM; German Creek FM; Aldebaran SS; Cattle Creek FM	Blenhein FM; Collinsvile CM; Tiverton FM; Lizzie Creek/ Bulgonnuna volcanics	Bandanna FM; Black Alley Shale/ Winnathoola CM; Tinowon FM/ Wallabella CM; Muggleton FM; Combarngo volcanics	Baralaba CM; Gyranda FM; Flat Top FM; Barfield FM; Oxtrack FM; Buffel FM; Camboon volcanics	Kianga FM; Back Creek FM
PERMIAN	EARLY	Back Creek GP					Roma granite	Camboon volcanics	Camboon/ Connors volcanics
CARBONIFEROUS	LATE			Timbury Hills FM	Timbury Hills FM		Timbury Hills/ Kuttung FM		Kuttung FM

1.4 Natural sources of hydrocarbons in the Bowen and Surat basins

1.4.1 Properties of Bowen and Surat basin coals

Bowen Basin

Coal seams of the Bowen Basin are classified into four distinct groups (numbered I through IV) (Mallett et al., 1995). Group I is the oldest and is highly variable in thickness and lithology, comprising good quality coking and non-coking coal towards the northern part of the basin. In the Capella region the coals are high in liptinite with a mean maximum vitrinite reflectance of ~0.77% and volatile matter contents of 37-40% (dry, ash-free basis, daf). At Cullin-la-Ringo the coals have low ash and sulphur with vitrinite contents ranging from 34 to 54% (Mallett et al., 1995).

Group II consists of several unconnected deposits of coal with variable properties, some of which are of economic interest. Ash yields of the Collinsville Coal Measures range between 12% for the Garrick Seam and up to 25% of the Potts Seam. Sulphur values are raised due to marine influence and all coal seams of the sequence are intruded in part, producing pronounced rank gradients (Mallett et al., 1995). Typical coals of the Blair Athol Coal Measures have variable ash yields and sulphur contents, but slightly lower than those of the Collinsville Coal Measures (Mallett et al., 1995).

Group III is laterally extensive and consists of multiple seams of high grade coking coal. In the northern Bowen Basin approximately 20m thickness of coal is present. Coal quality characteristics of the major economic seams are variable with volatile matter content ranging between 20 and 32%, and mean maximum vitrinite reflectance values between 0.98 and 1.45% (Mallett et al., 1995).

Coal quality of Group IV coals is the most diverse and the deposits are most widely distributed. The group contains coking and non-coking coal of major economic importance. In the central and northern Bowen Basin the coal-bearing formations are better developed and thicker, compared to the southern basin (Mallett et al., 1995). The coal seams are up to 6 m thick and have vitrinite reflectance values of 0.56 to 0.61%, and volatile matter content between 27 and 32% (Mallett et al., 1995).

Vitrinite reflectance values of the seams of the Permian German Creek and Moranbah Coal Measures in the northern Bowen Basin studied by Ward et al. (2005) show increases with increasing burial depth from 0.39% in the western part of the basin to over 3.5% in the east. Vitrinite reflectance studies of coals and dispersed organic matter by Othman and Ward (2002) show that the Early Permian Back Creek Group of the southern Bowen Basin have anomalously low reflectance values and a higher reflectance gradient compared to the overlying Late Permian, Triassic and Jurassic sequences.

For a suite of Bowen Basin and Illinios Basin coal samples studied by Mastalerz and Glikson (2000) the carbon content of solid bitumen is comparable to the carbon content of the associated vitrinite for vitrinite reflectance values below 0.67%. In all other samples bitumen shows higher carbon content. Mastalerz and Glikson (2000) attributes this to the loss of hydrogen as a result of generation of gaseous hydrocarbons. Sulphur, iron, and other minor elements in bitumen are present in almost identical amounts to those in the associated vitrinite, suggesting that the adjacent vitrinite is the source of bitumen Mastalerz and Glikson (2000). They also proposed that two types of solid bitumen could be present at the maturation stage corresponding to the onset of gas

generation: pre-gas bitumen which is more aliphatic, and at the higher maturation level the more aromatic post-gas bitumen was found.

Surat Basin

According to Scott et al. (2007) the Jurassic coals of the Surat Basin are dull, and rich in carbon (>80% dry, ash-free (daf)), with high volatile matter content (>30% as received (ar)) and moderate to high ash yield. The Walloon Coal Measures can be subdivided from bottom to top into the Taroom Coal Measures, the Tangalooma Sandstone, and the Lower and Upper Juandah Coal Measures, which have different coal character (Hentschel et al., 2016). It is a thick sequence of interbedded coal and sedimentary rocks with coal hosted mainly in the Taroom and Juandah Coal Measures. The coals range from sub-bituminous to high-volatile bituminous in rank (Scott et al., 2007). The middle Tangalooma to Lower Juandah contains fewer and thinner coals (Hentschel et al., 2016). The Juandah Coal Measures contains six coal seams with a mean aggregate thickness of 8m. Along the western flank of the Kumbarilla Ridge the Juandah Coal Measures contains two economic seams of interest, the uppermost of which has a maximum and mean thickness of 16 m and 10 m, respectively, and mean in situ ash of 28% (Goscombe and Coxhead, 1995). In the Chinchilla area the Juandah Coal Measures have ash yields of ~12% and volatile matter contents of ~42%. At Sefton Park and Rywung, the coal measure sequences contain two banded seams 1.5 to 5.8 m thick. Economic coal resources are also present at Glen Wilga, Haystack Road and Horse Creek (Goscombe and Coxhead, 1995). Three seams are typically present in the Juandah Coal Measures in the Wandoan area, with individual thickness ranging from 1 to 6 m. The seams occur at ~80 m depth with washed ash yields of ~9% and volatile matter contents of ~44% (Goscombe and Coxhead, 1995).

The lower Taroom coals are commonly thick, associated with sandstones (Hentschel et al., 2016). Around Taroom the Taroom Coal Measures have two coal seams of economic interest. The upper seam has a mean thickness of ~5m and the lower seam varies from 2 to 3m. Some of the coal resources in this area occur within 60 m of the surface (Goscombe and Coxhead, 1995) and extend south past Chinchilla. At Kogan Creek three main seams have a total thickness of 12m with minimum depths of 12 to 15 m below the surface (Goscombe and Coxhead, 1995).

1.5 Hydrocarbon distribution in the Bowen and Surat basins

1.5.1 Organic matter type and hydrocarbon potential of Bowen and Surat basin coals

From a petrological perspective the morphological units that coals are composed of are referred to as macerals, and these are classified into three main groups based on the origins of their precursor materials (Taylor et al., 1998). The vitrinite group macerals originate from the humification of cellular tissue of wood, leaves and roots. Inertinite macerals are similar in origin to vitrinite macerals although the remains are charred or partially charred in the case of inertinite. Liptinite is a collective term for macerals which originate from relatively hydrogen-rich plant materials such as spores, pollen, leaf cuticles, resin and algal remains (Taylor et al., 1998). Coal maceral groups can be related to kerogen (solid organic matter) types I to IV as shown in Table 1, and can also be represented on modified Van Krevelen diagram (Figure 3).

Types of Kerogen and Their Hydrocarbon Potential				
Environment	**Kerogen Type**	**Kerogen Form**	**Origin**	**HC Potential**
Aquatic	I	Alginite	Algal bodies	Oil
		Amorphous Kerogen	Structureless debris of algal origin	
			Structureless planktonic material, primairly of marine origin	
Terrestrial	II			
		Exinite	Skins of spores and pollen, cuticle of leaves and herbaceous plants	
	III	Vitrinite	Fibrous and woody plant fragments and structureless, colloidal humic matter	Gas, some oil
				Mainly gas
	IV	Inertinite	Oxidized, recycled woody debris	None

Based on the maceral compositions of typical coals from the Bowen and Surat basins as listed in Table 1 and the classification shown in Table 2, Bowen Basin coals are generally considered to be gas prone in their potential to produce hydrocarbons, along with some potential to produce oil as shown in the literature (Boreham et al., 1996; Carmichael and Boreham, 1997).

Also from Tables 1 and 2, it can be deduced that Surat Basin coals are also considered to produce mainly gaseous hydrocarbons but given their greater liptinite contents these coals have greater potential to produce heavier hydrocarbons if they were buried deep enough. On the modified Van Krevelen diagram in shown in Figure 3, Bowen Basin coals plot in the lower atomic H/C to atomic O/C region whereas Surat coals have slightly greater H/C to O/C ratios.

Microscopically the coal maceral components discussed here can be seen in Figure 4 for typical Bowen basin coals and Figure 5 for typical Surat Basin coals.

Maceral Group	Bowen Basin	Surat Basin
Vitrinite	Rich in vitrinite with typical Group III coals ranging in contents between 55 and 75% on a mineral-free basis (Mallett et al., 1995)	Vitrinite-rich coals with contents at typical deposits ~75% (Goscombe and Coxhead, 1995)
Liptinite	Low concentrations in the range of <1 to 4% (Mallett et al., 1995)	Rich in liptinite compared to most Permian coals, with contents up to ~16% (Goscombe and Coxhead, 1995) and above
Inertinite	Second largest maceral group present in most Bowen Basin coals, with contents ranging between ~24 and ~44% for typical Group III coals (Mallett et al., 1995)	Inertinite contents range from ~2 to ~10% for typical deposits (Goscombe and Coxhead, 1995)
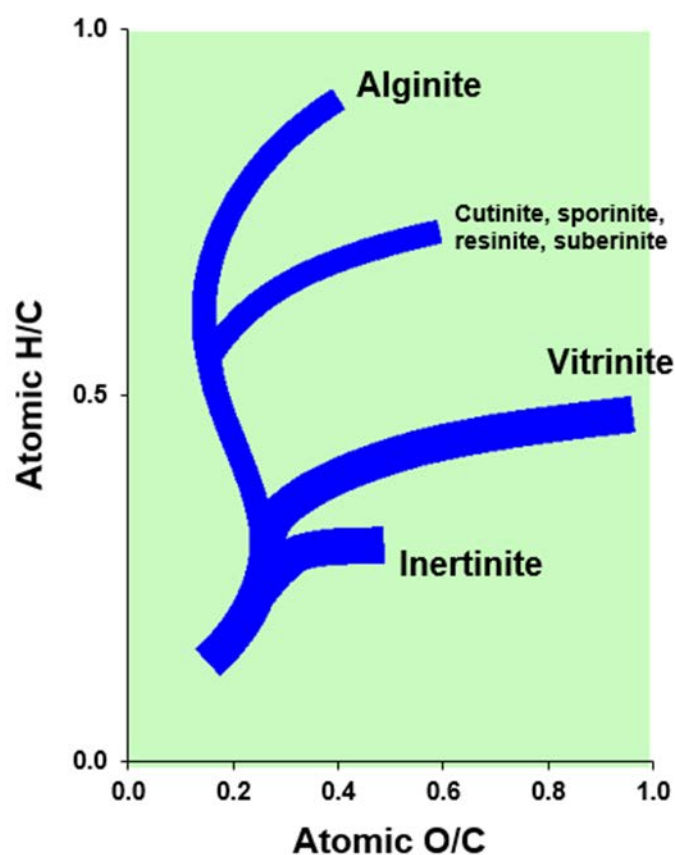
Figure 3 Modified Van Krevelen diagram showing the general plots positions based on coal maceral composition for typical Bowen and Surat basin coals
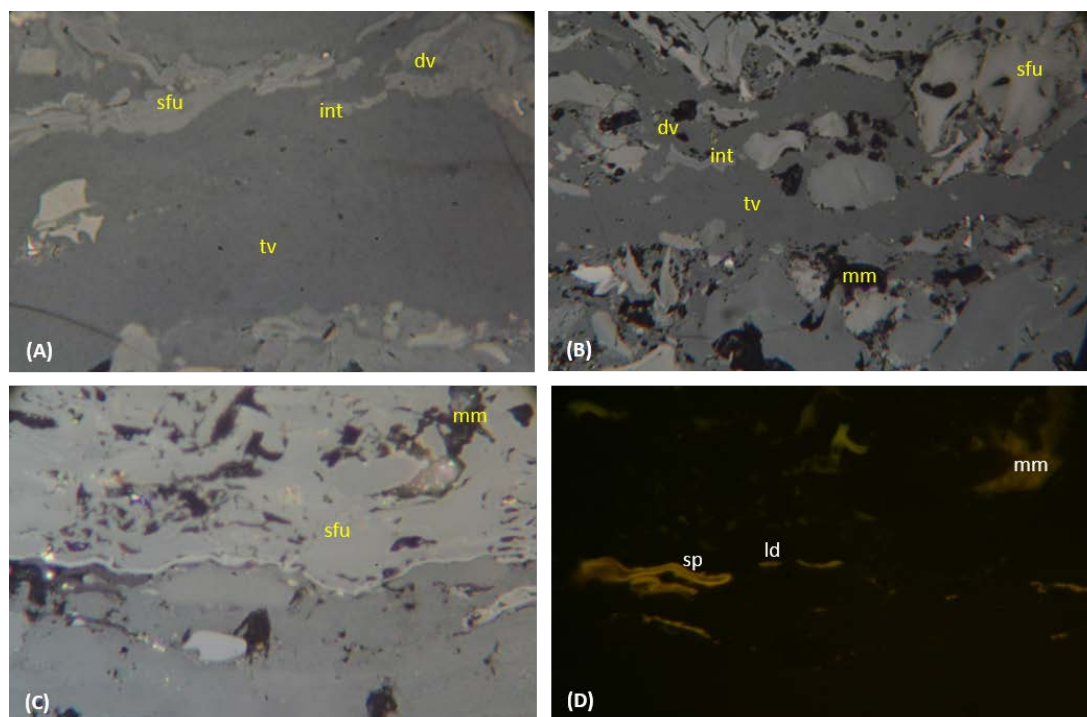
Figure 4 Photomicrographs of a coal sample from the Bowen Basin; (A) Reflected light image (field width = 0.16mm) of telovitrinite (tv), detrovitrinite (dv), semifusinite (sfu) and inertodetrinite (int); (B) Reflected light image (field width = 0.16mm) of semifusinite and inertodetrinite with telovitrinite and detrovitrinite bands; (C) Reflected light image (field width = 0.16mm) of semifusinite and inertodetrinite with mineral (mm) infilling cell lumens; (D) Image (C) in fluorescence mode showing fluorescing sporinite (sp), liptodetrinite (ld) and mineral.
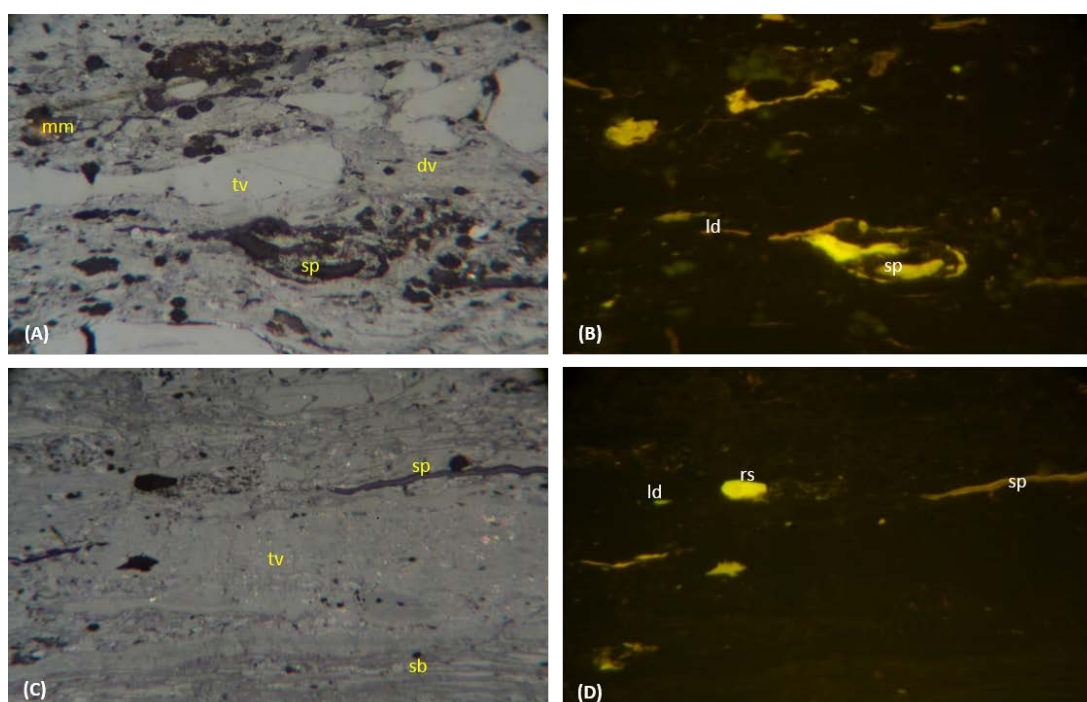
Figure 5 Photomicrographs of a coal sample from the Surat Basin; (A) Reflected light image (field width = 0.16mm) of telovitrinite (tv), sporinite (sp) and mineral matter (mm) in a groundmass of detrovitrinite (dv); (B) Image (A) in fluorescence mode showing fluorescing sporinite and liptodetrinite; (C) Reflected light image (field width = 0.16mm) of telovitrinite, sporinite and suberinite (sb) macerals; (D) Image (C) in fluorescence mode showing fluorescing sporinite, liptodetrinite and resinite.

1.5.2 Gaseous hydrocarbon distribution in the Bowen and Surat basins

Like other eastern Australian coals, the Bowen and Surat basins contain significant volumes of gas generated through either thermogenic, biogenic and/or magmatic processes, and the origin and distribution of these gases have been studied by various researchers. Smith and Pallasser (1996) concluded that thermogenic gases which were initially generated in the Sydney and Bowen basins were lost as a result of uplift and erosion. Isotopic data indicate that these lost gases were almost completely replaced by very dry biogenic methane (CH_4) produced through the microbial reduction of CO_2) and through the intrusion of magmatic carbon dioxide (CO_2) (Smith et al., 1996). Golding et al. (2013) reports high CO_2 concentrations in coal seams in the Oaky Creek area of the Bowen Basin and conclude that the CO_2 at Oaky Creek was emplaced during the Upper Triassic based on dating of illitic clay minerals and is magmatic or deep crustal in origin. Methane in the coals is of mixed origin with microbial reduction of CO_2 predominant in the high CO_2 coals producing biogenic CH_4.

A study on open system pyrolysis by Boreham et al. (1998) shows that there are two stages of CH_4 generation from Bowen Basin coals. The first stage, during which most of the CH_4 is generated, maximises at 570°C, with most of the heavier hydrocarbons (C_2-C_5) generated between 420 and 510°C. During the second stage only CH_4, carbon monoxide and CO_2 are produced. Upon comparing the pyrolysis data to compositional data for desorbed and produced coal seam gases from the Bowen Basin, Boreham et al. (1998) observed that CO_2 and heavier hydrocarbons are a minor component in the compositional data. This discrepancy was attributed to the "preferential migration of wet gas components by dilution of CH_4 generated during secondary cracking of bitumen, or kinetic effects associated with different activations for production of individual hydrocarbon gases" (Boreham et al., 1998).

Methane adsorption capacities of Bowen Basin coals related to coal properties were studied by Levy et al. (1997), who observed that the adsorption of CH_4 reduces by 0.12 mL g^{-1} of coal every 1°C increase in temperature, and by 4.2 mL g^{-1} of coal every 1 wt% increase in coal moisture content. With respect to carbon content Levy et al. (1997) found a linear, positive relationship with CH_4 adsorption for most-equilibrated coals, although on a dry basis high rank coal showed a sharp increase CH_4 adsorption capacity. The effect of coal composition of Bowen Basin coals on gas sorption capacity was also investigated by Laximinarayana and Crosdale (1999) who found that the Langmuir volume (V_L) for bright coals had a minimum V_L at 1.72% $R_{o,max}$ and dull coals had a minimum V_L at 1.17%. In high volatile bituminous coals, increases in vitrinite content are associated with increases in adsorption capacity, whereas higher ranks changes in maceral composition has little influence on adsorption capacity. Laximinarayana and Crosdale (1999) also observed that desorption rate is also a function of rank and that dull coals desorb more rapidly than bright coals. Diffusion rates are also higher at lower rank and changes coal pore structure with changing rank affects diffusion rate differences.

A reservoir study of the Rewan Group by Bashari (1998) shows that the conglomeratic and sub-lithic arenitic units have high permeabilities. According to Bashari (1998) porosity is best developed where early silicification has enhanced grain support and has minimised the effects of later compaction, as intense diagenetic alteration greatly reduced their porosity and permeability. In a study on the effects of matrix shrinkage in coal-seam gas reservoirs as a result of production from the MGP field in the Bowen Basin, Mazumder et al. (2012) observed a high level of growth in the

absolute permeability of coal seam during pressure drawdown, which is a result of matrix shrinkage caused by gas desorption.

Coal seam gas (CSG) is contained primarily within the seams of the Walloon Coal Measures of the Surat Basin. Recovery occurs generally from depths of 200 to 600 m below the surface, from seams of the Taroom and Juandah coal measures (Papendick et al., 2011), but gas production may also occur from shale and tight siltstone interburden that are interspersed between the coal seams, although this requires further investigation. The coals are in some cases very shallow allowing gas to desorb and be lost from the system (Scott et al., 2007). Scott et al. (2007) observed gas loss from the Walloon Coal Measures in the north-east Surat Basin which may be due to a reduction in confining pressure through tectonic movement and/or water movement.

Studies by Papendick et al. (2011) reported that an average well in the Dalby gas field contains 20 to 30 m of net coal and an average well the Roma gas field contains ~15 m of net coal. Individual seams of the Walloon Coal Measures can be thin and lateral discontinuous but have high seam permeabilities (Sander et al. 2014). Permeabilities can be as high as 200mD in the Roma field, whereas it can be lower ranging from 0.07 to 42.38mD in the Dalby field.

Gas contents generally range from 1 to 14m^3/t (daf), with an average of ~5m^3/t (daf) (Scott et al., 2007), whereas for the upper coal seams of the Juandah Coal Measures appear to be lower and more variable compared to the deeper seams (Scott et al., 2007). Gas contents are lower in coals of the Taroom Coal Measures compared to those of the Juandah Coal Measures (Scott et al., 2007). Hamilton et al. (2012) observed that while there is a general increase in gas content with increasing depth, gas content generally follows one of three depth trends where it either increases; increases then decreases; or decreases with depth. There is, however, considerable scatter in the distribution. Gas content layering also follows, rather than cross-cuts the stratigraphy (Hamilton et al., 2012). Hamilton et al. (2012) identified domains of different gas gradients, with the majority of very high gas gradient values occurring in coals within or above the Tangalooma Sandstone. This unit appears to form a regional-scale barrier for gas migration from underlying and higher rank coals, and to meteoric and biogenic recharge from above. Increased ethane concentration was observed in the upper Taroom and Tangalooma units supporting this interpretation. Scott et al. (2007) found that gas contents of the Walloon Subgroup also vary with coal petrology, although the variation is only subtle. Upper Juandah Coal Measures seam have lower vitrinite contents and lower gas contents, whereas lower Juandah and Taroom coals have higher vitrinite contents and higher gas contents (Scott et al., 2007).

The Walloon Subgroup CSG consists almost entirely of CH_4 (>98%; air-free basis), with only minor amounts of CO_2 and nitrogen (N_2), and very low levels of ethane (<1%; Hamilton et al., 2012). CH_4 in the Walloon Coal Measures is mainly of biogenic origin (Papendick et al., 2011), but compared to other low-rank CSG plays Hamilton et al. (2014b) found that the Walloon Subgroup differs particularly in methane carbon isotopic signature, as these values do not indicate strictly biogenic origins as could be expected. Carbon isotope values for CH_4 indicate thermogenic or mixed gas ($\delta^{13}C$ −58.5‰ to −45.3‰), with $\delta^{13}C$ values for CH_4 becoming more thermogenic from the top of the Juandah Coal Measures to the base of the Tangalooma Sandstone. In the Taroom Coal Measures, the $\delta^{13}C$ values for CH_4 decrease with increasing depth. Based on stable carbon isotopes alone Hamilton et al. (2014b; 2015) interpret this pattern as a transition from microbially- to thermogenically-sourced CH_4 in the central coal seams; based on the other data such as $\delta^{13}C$ values

for CH$_4$ and δD values for CH$_4$ Hamilton et al. (2014b; 2015) concludes that microbial CO$_2$ reduction is the primary source of Walloon Subgroup CH$_4$, and that stratigraphic variations in gas content mainly reflect the extent of microbial methanogenesis. Since the Walloon Coal Measures are only of a sub-bituminous rank, it is believed that thermogenic gas may have migrated into this stratigraphic horizon from further below at some locations. The quantity of thermogenic gas migration remains unclear (Towler et al., 2016).

1.6 Hydrogeology of the Bowen and Surat basins

A schematic hydrostratigraphy of the Surat and Bowen basins is shown Figure 6. A study by Kinnon et al. (2010) aimed at correlating water quality and stable isotope data with gas and groundwater production and flow pathways in the Bowen Basin, found that faults acts as a barrier to water and gas flow along strike. Significant differences also exist in stable isotope values of production waters. Production waters with more positive δD and δ^{18}O compositions were associated with areas of higher water production and shallower depths, whereas more negative δD and δ^{18}O compositions were associated with lower water production and high gas production (Kinnon et al., 2010). Production gases with more negative CH$_4$ δ^{13}C values characterize the zones of meteoric recharge in shallow, up-dip areas, with gas production data and CO$_2$ δ^{13}C values indicating ^{13}CH$_4$ stripping by the recharge waters and/or increased biogenic activity (Kinnon et al., 2010). Smaller carbon isotopic fractionation values are associated with zones of meteoric recharge, whereas higher isotopic fractionation values are associated with high gas production domain (Kinnon et al., 2010).

Baublys et al. (2015) conducted a related study for the Surat Basin by investigating the relationships between co-produced water compositional and stable isotopic data, and production gas stable isotope compositions of the Walloon Subgroup CSG play. It was observed that water compositions were distinct for each of the production regions. Near Roma waters have the lowest median values for alkalinity (861 mg/L), and Cl$^-$ (588 mg/L) and a δ^{13}C$_{DIC}$ of 14.2‰; at the Kogan Nose waters have the highest median values for Na$^+$ (1955 mg/L), Cl$^-$ (2280 mg/L) and δ^{13}C$_{DIC}$ of 20.0‰; and, at the Undulla Nose waters had the highest median alkalinity (1841 mg/L), excess Na$^+$ and lower than expected median δ^{13}C$_{DIC}$ of 14.0‰. Carbon isotope values for CH$_4$ from both the Juandah and Taroom coal measures indicate mixed 'thermogenic/microbial' origin (Baublys et al., 2015). Groundwater residence time does not increase consistently with increasing distance from the subcrop margin and the authors suggest that additional work is required to fully understand the sources of chloride in Walloon Subgroup waters and its possible association with nutrients such as nitrogen (Baublys et al., 2015).

In an assessment of the hydrochemical variability of CSG water from several sites in the Surat and Clarence-Moreton basins, Owen et al. (2015) found a strong positive linear correlation between the Na/Cl and alkalinity/Cl ratios; a decaying trend between the Na/Cl and Na/alkalinity ratios; inverse linear relationships between increasing chloride concentrations and decreasing pH for high salinity waters; and high residual alkalinity for lower salinity waters (Owen et al., 2015). Organically-bound chlorine held in the coal matrix appears to influence chloride and sodium concentrations in more saline waters, whereas high concentrations of bicarbonate in low salinity waters could be associated with a number of different factors such as coal degradation, methanogenic processes, and variability in gas reservoir characteristics. The authors conclude that where coal maceral content and the

dominant methanogenic pathway are similar, and where organic-bound chlorine is relatively abundant, distinct hydrochemical responses may be observed (Owen et al., 2015).

Surat Basin

Age	Surat Basin		GAB
Cenozoic	Colluvium		
	Alluvium (Condamine)		
	Chinchilla Sands		
	Main Range Volcanics		
Cretaceous	Griman Creek Formation		
	Surat Siltstone		
	Wallumbilla Formation — Coreena Member		
	Wallumbilla Formation — Doncaster Member		
	Bungil Formation — Minmi Member	Kumbarilla Beds	
	Bungil Formation — Nullawart Sst Member		
	Bungil Formation — Kingull Member		
	Mooga Sandstone — Southlands Formation		
Jurassic	Orallo Formation		
	Gubberamunda Sandstone		
	Injune Creek Group — Westbourne Formation		
	Injune Creek Group — Springbok Sandstone		
	Walloon Coal Measures		
	Hutton Sandstone		
	Evergreen Formation		
	Boxvale Sst		
	Precipice Sandstone		

Bowen Basin

Age	Bowen Basin		
Triassic	Moolayember Formation		Wandoan Formation
	Clematis Group Sandstones	Snake Creek Mst Mem	
		Showgrounds Sandstone	
Triassic	Rewan Group		
Permian	Bandanna Formation	Blackwater Gro	Baralaba Coal Measures

Figure 6 Hydrostratigraphy of the Surat and Bowen basins. Adapted with modified from Queensland Water Commission (2012).

2 Physico-chemical characteristics of hydrocarbons and other organic compounds

2.1 Hydrocarbon formation and composition in coal

Coal is an organic sedimentary rock composed of macerals and minerals formed from mostly partially decomposed plant debris which collected under waterlogged swampy conditions (e.g. Given, 1988; Speight, 2013). The original plant constituents have undergone considerable change through both physical and chemical interactions with their environment (Speight, 2015). Coal can also be considered as a complex chemical system composed of mostly high molecular weight organic material (Figure 7), although mobile, lower molecular weight compounds also occur and can be trapped within the pore system of the coal (Figure 8). Therefore, coal can be thought of as a two-component system composed of a mobile phase and a macromolecular network of higher molecular weight constituents (Given, 1984a,b; Given et al., 1986). Identification of the molecular constituents of coal is a difficult task and a distinction needs to be made between understanding the nature of the chemical constituents of coal and delineating the molecular structure.

The majority of organic matter in coal is derived from lignin, but some originates from other material and is derived from highly modified carbohydrates, polymerised terpenes, and other alkenes (Wilson, 1994). Humic materials may be intermediates from oxidation, or the coals may be derived directly from lignin. The detection of the physically smaller volatile compounds, which are the subject of this review, is unlikely in any technique in which the macromolecular component is also observed. However, they may be present in significant quantities, much greater than would be expected given their volatility. This is because some compounds may be entrapped as guests in host-guest complexes in the coal (Derbyshire et al., 1989).

In general, gas formation predominates over oil formation during the coalification (the formation of coal from plant material via bio- and geochemical means) in coal formations. Three main changes that occur during coalification involve the cracking of heteroatoms such as oxygen containing groups, degradation of hydrogen-containing alkyl side chains and increasing aromaticity (Stach 1975; Teichmüller and Teichmüller, 1979). During this process, all types of coal exhibit an increase in C and a decrease in H and O content. The change in H/C ratio reflects increased aromatization of the lignin structure through loss of functional groups and an increase in the number of polynuclear aromatic structures (e.g. Orem and Finkelman, 2005). The characteristics of the hydrocarbons generated by coal are fundamentally influenced by the constituent macerals and the degree and setting of coalification (e.g. Song et al. 2013). Since coal is a hydrogen-deficient substance, it is assumed that the basic structure of coal is probably built up of a large number of interlocked benzene rings with hydrogen occurring in the aliphatic side chains emanating from the benzene rings (e.g. Speight, 2013). Reactive hydroxylic, carboxylic, carbonyl and methoxyl functional groups can also be bound to aromatic and aliphatic components in coal and occur at the surface edges of coal. These functional groups can exhibit polarity, thereby affecting the surface chemistry of coal (e.g. Krzyżanowski and Żyła, 2007).

The identification of the chemical constituents of coal can be classified into 1) chemical techniques, 2) spectroscopic techniques, and 3) physical property methods. These techniques have been previously summarized in more detail by Schinteie et al. (2015; see also Pullen 1983; Speight, 2015). Determining the hydrocarbon composition of coal is a complex task littered with several caveats. Most common organic solvents (e.g. benzene, methanol, chloroform), for example, dissolve little of the true coal substance and usually extract only material occluded with the coal matrix (Speight, 2015). Other limiting factors are coal rank and composition, which influences the nature and quantity of extracts obtained by the solvent extraction of coal (Speight, 2013 and references therein). Nevertheless, some basic aspects of soluble hydrocarbons in coal can be described.

Evidence accumulated since the mid-1900s have shown that low molecular weight organic compounds form important constituents of coal. How these low molecular weight constituents exist in conjunction with the main macromolecular body of the coal is currently uncertain. IR investigations have established that coal contains various aliphatic and aromatic carbon-carbon and carbon-hydrogen bonds but few, if any, isolated alkene (>C=C<) or alkyl (>C≡C<) bonds (e.g. Speight, 1978).
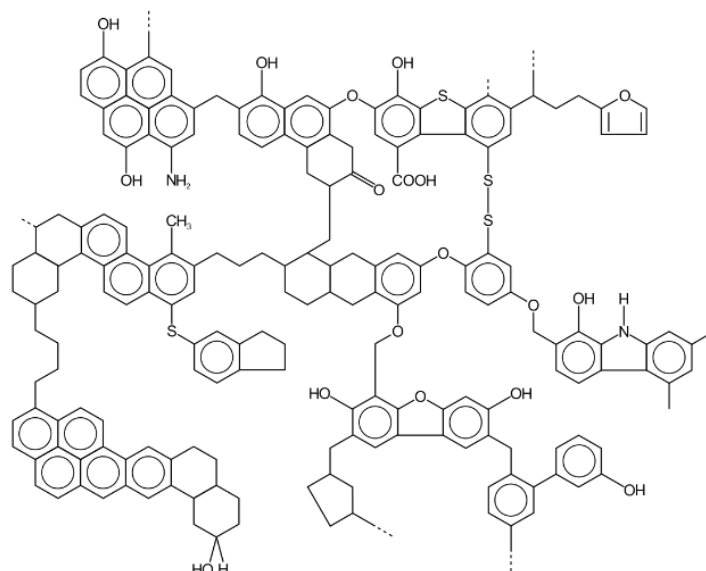
Figure 7 Coal has a complex, heterogeneous structure that includes aromatic and aliphatic components. Image courtesy: Karol Głąb

2.1.1 Low molecular weight constituents of coal

Non-destructive solvent extraction of coal demonstrates that it contains low molecular weight compounds that appear trapped within the pore system of coal (Vahrman, 1970; Bartle et al., 1978, 1982; Davis et al., 1989; Littke et al., 1990; Smith and Smoot, 1990; Pickel and Götz, 1991). These extractable low molecular weight constituents are likely to influence coal properties such as the atomic hydrogen/carbon ratio and the volatile matter content (Speight, 2013). However, uncertainty exists on the chemical relationships between many of the extractable lower and non-extractable higher molecular weight compounds and their respective origins.

Depending on type and rank of coal, various constituents of coal can be extracted with organic solvents. The nature and quantity of the extracts also depend on the length of extraction, the solvent used, and the grain size to which the coal has been mcaulground.

Variations in the makeup of these low molecular weight constituents is presumed largely due to the diversity of the original materials rather than differing conditions during coalification. Due to local and regional variations in the distribution of floral species as well as their occurrences in geologic time as a result of plant evolution, the relative amounts of low molecular weight constituents can vary considerably from one location to another and in different geologic ages. (Speight, 2013). However, in general, lignite and anthracite coals contain much lower proportions of volatile organic matter <C_{10}) than their bituminous counterparts. Therefore, regional variations in the physical maturation conditions of coal need to be taken into consideration (see Schinteie et al., 2015 and references therein).

Saturated compounds

Saturated compounds have been solvent extracted from coal and their yields vary significantly with coal rank (e.g. Raj, 1976). *n*-Alkanes have been extracted from all coal ranks and ranged from C_{13}-C_{33}. In lower rank coals, branched alkanes tend to predominate over *n*-alkanes. Cycloalkanes, isoprenoids, steranes and terpanes have also been extracted from various coals (e.g. Bartle et al., 1978). The branched and cyclic alkanes are believed to originate from coal/peat-forming living matter that were either the alkanes themselves or possessed oxygen-containing functional groups (e.g. terpenoids). Therefore, variations in lower molecular weight constituents appears to be related to the original coal-forming matter rather than the condition acting on the coalification process. Nevertheless, coalification can have a substantial impact with regards to the quantity of volatile organic compounds contained within coal. Lignite and anthracite coal, for example, appears to possess a lower proportion of volatile organic compounds (<C_{10}) than their bituminous counterparts. In addition to volatile hydrocarbons, organic acids of various types have also been shown to occur.

Aromatic compounds

The relative abundance of aromatic structures in coal increases during coalification (e.g. Teichmüller and Teichmüller, 1968). Solvent extractable, low molecular weight aromatics originate from either previously trapped non-aromatic biological precursors (e.g. resin acids) that were consecutively aromatized (Skrigan, 1964) or through release from the coal matrix by partial breakup of the polymer network during coalification (e.g. Radke et al., 1982). GC-MS of solvent extracts revealed a wide range of aromatic compounds, ranging from benzene and their alkyl homologues to highly condensed PAH (e.g. benzopyrenes). Some aromatic compounds also contain heterocyclic structural elements containing nitrogen, sulfur and/or oxygen (i.e. NSO compounds; e.g. Radke et al., 1982).

Below we list the most commonly studied aromatic compounds used for groundwater degradation assessment.

- Benzene, toluene, ethylbenzene and xylenes (BTEX). The term BTEX is an abbreviation used for four related compounds that are found in coal, crude oil and a variety of petroleum-

derived products (e.g. Leush and Bartkow, 2010). BTEX compounds have a number of different sources and can be introduced into the environment through natural and artificial means. Importantly, these compounds may dissolve and are highly mobile in water and can be detected in surface and groundwater contaminated sites, including those in close proximity to natural oil, coal and gas deposits (e.g. Leush and Bartkow, 2010).

- Polycyclic aromatic hydrocarbons (PAHs). These compounds are produced in coal as lignin-rich organic matter that undergoes defunctionalisation and condensation during the normal coalification processes. Their presence in groundwater is a result of leaching of coals (Orem et al., 1999).

2.1.2 High molecular weight constituents of coal

Considerable difficulty has been experienced when trying to identify high molecular weight constituents of coal. These constituents are difficult, if not impossible, to extract with organic solvent and also prove problematic when trying to separate them (e.g. via distillation) individually or as compound classes (Davidson, 1980). Therefore, high molecular weight constituents of coal are often inferred via a range of physico-chemical techniques (e.g. absorption spectroscopy, X-ray diffraction, electron spin resonance; Speight, 2013). Due to the complex, heterogenous nature of coal as well as uncertainties in characterizing the high molecular weight constituents, care must be adopted when presenting data in terms of an "average" coal structure (Speight, 2013). Due to the largely insoluble nature of the high molecular weight constituents in water, these compounds will not be further discussed here.
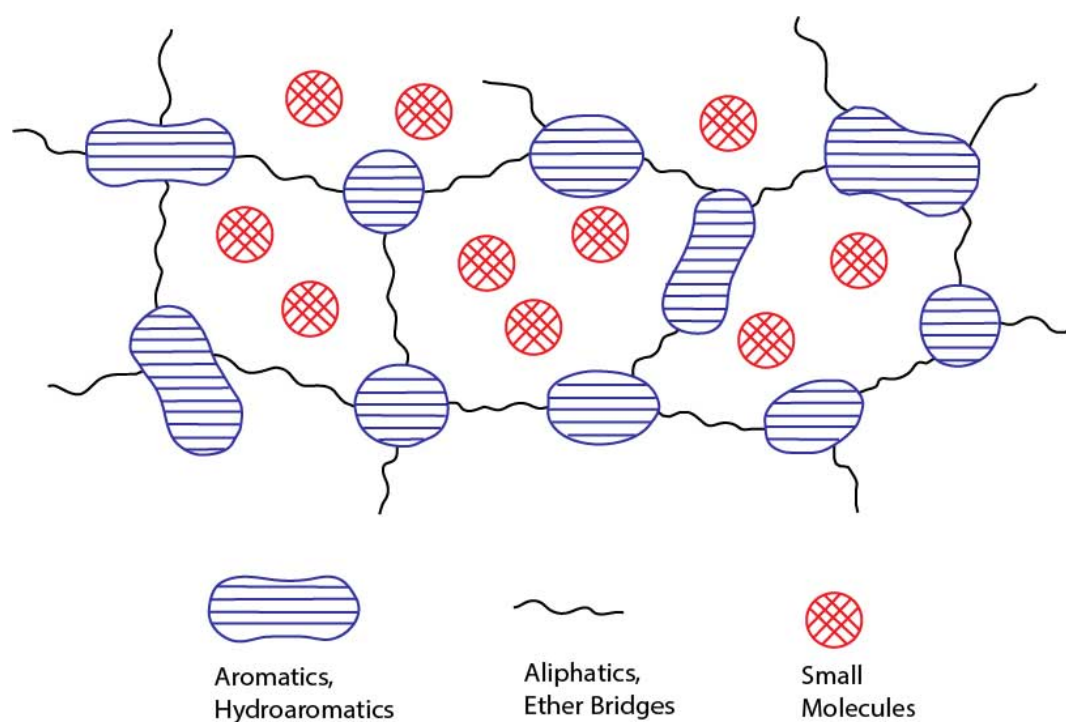
Figure 8 Conceptual model of coal as a two-component system involving a three-dimensional cross-linked network with small molecules scattered throughout (adapted with modifications from Haenel, 1992).

2.2 Release of hydrocarbon/organic compounds into groundwater

The environmental fate of hydrocarbon and other organic compounds in the subsurface can at least partially be explained and predicted by their physical and chemical properties. Indeed, it is widely acknowledged that organic and inorganic compounds can be absorbed, precipitated or otherwise released into the surrounding groundwater environment as a result of natural physico-chemical processes. Key properties that require consideration are: solubility, sorption, volatility, density, chemical stability, and biodegradability. These properties are separately discussed in detail below.

Naturally occurring hydrocarbons and other organic compounds present a potential risk to humans due to their toxicity, carcinogenicity, and the effects of chemical reactions with natural systems (e.g. oxygen consumption; Deutsch, 1997). Typical risks to human health from hydrocarbon exposure in the shallow subsurface typically arise through 1) exposure to vapour emissions that migrated to the surface in groundwater; and 2) from direct exposure (dermal, ingestion, inhalation pathways) to hydrocarbons in the groundwater. While dilution can reduce the concentration of compounds in groundwater, it is not by itself considered as natural attenuation. Processes leading to mass reduction are deemed necessary to be regarded as natural attenuation.

Previous studies from Australia and from other parts of the world have shown that hydrocarbons and other organic compounds can leach from coals (e.g. Orem et al., 2014; Orem et al., 1999; Stearman et al., 2014; Taulis and Stearman, 2015).

The physico-chemical characteristics of these compounds is related to their various chemical structures. With respect to groundwater contamination, these hydrocarbons are typically placed into three groupings:

1) Aliphatic hydrocarbons, which are comprised of saturated straight-chain or branched-chain hydrocarbons;

2) Monocyclic aromatic hydrocarbons, which are comprised of benzene, toluene, ethylbenzene and the xylene isomers (BTEX);

3) Polyaromatic hydrocarbons, which refer to hydrocarbons containing to or more fused aromatic ring structures.

The specific composition of hydrocarbons in groundwater will principally depend on the source.

Key hydrocarbon physico-chemical properties of concern are:

- Solubility

- Sorption

- Volatility

- Biodegradability

- Chemical stability

- Density

- Toxicity

- Abiotic chemical reactions

These physico-chemical properties are described and discussed in greater detail below. Effects of reservoir pressure and lithostatic pressure have been previously investigated by Taulis and Stearman (2015) through a Triaxial leaching experiment. The results were not found to be significant and are also not discussed further here.

2.2.1 Solubility

Solubility pertains to the maximum amount of a substance (gas, liquid, or solid) that will dissolve in a specified amount of solvent at a defined temperature and pressure (e.g. US-EPA, 1997). Solubility in water affects volatilization of chemicals from water bodies and is affected by temperature, the presence of dissolved salts and other organic matter, and surfactants. Since solubility in water is a function of temperature, most organic compounds become more soluble with increasing temperature (e.g. benzene). However, there are some chemicals whose solubility may decrease at higher temperatures. Thus, solubility depends on the nature of the chemical and the temperature range involved (Lyman et al., 1990). Apart from temperature, other factors that affect solubility include pH, pressure, and the presence of additional chemical species (e.g. Sawamura et al., 1989; Pinal et al., 1990; Keeley et al., 1991).

The presence of dissolved salts can lead to moderate decreases in solubility. Salts readily dissociate in water to yield anions and cations and in a process called 'salting out', the ions interact with the water molecules directly contacting organic solutes, resulting in a decrease in solubility (e.g. Zhang and Cremer, 2006). Franz Hofmeister, in the early 20th century, organized various anions and cations by their ability to salt out proteins. The ordering of cations and anions is called the Hofmeister Series (Hofmeister, 1888). The cations are arranged as follows:

$$NH_4^+ > K^+ > Na^+ > Li^+ > Mg^{2+} > Ca^{2+}$$
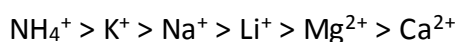
where ammonium has the highest ability to precipitate other organic solutes. The order for anions is:

$$F^- \geq SO_4^{2-} > H_2PO_4^- > H_3CCOO^- > Cl^- > NO_3^- > Br^- > ClO_3^- > I^- > ClO^-$$
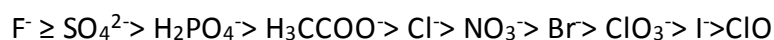
While the salinity of water from aquifers in the Bowen and Surat basins is generally fresh to brackish (averaging 1,900 mg/L), salinity of water in the coal measures is typically slightly higher. For example, water in the Walloon Coal Measures averages ~2,500 mg/L and ranges up to 6,000 mg/L; DNRM, 2016; Underschultz et al., 2018). Such salinities could potentially also play a part in lowering the solubility of hydrocarbons and other organic compounds.

The presence of organic matter may increase the solubility of many organic chemicals in water. This mechanism is based on the formation of hydrogen bonds or the partitioning of hydrophobic compounds with organic compounds such as humic acids so as to increase their water solubilities (e.g. Nanny and Maza, 2001; Ma et al., 2012). Benzene, for example, was shown to interact with dissolved humic acids at all pH values, although these interactions increased with decreasing pH and generally were proportional with the percent aromaticity of humic acid (Nanny and Maza, 2001). Sorption of organic compounds to humic acids, for example, also has the added effect of increasing the bioavailability of an organic compound to biodegradation (Smith et al., 2009). Humic and fulvic acids contain hydrophobic aromatic and aliphatic moieties (Stumm and Morgan, 1996) that can interact with dissolved organic compounds.

Surfactants have also been shown to increase the solubility of organic compounds by forming organic droplets into which the solute partitions (Lyman et al., 1990). A 'surfactant' is a contraction of the words 'Surface Active Agents' and work by lowering the surface (or interfacial) tension between two liquids or between a liquid and a solid. In the bulk aqueous phase, surfactants form masses, such as micelles, where the hydrophobic tails form the core and the hydrophilic heads are immersed in the surrounding liquid. Such masses have the capacity to disperse organic compounds in water. Natural surfactants exist. Microorganisms, for example, produce both high molecular weight and low molecular weight natural surfactants (Holmberg, 2001). Sugars and amino acids are the two most important examples of surfactant polar headgroups of natural origin. However, these products are usually present in relatively small quantities (Holmberg, 2001) and their effects on the solubility of organic compounds may therefore be limited.

2.2.2 Sorption

This is a process that leads to the partition of a dissolved phase (e.g. hydrocarbons) to solid phase sorbents. It ultimately leads to the immobilization of the dissolved phase through preferential attachment to a solid surface (sorption site; e.g. Stumm and Morgan, 1996). The substance being adsorbed is the adsorbate and the adsorbing material is termed the adsorbent. The adsorbate (i.e. adsorbed phase) can be immobilized temporarily or semi-permanently. Since sorption is a reversible process, consideration, must also be given to desorption. Sorption occurs through the forces exerted by atoms, molecules, and ions at the solid-water interface including surface complexation reactions with functional groups, electric interactions, and hydrophobic expulsion (see Stumm and Morgan,

1996 for detailed description of these processes). In regards to hydrocarbons and other organic compounds, the hydrophobic (i.e. "water-hating") effect is perhaps one of the most important factors leading to their sorption onto various surfaces. Due to their incompatibility with water, these hydrophobic substances tend to avoid contact with water and seek to associate with other nonpolar environments (e.g. organic particles; Tanford, 1980; Stumm and Morgan, 1996). While most hydrocarbons or other organic compounds are predominantly hydrophobic, they can contain hydrophilic (i.e. "water-loving") structural units through either heteroatomic functional groups (e.g. carboxylic acids) or possess some polar charge through the nature of their hydrocarbon bonds electron configurations (e.g. double bonds in alkenes). Such compounds with both hydrophobic and hydrophilic structural units are known as amphipathic and can satisfy each medium at the oil-water interface (Tanford, 1980; Stumm and Morgan, 1996). In an aqueous solution, such compounds tend to migrate to the surface (e.g. air-water interface) or form micelles through self-association. It should be pointed out that the attraction of nonpolar structural units to each other is the result of the strong attractive forces between water molecules and not due to any particular affinity between nonpolar molecular units (Stumm and Morgan, 1996).

The hydrophobicity of an organic compound represents the affinity it has for a hydrophobic environment. It is commonly measured by its distribution in a biphasic system consisting of n-octanol ($CH_3(CH_2)_7OH$) and water (e.g. Wermuth et al., 1998). *n*-Octanol has become a reference phase for organic phase water partitioning of organic solutes since octanol contains both a polar OH group and a hydrophobic hydrocarbon group. Therefore, it can dissolve both polar and non-polar compounds (Stumm and Morgan, 1996). The distribution equilibrium of a compound between water and n-octanol is known as Kow. It is determined experimentally and expressed as:

$$Kow = [A(oct)]/[A(aq)]$$

where A(oct) is the molar concentration of the organic solute associated with n-octanol, and A(aq) is the molar aqueous concentration of the organic solute. Kow coefficients are usually inversely proportional to water solubility (Stumm & Morgan, 1996).

Importantly, sorption influences the distribution of substances between the aqueous phase and particulate matter. The results affect relative residence times, residual concentrations and the ultimate fate of these substances (Stumm and Morgan, 1996).

In order to study the transfer of substances from a liquid or gaseous mobile phase to a solid phase, isotherms are used to describe and predict the mobility of this substance in the environment (e.g. Limousin et al., 2007). Isotherms are curves used to describe and predict the mobility of this substance in the environment. Furthermore, these retention/release phenomena can be strongly kinetically controlled, so that time-dependence of the sorption isotherm must be specified (Limousin et al., 2007). Sorption is measured by the partition co-efficient KD. It can be measured directly from column or batch tests. Alternatively, it can be estimated from the product of the soil-carbon sorption co-efficient (K_{OC}) and the fraction of organic carbon (f_{OC}) in a soil or aquifer.

Sorption or hydrocarbons and other organic compounds is complex and depends on the degree of coalification (e.g. Helle et al., 2003; Karacan et al., 2003; Valhaluru et al., 2003). Coalification changes coal type, the content of oxygen-containing functional groups, and the pore structure (e.g.

Zhou et al., 2015). While coal is mostly apolar, surface functional groups such as oxygen, play an important part in sorption since they are more electronegative than carbon and form partially charged poles, thereby contributing to hydrophilic properties in coal surfaces (e.g. Orzechowska-Zięba and Nodzeński, 2017). Porosity of coal is another property that affects hydrocarbon adsorption, since it affects the surface area onto which hydrocarbons can be sorbed. Meso- (2-50 nm diameter) and macropores (>50 nm Rouquerol et al., 1994) have been identified as the key sites of molecular adsoption (e.g. Krzyżanowski and Żyła, 2007). While numerous experiments have been conducted on the sorption of hydrocarbons on activated carbon (i.e. processed carbon with small, low-volume pores to increase surface area; e.g. Amstaetter et al., 2012; Chada et al., 2012) extrapolation of this data to complex natural settings need to be treated with caution. Activated carbon blended in sediment often sorbs around one order of magnitude less extensively than their clean counterparts (Cornelissen et al., 2006; Werner et al., 2006; Hale et al., 2009) and may be caused by pore throat clogging and/or competition among various compounds for soption sites (Kwon and Pignatello, 2005).

Traditionally, hydrocarbon adsoption onto coal has focused on gases, since these rocks act as collectors of gases in their porous structures (e.g. Walker et al., 1988). Thus far, only a few studies have been conducted on the sorption and desorption properties of relatively higher molecular weight hydrocarbons on coals (e.g. Krzyżanowski and Żyła, 2007; Baran et al., 2013; Orzechowska-Zięba and Nodzeński, 2017). Porosity and the presence of polar functional groups on coal surfaces have been shown as key determiners in the sorption capacity of hydrocarbon compounds onto coal. Relatively younger coals at a lower degree of coalification favoured the sorption of benzene and any alkyl derivatives (Krzyżanowski and Żyła, 2007 and references therein). It was noted that less mature coals possessed a large number of meso- and macro-pores than more mature coals. These pores were hypothesized to favour the sorption of benzene to a greater degree than a microporous texture of more mature coals of a higher degree of metamorphism (Krzyżanowski and Żyła, 2007). While coal is typically regarded as an apolar sedimentary rock, the occurrence of polar functional groups on lower ranked coal allows for the greater adsorption of hydrocarbons and other organic compounds with polar structural units. For example, alkenes (unsaturated hydrocarbons with a double bond) up to C_8, exhibited higher sorption onto some coal surfaces than alkanes (saturated hydrocarbons with only single bonds; Orzechowska-Zięba and Nodzeński, 2017). Orzechowska-Zięba and Nodzeński (2017) hypothesized that electron configuration in these double bonds allowed for their preferential adherence via polar functional groups onto coal surfaces. Therefore, coals with significant amounts of polar functional groups on their surfaces may control the sorption of apolar ones. Benzene also possesses an electron configuration that imparts polar properties, enabling it to bind to both polar and apolar structural groups on coal surfaces (Krzyżanowski and Żyła, 2007). However, such research on higher molecular weight hydrocarbons is at an infancy and significantly more work needs to be done in this particular area of research to better understand sorption of a range of naturally occurring compounds onto coal surfaces.

In soil, the higher the organic carbon fraction (fraction organic carbon – foc), the greater the sorption capacity and retardation (e.g. Sadler and Connell, 2003). Caution needs to be applied when using overseas soil data and applying it to an Australian context. Due to their age, many Australian soils have lower organic matter content than their overseas equivalents (e.g. Sadler and Connell, 2003).

Partitioning of hydrocarbons and other organic compounds between sediments and water is determined by the partition coefficient (K_p) of the sediment and is dependent on the concentration

of organic carbon in the sediment (e.g. Leo et al., 1971). The partitioning coefficient is expressed as follows:

$$K_p = K_{OC} * f_{OC}$$

where K_{OC} represents K_p corrected for the fraction of organic material present in the sediment and is specific for an organic substance in the sediment. As mentioned above f_{OC} represents the fraction of organic material in the sediment.

The K_{OC} of coal, in particular, has been shown as significantly higher than many other organic substances such as humic acids or cellulose (e.g. van der Heul, 2009). Ghosh et al. (2003) analysed polyaromatic hydrocarbons (PAHs) at a microscale in sediment from urban locations at Harbor Point (USA) and noted an association of PAHs mainly with coal tar pitch residue. However, PAHs present in semisolid coal tar pitch are more bioavailable than PAHs sorbed onto carbonaceous particles such as coal, coke, charcoal, and cenosphere. Therefore, differences in the partitioning coefficients of various organic-rich materials can significantly affect the concentrations of hydrophobic compounds in the environment.

2.2.3 Volatility

This process refers to the partitioning of vapour-phase constituents from a dissolved phase. It is essentially the transportation of chemicals from water bodies into the atmosphere (Smith et al., 1980). Volatilized compounds migrate as vapours upwards to the surface and can accumulate under or within structures, re-dissolve into soil moisture in the vadose zone, or are emitted into the atmosphere. Volatilisation involve a mass transfer process, which results in a decline in the total mass of dissolved hydrocarbons.

The equilibrium distribution of a volatile compound between the liquid and gaseous phases is described by Henry's law (e.g. Lee et al., 2004). This law provides an indication of processes that control the rate of volatilisation and is critical when modeling the transport and fate of volatile compounds in the environment (e.g. Bamford et al., 1999). For example, one compound with a high Henry's law constant will volatilize from water into air and be distributed over a large area, while another compound with a low constant tends to persist in water and may be adsorbed onto soil (e.g. Ameji et al., 2015). However, it should be kept in mind that any constants derived from Henry's Law are valid only for ideal solutions and these may not be applicable in complex real world situations (Stumm and Morgan, 1996).

Henry's Law can be expressed in one of two forms:

$$K_H = \text{Concentration in gas phase/Concentration in liquid phase}$$

or

$$K_H = \text{Liquid vapour pressure/Chemical solubility}$$

Where K_H is the Henry's Law constant.

The term volatile organic compound (VOC) refers to an entire set of vapour phase atmospheric organics excluding carbon monoxide (CO) and carbon dioxide (CO_2; Seinfield and Pandis, 1998). More specifically, Atasoy et al. (2004) defined VOCs, including aromatic hydrocarbons, as vapour phase atmospheric organics with a vapour pressure greater than 1mmHg. The rate at which a compound may volatilise is indicated by the physico-chemical properties of the chemical compounds.

Rates by which organic compounds volatilize are dependent on their physico-chemical properties. For example, compounds with high molecular weight and low vapour pressure usually evaporate slowly (Mackay & Wolkoff, 1973). Also, compounds with low Henry's law constants volatilise much more slowly than those with high Henry's law constants (Lee et al., 2004; Chao et al., 2005).

Volatilization essentially occurs in three stages, consisting of the diffusion of solutes from the bulk of the water to the water-air interface, the transfer across this interface, and finally the diffusion from the interface to the bulk of the air phase (Mackay et al. 1979). The nature of this transfer depends on the physico-chemical properties of the solute in question, the co-presence of other pollutants and their properties, velocity, depth, and turbulence of the water body and the atmosphere above it (e.g. Lee et al., 2004; Thomas, 1990). It can also be explained through thermodynamics; an evaporation process depends on the availability of thermal energy and the vapour pressure deficit between the evaporating surface and the overlying air (e.g. Gianniou & Antonopoulos, 2007). In particular, a continuous supply of heat to meet the latent heat requirement is necessary and the partial pressure in the atmosphere must be lower than the vapour pressure of the surface of the evaporating body. Volatilization in the natural environment is controlled by factors that change rapidly and over a wide range and, consequently, are often nonlinearly interdependent and do not behave in a simple, deterministic way (Thomas, 1990). For example, while chemical compounds of low-molecular weight and high vapour pressure have shown to volatilise rapidly, some high-molecular-weight, low solubility compounds may volatilise at an appreciable rate due to their high activity coefficient in aqueous solution (Smith et al., 1980). Therefore, an understanding of the relationship between VOC emission rate and the system parameters affecting the emission is necessary. Additional complicating factors to consider are the diffusivity coefficient and the presence of modifying materials such as adsorbents, organic films, electrolytes and emulsions as well as the physico-chemical properties of the water body and atmospheric conditions (Thomas 1990).

Currently, accurate Henry's Law constants are unavailable for a large range of hydrocarbons, including many organic compounds. This is especially the case for those compounds that exhibit a low volatility (Chao et al., 2017). Nevertheless, a comprehensive list of a wide range of hydrocarbons and other organic compounds can be found in Sander (2015).

2.2.4 Biodegradability

This is a process by which hydrocarbons are broken down by microbially-facilitated chemical reactions. These reactions are mainly oxidation-reduction reactions that lead to the production of carbon dioxide and, under certain circumstances, methane. From a natural attenuation perspective,

biodegradation acts as a mass conversion process that results in a decline in the total mass of dissolved phase hydrocarbons in groundwater. Biodegradation is generally regarded as the most important parameter in natural petroleum attenuation.

This parameter is typically measured by the half-life of particular compound; a greater half-life denoting a greater persistence of the compound in the environment. Lighter hydrocarbons typically exhibit relatively short half-lives. Hydrocarbons with more complex molecular structures, in turn, generally have a greater half-live.

2.2.5 Density

Hydrocarbons typically exhibit a density less than that of water. However, variations between individual compounds exist. Density plays an important role in the movement of hydrocarbons in the environment through the effects of buoyancy.

2.2.6 Toxicity

This property affects the biodegradability of hydrocarbons as many compounds at high concentrations are toxic to biodegrading microbes. Therefore, toxicity will limit mass breakdown.

2.2.7 Abiotic chemical reactions

Abiotically driven chemical reactions of hydrocarbons can occur under highly oxidizing or reducing environments. Oxidation, for example, has been shown to influence the mobile, extractable phase of coal more than the residual network (Khan et al., 1988). Exposure to light may also cause significant degradation of many hydrocarbons and other organic compounds. Aromatic hydrocarbons, in particular, are able to absorb both visible and ultraviolet light through their ring structures (van der Heul, 2009). Photo-degradation of hydrocarbons can be classified as either direct or indirect photolysis (Plata et al., 2008). Direct photolysis results when a compound absorbs energy from light and degrades further. Indirect photolysis, by contrast, takes place when a different compounds absorbs light energy and reacts to degrade the compounds of interest.

2.3 Hydrocarbon and other organic compounds suitable as indicators of groundwater quality

Profiling of hydrocarbons and other organic compounds in groundwater is typically made difficult by their natural attenuation (also known as weathering). Through volatilisation, leaching, chemical reactions and biodegradation, the profile of these compounds will change with time (e.g. Wang and Stout, 2007). Therefore, indicator compounds will need to withstand natural attenuation for considerable periods of time. In addition, it would be desirous for such compounds to yield information regarding their original source(s). Knowing the provenances of these compounds would

provide key insights into the major natural hydrocarbon emitters in the environment. Finally, such indicator compounds also need properties that allow them to be soluble in groundwater.

The predominance of aromatic hydrocarbons as aqueous contaminants is not surprising (Figure 9). Previous experimental measurements (McAuliffe, 1966; Peake and Hodgson, 1966, 1967; Price, 1976) have shown that solubilities of many hydrocarbons in water are extremely low, even in the range of temperature and pressure conditions encountered under geologic settings. The exception to this observation are gases and low molecular weight aromatics such as benzene, toluene and xylenes (Figure 9). Indeed, for compounds with the same carbon number, aromatics are three orders of magnitude more water soluble than saturates at 25°C (e.g., Vandenbroucke, 1993). Therefore, the relatively small aromatic BTEX compounds would act as ideal indicator compounds based on their solubility properties. However, such compounds are considerably volatile and not necessarily informative as they are widely occurring in both natural (coal, crude oil) and artificial sources. While low-molecular weight PAHs such as naphthalene or phenanthrene are often selected as indicator compounds of contamination, they also biodegrade relatively quickly (Sadler and Connell, 2002) and are not necessarily source-specific. However, these compounds are typically selected as indicators of contamination because of their abundance and relative ease of measurement (Sadler and Connell, 2003).
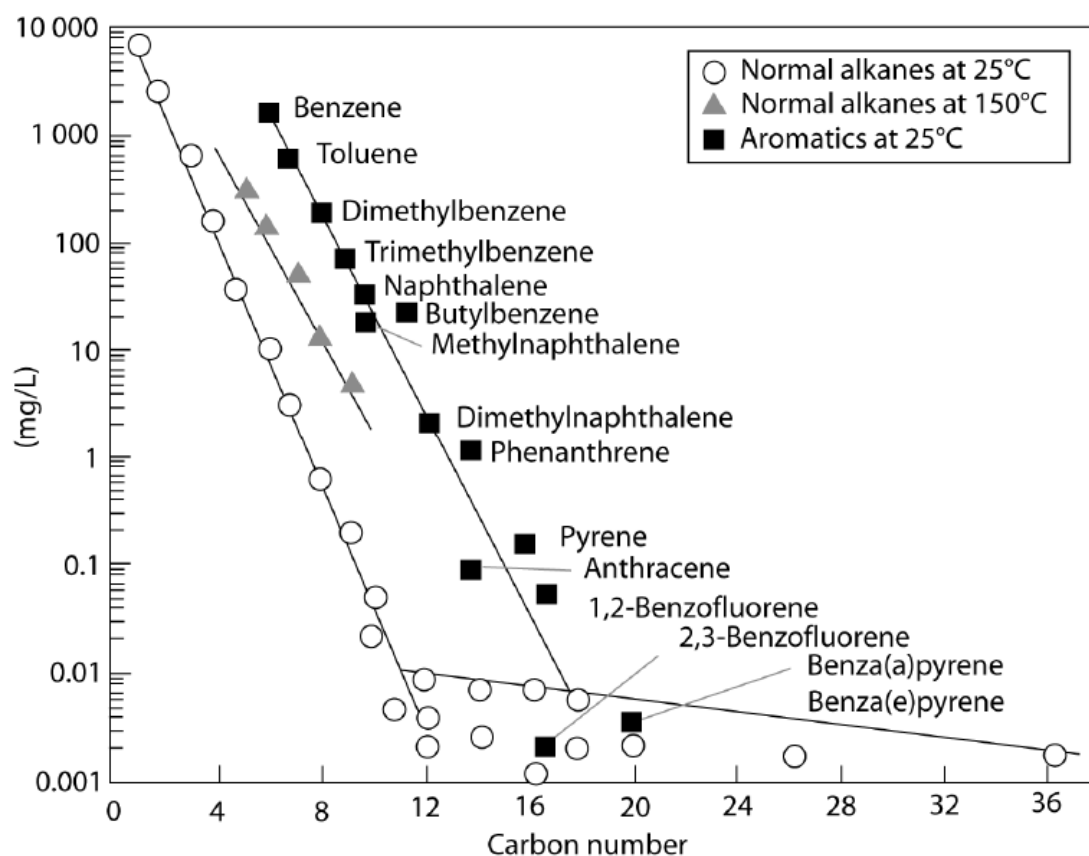
Figure 9 Solubility of *n*-alkane and aromatics in water according to carbon number. Y axis is in logarithmic scale. Source: Huc 2013 (After McAuliffe 1980).
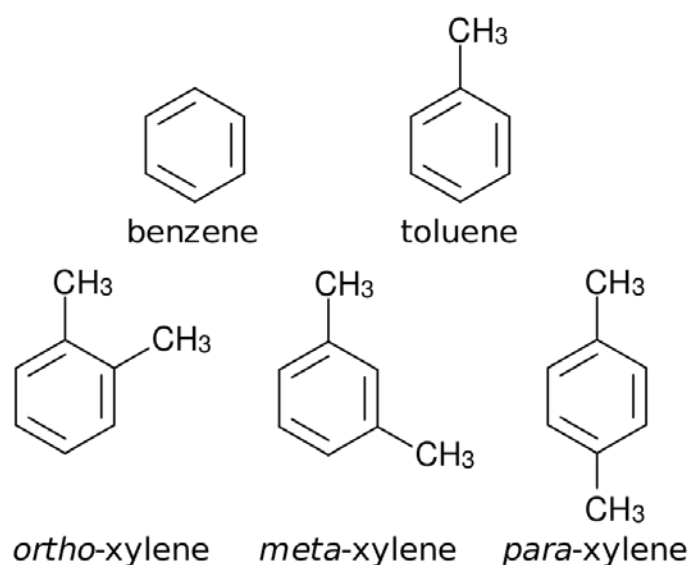
Figure 10 Various monoaromatic compounds

Several hydrocarbon compounds exist that are significantly less volatile and provide substantial information regarding their source(s). These compounds are often referred to as 'biomarkers' due to their origin from biochemically-derived precursor compounds (e.g. Peters et al., 2005). Biomarkers include compounds such as the acyclic isoprenoids pristane and phytane, as well as the polycyclic aliphatics steranes and hopanes (Figure 11). Since many of these compounds can be source-specific, they are often employed as crude oil signatures in petroleum exploration and forensic oil spill characterization (e.g. Peters et al., 2005, Wang and Stout, 2007). Based on both field and experimental work, these compounds exhibit differential resistance to biodegradation. Consequently, biodegradation schemes have been devised to identify the sequential removal of these compounds from petroleum accumulations (Figure 12). These schemes assess the extent of biodegradation based on the relative abundance of various hydrocarbon classes. While n-alkanes are significantly prone to biodegradation, hopanes and steranes, by contrast, are significantly more recalcitrant. Therefore, a range of biomarkers can be used as potential indicators of groundwater quality at a range of different biodegradation states. Nevertheless, these biomarkers are significantly less soluble in water as can be seen when *n*-alkane solubilities are compared with aromatic compounds (Figure 9). Previous investigations into the effects of water washing on crude oils (e.g., Zhang and Zhang, 2000) has shown that a number of polycyclic aliphatics such as pregnane, homopregnane, diasteranes can exhibit some solubility in water. Future studies could investigate their transportation and residence times in groundwater. Another potential candidate as indicator compounds for groundwater quality are the aromatic biomarkers. These compounds are composed of mixed structures of aromatic and saturated rings (e.g. Peters et al., 2005; Yang et al. 2013). Aromatic hopanoids, for example, originate from bacterial precursors, while tera- and pentacyclic aromatics with oleanane, lupine or ursane skeletons indicate higher plant input (Peters et al., 2005 and references therein). Although these biomarkers are typically found in relatively low concentrations in oils and coals (e.g. Peters et al., 2005), their specific fingerprints as well as their reportedly high weathering resistance make them desirable biomarkers for the characterization, correlation, differentiation, and source identification in environmental forensic investigations (Yang et al., 2013). Their relative resistance to biodegradation is particularly noteworthy. For example, Bao and Zhu (2009) observed that the concentrations of alkyl naphthalenes, alkyl phenanthrenes,

alkyl dibenzothiophenes declines, and the concentration of triaromatic steroids rose with increasing biodegradation degree in oils. However, while aromatic biomarkers are highly resistant to biodegradation, they can still be degraded under severe biodegradation conditions, resulting in significant changes to their molecular ratios (e.g., Yang et al., 2003).
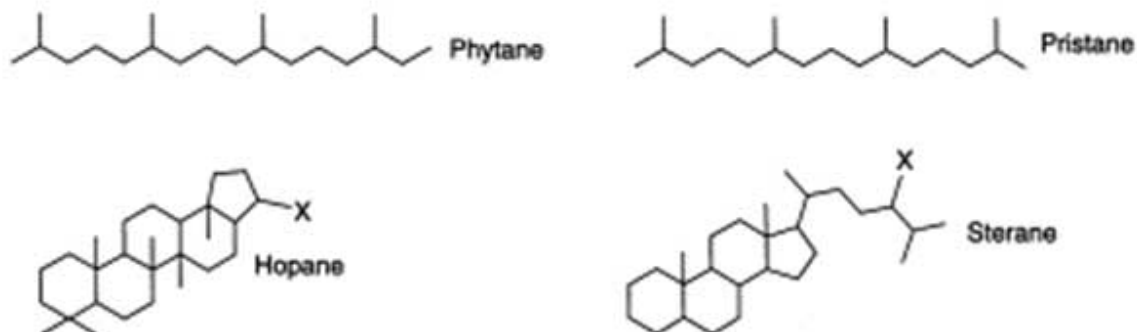
Figure 11 Common hydrocarbon biomarkers. X denotes alkyl group.

Apart from the relatively small and volatile BTEX and PAHs compounds, some aromatic compounds serve as potential indicator compounds of water quality degradation due to hydrocarbons. As shown in Figure 12, some methylated aromatic compounds (e.g., tetramethylnaphthalenes), exhibit significantly greater resistance to biodegradation than numerous acyclic biomarkers. Furthermore, their aromatic chemical structure may impart greater solubility in water. Indeed, Eaganhouse et al. (1993), for example, noted that the aromatic hydrocarbon 1,2,3,4-tetramethylbenzene was one of the most abundant and stable oil constituents in groundwater affected by a pipeline rupture near Bemidji, Minnesota. This compound was commended for its use as a marker for the contamination plume. PAHs can also provide indications of the coalification stage of their original host rocks. In low maturity coals, PAHs often reflect their biogenic origin, while in bituminous coals increased alkylation of PAHs is observed. With further thermal maturation, anthracite is observed (Achten and Andersson, 2015). Identifying these compounds in the environment may therefore help with determining potential sources of these PAHs.

Another potential candidate to serve as indicator compounds of water quality, are polar organic compounds. Their polarity affords significantly more solubility in water than their more hydrophobic hydrocarbon counterparts. Polar polycyclic aromatic compounds, for example, have been previously shown to exhibit greater leaching from contaminate soil and thereby risk groundwater contamination (Larsson et al., 2018). Indeed, Andersson and Achten (2015) suggested the addition of several polar PAHs to the list of compounds that should be investigated for their evaluation of toxicity in the environment. Some polar organic compounds, such as phenols, are appreciably soluble in water (e.g. Huyskens et al., 1975), but can be readily biodegraded (e.g. van Schie and Young, 2000). Other polar compounds occur in coal but are poorly studied and little is known regarding their solubility and transportation in water.

The occurrence of some organic and inorganic chemical species can indirectly indicate the former occurrence of hydrocarbons and other organic compounds in an environmental setting. Their

distribution pattern within a plume may provide indications reaction types the natural attenuation capacity (Beck and Mann, 2010).

Biological degradation of hydrocarbons can result in the formation of various metabolic by-products (e.g. volatile fatty acids, ferrous iron, and methane) due to the reaction between an electron donor and electron acceptor. These metabolic by-products can serve as an indicator of biodegradation (Beck and Mann, 2010).

Finally, another indirect line of evidence relies on electron mass balance calculations to estimate the attenuation capacity of the groundwater system. Here, a change in the electron acceptor/metabolic by-product concentrations (O_2, Mn^{4+}, NO_3^-, Fe^{3+}, SO_4^{2-} and CH_4) between plume and background values is measured as well as the stoichiometry of the hydrocarbon degradation reactions to estimate the contributions of various biodegradation processes (Beck and Mann, 2010).
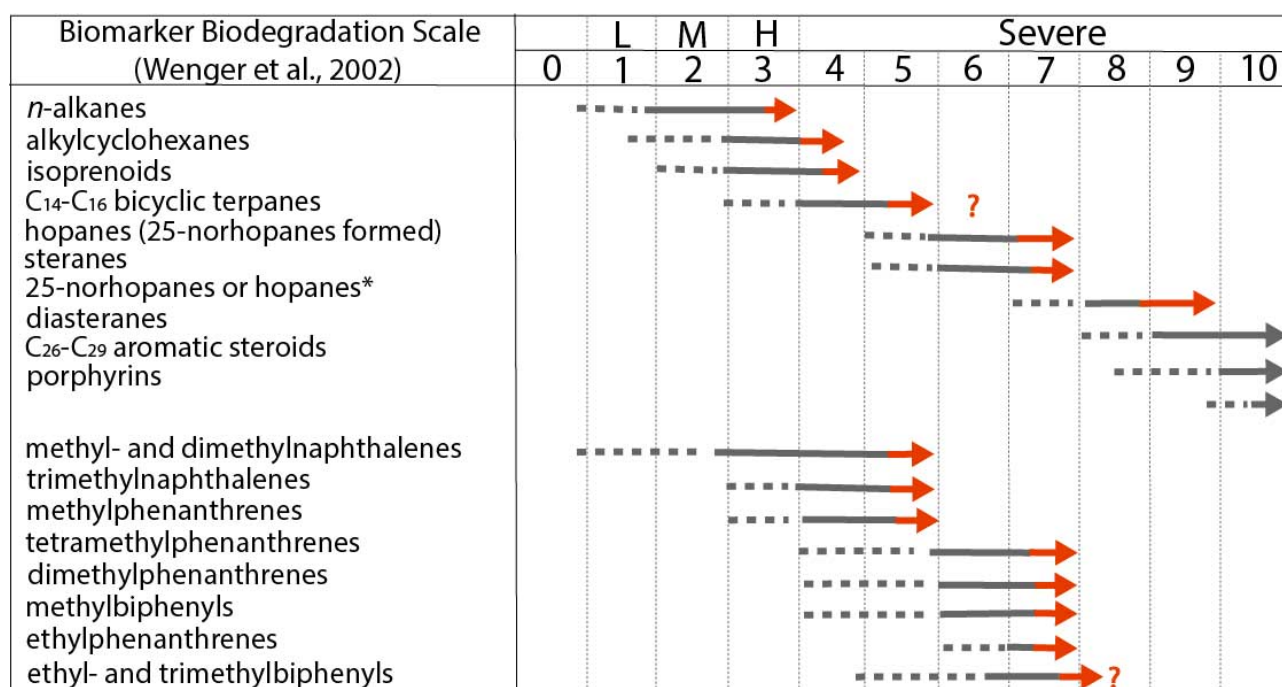
Figure 12 Extent of hydrocarbon biodegradation of a mature crude oil ranked on a scale of 1-10 based on differing resistance of compound classes to microbial attack. Arrows indicate where compound classes are first altered (dashed grey lines), substantially depleted (solid grey lines), and completely eliminated (solid red lines). Degree of biodegradation from Wenger et al. (2001) reflects changes in oil quality: L = lightly biodegraded; M = moderately biodegraded; H = heavily biodegraded. Figure adapted with modifications from Peters et al. (2005).

3 Biological attenuation of hydrocarbons

3.1 Microbial catabolism of hydrocarbons

Most of our understanding of microbial catabolism of hydrocarbons, stems from the study of microbial degradation of materials found on the surface of the earth rather than in the subsurface. In terrestrial settings, outside of industrial applications; hydrocarbons are mostly perceived as contaminating materials from anthropogenic activities including oil production, coal mining, surface spills of hydrocarbons or subsurface leaking tanks (Fuchs et al., 2011). In the subsurface, however, hydrocarbons represent a major source of carbon for microbes and layers of rocks rich in organic matter (such as coal) can represent something of an oasis for microbial life.

3.2 Microbial lineages in coal seams

In the subsurface where cleat systems are filled with formation water coal seams are host to a range of microbes from two of the three domains of life (Figure 13). There is no evidence to date that microscopic eukaryotes occur in in-tact deep surface systems. However, in deep mines, or other areas where coal is exposed to oxygen, eukaryotes can be found and are involved in degradation of coal to a range of other compounds.

Phylogenetic Tree of Life

Bacteria   **Archaea**   **Eukaryota**

Spirochetes
Green Filamentous bacteria
Gram positives
Proteobacteria
Cyanobacteria
Planctomyces
Bacteroides Cytophaga
Thermotoga
Aquifex

Methanosarcina
Methanobacterium
Methanococcus
T. celer
Halophiles
Thermoproteus
Pyrodicticum

Entamoebae
Slime molds
Animals
Fungi
Plants
Ciliates
Flagellates
Trichomonads
Microsporidia
Diplomonads

Figure 13 A modern phylogenetic view of life. Only organisms from the Bacteria and Archaea occur in in-tact subsurface coal seams, though where mining occurs or the coal outcrops on the surface other microbes such as fungi play roles in coal degradation and alteration.

3.3 Life strategies in the coal environment

In the subsurface, light and oxygen are lacking, and alternative strategies are required for the production of energy by microorganisms. Within the bacterial and archaeal domains, a range of metabolic life strategies are employed (Figure 14). Many organisms in these settings obtain their energy by reducing a range of compounds including sulfate, nitrate, ferric iron, other metals or metalloids or carbon dioxide.

Carbon, as opposed to energy generation, can be obtained through either carbon fixation from carbon dioxide (or carbon monoxide) or using more complex organic compounds derived from coal. Unlike eukaryotes, which are typically limited to one mode of growth, many bacteria and archaea have multiple means of deriving energy and carbon; this is termed mixotrophy. Obligate anaerobic bacteria can only grow where oxygen is absent, whereas facultative anaerobic bacteria have the capability to grow in the presence or absence of oxygen and may derive different forms of cell carbon in these environments. For example, an organism may fix carbon dioxide under anoxic conditions but may cleave aromatic compounds in the presence of oxygen. Some obligate anaerobes are aero-tolerant – that is, oxygen does not kill the organism – however, other anaerobes perish in the presence of oxygen.
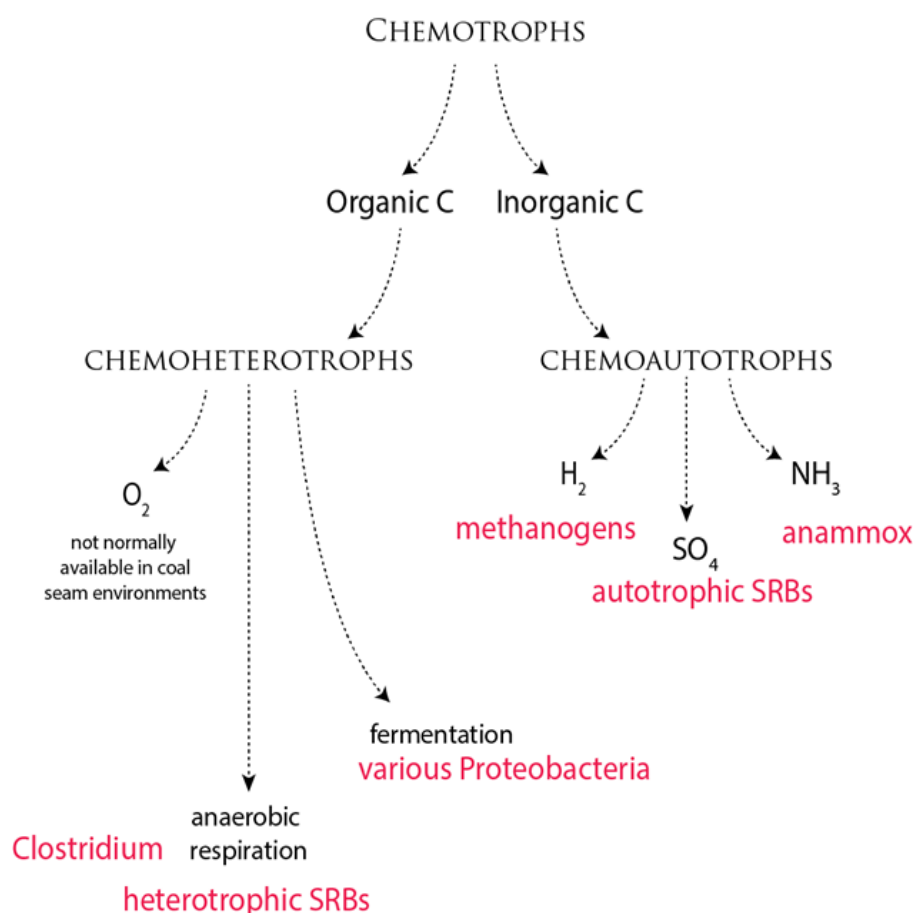
Figure 14 Various chemotrophic strategies

3.4 Origins of PAHs and aliphatic compounds

Microbial degradation of coal requires an array of enzymatic activities. In oxic environments, the degradation of aromatic compounds is facilitated by various redox enzymes (laccases) and hydrogen peroxide reducing enzymes (peroxidases), which occur in a variety of organisms (Quigley and Crawford, 1993). The process of lignin degradation by both aerobic fungi and aerobic bacteria is well studied (see reviews by Leonowicz et al., 1999; Li et al., 2009), but other processes are required for anoxic environments (Carmona and Díaz, 2005). The early anaerobic reactions for degradation of aromatic components of coal are likely to be primarily limited to bacteria (Lovley et al., 1989; Lovley et al., 1996; Gibson and Harwood, 2002). They may be focused on fermentation of interlinking oxygen bridges (Strąpoć et al., 2008). In parallel, aliphatic compounds may be degraded by other bacteria such as *Cytophaga* and *Flavobacterium* (Rahman et al., 2002). The process of coal degradation is not well characterised, but may be analogous to the degradation of lignin (Deobald, 1993). Anaerobic depolymerisation of lignin proceeds via vanillin, vanillic acid and fatty acids as intermediates (Chen et al., 1987). It seems likely that early polyaromatic hydrocarbons (PAHs) may include compounds such as fluorene, anthracene and phenanthrene (Figure 15).
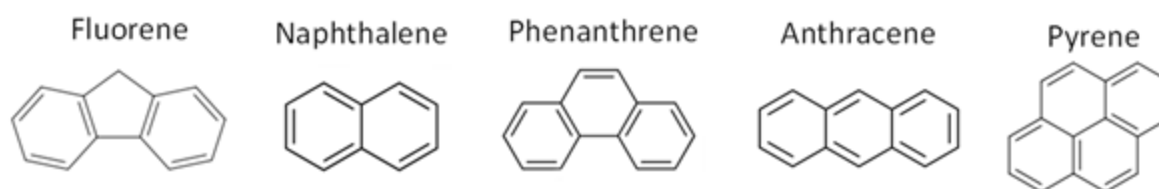
Figure 15 Simple polyaromatic compounds may be intermediates of microbial coal degradation.

These simpler aromatic compounds are then dehydroxylated and decarboxylated, and bound to coenzyme A prior to cleavage of aromatic rings (Harwood et al., 1999; Boll and Fuchs, 2005). After ring cleavage, compounds such as lactate, butyrate and propionate result (Figure 16). These compounds can be fermented to acetate or syntrophically degraded to H_2 and CO_2, if coupled with hydrogenotrophic methanogenesis. In turn, acetate may be fermented by bacteria to CO_2, H_2, alcohols and acids, or to methane via acetoclastic archaeal methanogenesis. The produced H_2 and CO_2 may be used for either acetogenesis or for hydrogenotrophic methanogenesis (Figure 16).

Along with aromatic compounds, coal is likely to include a range of degradable aliphatic compounds. These are likely degraded via one of the two primary anaerobic aliphatic degradation methods: beta-oxidation or fumarate addition (Fuchs et al., 2011; Rabus et al., 2016). The diversity of microbes in coal seam environments is such that the microbes are likely living in different niches, with some species specialising in the degradation of aromatic compounds, others in the degradation of aliphatic compounds, and still others specialised in recycling OM from cells into ever-simpler carbon compounds. Eventually, these end up as precursors of methanogenesis: acetate, formate, simple methyl-containing compounds, hydrogen and carbon dioxide.
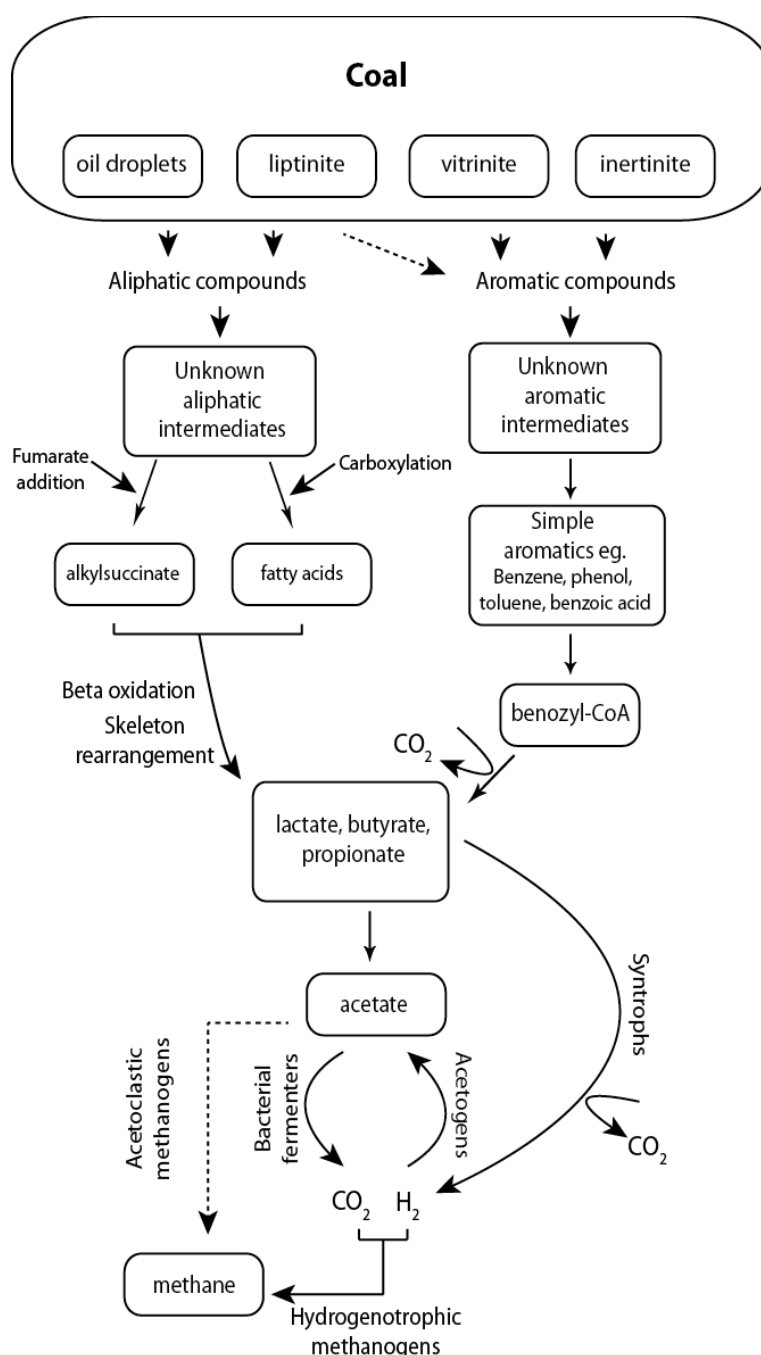
Figure 16 A schematic for the degradation of coal components to methane. Coal is composed of aromatic and aliphatic compounds, which are sequentially degraded via a series of different enzymatic reactions.

3.5 Microbial communities associated with coal seams

Microbial communities associated with coal seams have been analysed using modern molecular ecology techniques (e.g. Shimizu et al., 2007; Strapoc et al., 2008; Green et al., 2008; Li et al., 2008; Penner et al., 2010; Midgley et al., 2010; Vick et al., 2018; Reviewed in Ritter et al., 2015). These studies indicate that the communities in coal are highly variable and diverse. Some broad generalisations, however, are possible.

Betaproteobacteria are a highly versatile group of aerobic and facultative bacteria, some of which fix nitrogen in plants. Most of the comamonads detected in coal appear to be allied to the genera Acidovorax, Comamonas or Delftia. No coal seam-derived comamonads have yet been brought into pure culture, and even microbial enrichment cultures do not appear to contain members of this lineage. Cultured representatives of Acidovorax, Comamonas or Delftia from other environments can grow anaerobically using nitrate as an electron acceptor. The absence of nitrate in many of the media used to enrich microbial communities from coals may be a cause of their absence, although our recent attempts to culture these taxa in the presence of nitrate have been unsuccessful.

In addition to comamonads, numerous other alpha, beta, delta and gammaproteobacterial lineages, commonly from the orders Alteromonadales, Burkholderiales, Campylobacterales, Desulfuromonadales, Desulfovibrionales, Enterobacteriales, Rhizobiales, Rhodobacterales and Rhodocyclales, also occur in coal seam environments (Shimizu et al., 2007; Li et al., 2008; Midgley et al., 2010; Penner et al., 2010). Of these groups, the Desulfuromonadales are likely the most common, with members of the families Desulfuromonadaceae and Geobacteraceae being the most abundant (Li et al., 2008; Penner et al., 2010; Midgley et al., 2010). Both the Desulfuromonadales and its related group, the Desulfovibrionales, contain an array of organisms capable of various types of sulphur reduction, and many members of both of these groups have alternate fermentative modes of metabolism such that they are not limited to sulphur reduction for growth.

Coals also contain a diverse array of Enterobacteriales taxa, where most members are from the family Enterobacteriaceae and have affinities to the genera *Citrobacter, Escherichia, Pantoea and Shigella*. *Citrobacter* and *Pantoea* aside, it is difficult to ascertain the specific identity of these genera, because some *Escherichia* and *Shigella* are identical in their 16S DNA sequences. Alphaproteobacterial lineages are rare for coal seam environments, though organisms with affinities to Rhizobiales, Rhodobacterales and Sphingomonadales are present in some samples (Li et al., 2008; Penner et al., 2010). These taxa appear to be more common in coal than in associated waters. Most of the alphaproteobacterial lineages detected in coal seam environments have been facultative anaerobes (i.e. also able to survive with oxygen present, having respiratory-type metabolisms), probably using compounds such as nitrate as an electron acceptors.

Along with the Proteobacteria, a range of Firmicutes taxa occur in coal seams. Most commonly the organisms detected are clostridia from the families Clostridiaceae, Eubacteriaceae, Peptostreptococcaceae, Veilonellaceae, Incertae Sedis XI and Incertae Sedis XII sensu (Strapoc et al., 2008; Shimizu et al., 2007; Strapoc et al., 2008; Li et al., 2008; Midgley et al., 2010). Several Bacteroidetes taxa, most commonly with affinities to the family Rikenellaceae, have also been detected in coals (Shimizu et al., 2007; Strapoc et al., 2008; Li et al., 2008).

Archaea also occur in coals seam environments. For example, at one field site in the Illinois Basin, archaea from the Methanocorpusculaceae family are present (Strapoc et al., 2008), whereas at a site in the Powder River Basin, archaeal taxa from the Methanosarcinaceae predominate (Green et al., 2008). In contrast, some sites in eastern Australia have mixtures of cren-archaeal and eury-archaeal taxa from the Archaeglobaceae, Methanobacteriaceae, Thermococcaceae and the Desulfurococcaceae families (Li et al., 2008; Midgley et al., 2010). One Japanese coal aquifer appears to have the most diverse range of archaea examined thus far, and includes representatives from the Desulfurococcales, Methanobacteriales, Methanomicrobiales, Methanosarcinales and Thermoproteales orders and the Thermoplasmata class (Shimizu et al., 2007). In Australia, only two

published studies, both from CSIRO, have been undertaken on the microbial communities associated with coal seams (Li et al., 2008; Midgley et al., 2010). Data from Li et al. (2008) suggest that microbial consortia in a brown coal from the Port Phillip Basin in Victoria are dominated by proteobacterial lineages, though some other phyla, notably the Bacteroidetes and Firmicutes, were also detected. Midgley et al. (2010) detected a range of bacterial taxa from the phyla Firmicutes, Proteobacteria and Actinobacteria (in order of decreasing abundance). Li et al. (2008) did not detect methanogenic archaeal species in either the coal nor formation water samples, although Midgley et al. (2010) detected methanogenic archaea from the family Methanobacteriaceae.

More recently, a number of studies have used ecogenomics or metagenomics to try to understand microbial diversity in the coal system (Guo et al., 2012; Wei et al., 2013; Ghosh et al., 2014; Wei et al., 2014; Guo et al., 2015; Lawson et al., 2015; Susilawati et al., 2015a; Zhang et al., 2015a; Susilawati et al., 2015b; Raudsepp et al., 2016; Vick et al. 2016; Vick et al., 2018). By and large, these studies mirror previous work, although changes in methods used mean that many report greater diversity than earlier studies. Earlier work emphasised how variations in abiotic factors (e.g. coal type, water chemistry and physicochemical descriptors such as temperature) relate to differences in community composition.

Vick et al. (2018), in particular, offers interesting insights into the microbial communities in the Surat and Bowen Basins. The study by Vick and co-workers assigns Coal Seam MicroBiome (CSMB) numbers; a reference number for coal-associated microbial 'species' ≈ OTUs. The use of the reference numbers means that microbial communities can be easily compared across seams globally. The study also includes the most comprehensive microbial surveys of the Surat and Bowen Basins conducted to date. The study reports that ~861 OTUs where observed in the Bowen Basin formation waters, while ~1356 OTUs were observed in the Surat Basin. Almost twice as many OTUs (2789) were reported for the Sydney Basin. There was considerable overlap between the three basins with just 55 and 179 OTUs demonstrated to be endemic to the Bowen and Surat Basins, respectively.

3.6 Strategies for dealing with the diverse range of aromatic and aliphatic hydrocarbons

Regardless of whether microbes are living on coal the surface or in subsurface, the array of different hydrocarbons encounter are incredibly diverse. For this reason microbes tend to use a range of biochemical pathways to convert this diversity into a smaller subset of central metabolites which are then 'funnelled' into a central degradation pathway (Fuchs et al., 2011). For aromatic compounds, these key metabolites are catechol, protocatehuate and benzoyl-CoA (Figure 17).
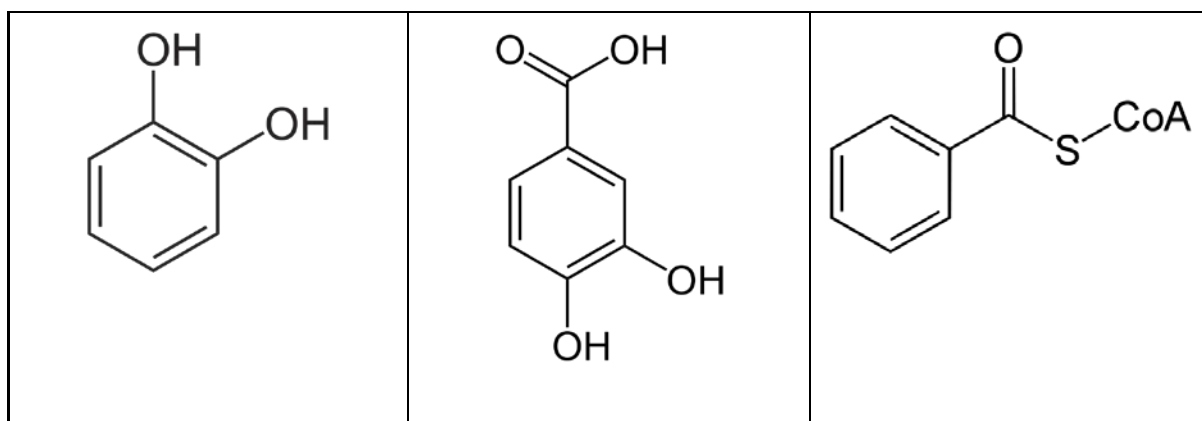
Figure 17 Left to right: Catechol, protocatehuate and benzoyl-CoA. These three compounds represent key central intermediates through which degradation of aromatic hydrocarbons proceeds. The use of catechol and protocatehuate is more common in aerobic taxa, while the benoyl-CoA tends to be central immediate in anaerobic organisms.

For aliphatic compounds, the plant cuticle on the surface of leaves, and plant oils likely represent the major sources of these compounds in non-geological settings (Fernández et al., 2016). The plant cuticle is composed of two main monomers, cutin and cutan (Deshmukh et al., 2005; Riederer and Muller, 2008). Cutin is comprised primarily of aliphatic monomers such as 16-hydroxy palmitic acid that are bound together in a linear polyester.

The structure of the cutan monomers are less well understood (Domínguez et al., 2011), however, they likely contain aromatic subunits and are more difficult to degrade (Deshmukh et al., 2005). In contrast, plant oils tend to be triglycerides and typically include even-numbered fatty acids such as oleic, stearic or palmitic acid (Wool and Sun, 2011).

Alphatic compounds are degraded differently to aromatic compounds and by differing groups of organisms. Under oxic conditions, the most readily degraded of the aliphatic compounds are n-alkanes for which degradation is dependent on the length of the alkane (Abbasian et al., 2015). Very short chain alkanes (C1-C4) are degraded by methane monooxygenases, lengths from C5-C16 are degraded by alkane monooxygenases or cytochrome P450s, while longer chain alkanes (C15+) are frequently degraded by dioxygenases (Abbasian et al., 2015). Alkenes are also readily degraded via similar enzymes to those used in alkane degradation (Grossi et al., 2008). Of the more difficult types, branched chain alkanes tend to have slower degradation rates than either n-alkanes or alkenes (Alvarez et al., 2009). Similarly, cyclicaliphatic compounds are relatively abundant in coal-associated environments and are more resistant to decomposition than straight chain aliphatic compounds. Under anoxic conditions the rates of degradation of all aliphatic compounds are markedly slower. Nevertheless, anaerobic aliphatic degradation is common and undertaken by a diverse group of bacteria. Fungal degradation of aliphatic compounds is also possible, though the range of organisms that can degrade these compounds is smaller and the pathways are less well studied. For example, *Mortierella* is known to convert aliphatics to ω-hydroxic and ω-dioic acids via alcohol dehydrogenases (Waché, 2013). Similarly, Aspergillus and other mold species are known to undertake subterminal oxidation of aliphatic compounds various alcohols (Pelz and Rehm, 1973).

For aromatic compounds, the most abundant extant source of plant aromatic compounds is lignin. Lignin is a heterogeneous, complex, cross-linked polyaromatic compound that allows flexible

cellulose microfibrils to be reinforced, creating woody tissues. Most of the monomers in lignin are p-coumaryls, coniferyls, and sinapyl alcohols (Li and Chapple, 2010).

Microbial activities towards aromatic and aliphatic compounds found in coal are largely analogous to those used to degrade portions of the living or moribund plant material, though in the coal these compounds are the most abundant forms of carbon.

In broad terms the catabolism of these compounds can be divided into two groups: catabolism under oxic and catabolism under anoxic conditions. The organisms that operate in these two groups are also clearly demarcated. That is, in the oxic setting both fungi and obligate and facultatively aerobic prokaryotes (bacteria and archaea) are involved in the degradation of aromatic and aliphatic compounds while degradation of these compounds in anoxic settings will only involve obligate and facultatively anaerobic prokaryotes. There are some anaerobic fungi, notably the chytrids of the phylum Neocallimastigomycota, however, these are limited to animal digestive tracts (Griffith et al., 2010).

3.7 Bacterial degradation of aromatic and aliphatic compounds

3.7.1 Aromatic compounds

Many bacterial taxa probably play roles in degrading aromatic compounds. Genera previously implicated in oxic processes include: *Achromobacter, Alcaligenes, Arthrobacter, Acidovorax, Bacillus, Brevibacterium, Burkholderia, Chryseobacterium, Cycloclasticus, Marinobacter, Mycobacterium, Nocardioidetes, Pasteurella, Palaromonas, Psedomonas, Ralstonia, Rhodanobacter, Rhodococcus, Staphylococcus, Strenotrophomonas, Sphingomonas, Terrabacter* and *Xanthomonas* (incomplete listing obtained from (Seo et al., 2009). Unlike fungi which are almost exclusively aerobic (a small number of groups notwithstanding), different bacteria can degrade BTEX and PAH compounds under both oxic and anoxic conditions though the pathways used and the organisms involved vary by oxygen status.

Bacteria have been demonstrated to aerobically use naphthalene (Cerniglia, 1992; Albert et al., 1996; Goyal and Zylstra, 1997), fluorene (Boldrin et al., 1993; Grifoll et al., 1995; Wattiau et al., 2001), phenanthrene (Moody et al., 2001; Moser and Stahl, 2001; Prabhu and Phale, 2003), fluoranthene (Juhasz et al., 1997; Boonchan et al., 1998; van Herwijnen et al., 2003), pyrene (Jimenez and Bartha, 1996; Vila et al., 2001) and benzo(a)pyrene (Grosser et al., 1991; Juhasz et al., 2002; Ye, Akmal Siddiqi, Maccubbin, Kumar, & Sikka, 1996) as a sole sources of carbon.

In comparison, anaerobic PAH degradation is relatively more poorly studied (Spormann & Widdel, 2000). Degradation of these compounds can occur under nitrate-, sulfate- or metal-reducing and in carbon dioxide reducing (methanogenic) environments (Spormann & Widdel, 2000). The mechanism of degradation differs markedly from processes in oxic environments. While many aerobic PAH degradations begin by using (di)oxygenase enzymes, carboxyl groups are typically added to aromatic rings by anaerobic bacteria (Annweiler et al., 2002). For example, Woline*lla succinogenes* is known degrade toluene in anoxic condition (Meckenstock, 1999). Perhaps the best studied anaerobic monoaromatic degraders are related to the genera *Azoarcus* or *Thauera* (Achong et al., 2001; Leuthner, 1998; Leuthner and Heider, 2000; Leuthner et al., 1998; Meckenstock, 1999; Zhou et al., 1995). Bacteria have also been anaerobically shown to degrade benzene (Abu Laban,

Laban, Selesi, Jobelius, & Meckenstock, 2009; Aburto-Medina and Ball, 2014; van der Zaan et al., 2012) and polyaromatic hydrocarbons (Ambrosoli et al., 2005; Braun et al., 2015; Meckenstock et al., 2016).

3.7.2 Aliphatic compounds

Numerous bacteria have been shown to grow on aerobically straight chain and branched alkanes including *Bacillus, Mycobacterium, Rhodococcus* and *Acinetobacter* (Nhi-Cong et al., 2009; Parthipan et al., 2017); (Throne-Holst, Wentzel et al., 2007)(Parthipan et al., 2017). Similarly, capacity for degradation of alkenes have also been observed in several bacterial groups including *Xanthobacter* (Zhou et al., 1999) and *Rhodococcus* (*Nocardia*) species (Saeki et al., 1999). *Cycloaliphatic* compounds have also been shown to be degraded by Pseudomonas (Anderson et al., 1980; Saeki et al., 1999), *Acinetobacter* (Trudgill, 1991) and *Rhodococcus* (Yi et al., 2011) species.

Under anoxic conditions, numerous nitrate- and sulphate reducing bacteria have been also shown to degrade aliphatic compounds including alkanes, alkenes and cyclic aliphatic compounds (Musat et al., 2010; Spormann and Widdel, 2000; Callaghan et al., 2012; Kung et al., 2014; Jaekel et al., 2015).

3.8 Fungal degradation of aromatic and aliphatic compounds

3.8.1 Aromatic compounds

Fungi

The ability to degrade of aliphatic compounds is phylogenetically widespread in the fungal kingdom, though a relatively smaller number of species from the estimated tens of millions of fungal species (Bass and Richards, 2011) appear to be involved.

Three broad, polyphyletic groups of fungi have been comparatively well studied with regard to their abilities to degrade aromatic compounds: the white rot, brown rot and soft rot fungi (Goodell et al., 2008). All of these groups of fungi produce some form of ligninase. This is a collective term, rather than a specific enzyme. The enzymes involved in activity against aromatic compounds in fungi are generally of one of two kinds. The first, phenol oxidases (also called laccases) use oxygen. The second group include the various heme peroxidases (lignin or manganese peroxidase) and these enzymes use peroxidase as a co-factor (Dashtban et al., 2010).

White Rot Fungi

The best studied white rot fungus in the world is probably *Phanerochaete chyrsosporium* and much of our understanding of white rot activity is derived from this one fungus (Broda, 1994). In terms of the kinds of fungi that undertake white rot activity, most are basidiomycetes though they do not form a single monophyletic unit. The distribution of the different types of lignases, varies by fungal group. For example, lignin peroxidases have been found in the Polyporales, manganese peroxidases have been detected in both the Russulales and Polyporales, while versatile peroxidases have been observed the Agaricales (Zhou et al., 2014). Unlike the soft rot lignin degraders, most of the taxa

involved in white rot degradation of aromatic compounds require significant oxygen (Bruce & Palfreyman, 2002) and thus tend to only be functional in oxic, terrestrial habitats.

White rot fungi have demonstrated activity against a range of aromatic compounds including BTEX. For example, *P. chyrsosporium* has been demonstrated to completely degrade all BTEX compounds, and a variety of toluates, both individually and in mixtures to carbon dioxide. This process is relatively rapid, and in media in which these compounds were the only form of carbon, and complete degradation occurred in two days. Intriguingly, degradation of these compounds does not seem to require the production of extracellular lignases (Yadav and Reddy, 1993). Similar, Trametes versicolor, a member of the Polyporales, has also been demonstrated to rapidly degrade all BTEX compounds via the production of hydroxyl radicals (Aranda et al., 2010).

Along with monoaromatics, a host of white rot fungi (including: *Bjerkandera, Ceriporia, Dentipellis, Heterobasidionm, Mycoaciella, Peniophora, Phanerochaete, Phlebia, Phlebiella, Pseudochaete Rhizochaete* and *Trichaptum* species) have been shown to degrade the polyaromatic hydrocarbons anthracene, phenanthrene, fluoranthene and pyrene (Lee et al., 2014). Similar catabolic potential has been observed for *Pleurotus ostreatus* which has been shown to degrade anthracene, benzo[a]pyrene, pyrene and phenanthrene (Eggen and Majcherczyk, 1998; Novotný et al., 1999). Unlike BTEX compounds which are degraded in timescales of days by white rot fungi, removal of PAHs is slower is reported to take weeks or months (Eggen and Majcherczyk, 1998; Eggen and Sveum, 1999). For higher molecular weight compounds like benzo(ghi)perylene, benzo(a)pyrene, chrysene and dibenz(ah)anthracene, efficient oxidation by fungi was dependant on the solubilisation of these compounds (Zheng and Obbard, 2002). Such solubilisation is dependant on the production of surfactants which may be produced by microbes in situ. Regardless, even partial oxidation of these compounds results in increased biodegradation and bioavailability for bacterial communities. White rot and other aromatic degrading fungi may thus pay key ecological roles in initial processing of aromatic compounds (Andersson et al., 2003; Meulenberg et al., 2006).

Brown Rot Fungi

Phylogenetically all brown rot fungi are from the Basidiomycota and are distributed across the families: Auriculariaceae, Coniophoriaceae, Coprinaceae, Corticiaceae, Paxillaceae, Sparassidaceae, Stereaceae and Tricholomataceae (Worrall, 1989; Osiewacz, 2013). Unlike white rot fungi, brown rot fungi typically do not produce liginases (Cowling, 1961; Ritschkoff, 1996; Highley and Murmanis, 1985). Instead their attacks on aromatic compounds are facilitated by the creation of hydroxyl radiations produced via Fenton chemistry (Kerem et al., 1999; Paszczynski et al., 1999; Presley et al., 2016).

Brown rot fungi have been demonstrated to degrade polyaromatic hydrocarbons. For example, Laetiporus sulphureus, has been shown to degrade both pyrene and phenanthrene (Sack et al., 1997). Similarly, a 2011 study demonstrated brown-rot degradation of the halogenated polyaromatic hydrocarbon DDT (1,1,1-trichloro-2,2-bis (4-chlorophenyl) ethane) by *Daedalea dickinsii*, *Fomitopsis pinicola* and *Gloeophyllum trabeum* (Purnomo et al., 2011).

Soft Rot Fungi

Most soft rot fungi are micro fungi, that is, mostly ascomycetous fungi that do not produce large fruiting bodies (Savory, 1954). In broad terms, the ability of soft rot fungi to degrade aromatic compounds appears to be less than for white or brown rot fungi. Though the group is more poorly

studied than either brown or white rot fungi. In some settings, soft rot fungi are potentially more important, for example, in environments with lower oxygen (e.g. underwater), soft rot fungi may be more important than either brown or white rot fungi (Bruce and Palfreyman, 2002). In soft rot fungi, activity against aromatic compounds is thought to use a system for generating free radicals, in concert with phenol oxidases. While all soft rot fungi are cellulolytic, not all species can degrade lignin. Those that can include a large range of phylogenetically disparate ascomycetes including some *Acremonium, Allescheria, Ceriporiopsis, Coonemeria, Cladorrhinum, Graphium, Humicola, Lecythophora, Lulworthia, Monodictys, Paeciliomyces, Phialocephala, Phialophora, Phoma, Preussia, Sphaeropsis, Sporotrichum, Stachybotrys, Thielavia* and *Thermoascus* species (Levy, 1966; Tuomela, 2000; Bruce and Palfreyman, 2002). These fungi can operate under a diverse range of environmental conditions including at high osmotic stress (i.e. in seawater) and at high temperatures (Johnson, 1956; Meyers and Scott, 1968; Mouzouras, 1989; Bruce and Palfreyman, 2002).

Several studies have reported activities of soft rot fungi against aromatic compounds. For example, *Lecythophora hoffmannii*, has been demonstrated to degrade nine monoaromatic compounds (Bugos et al., 1988). Similarly, *Preussia, Chaetomium* and a *Stachybotrys* species were demonstrated to completely degrade phenols, coniferyl, vanillic, benzoic and hydroxybenzoic acids (Haider and Trojanowski, 1975).

Brown rot fungi, by contrast, are known to be able to cleave (via oxidation) Cα-Cβ bonds in lignin and brown rotted plant material is also enriched in lignin that has modified by the extensive removal of alky side chains. White rot fungi are in many ways the archetypal lignin degraders and their enzymes for these process, most notably lignin and manganese peroxidase and laccases have been particularly well studied.

3.8.2 Aliphatic compounds

Much of the research into fungal degradation of lipidic compounds has centred around infection of either plant or insect tissues. In these settings, fungi need to penetrate the cuticle in order to infect the host. This activity is certainly widespread in the fungi, though it is less studied than other aspects of fungal catabolism. In *Beauveria bassiana*, for example, lipidolytic activity is conferred by a suite of cytochome P450's which convert alkanes to alcohols via terminal oxidation, subsequent alcohol or aldehyde dehydrogenase activity further oxidises the product which is then degraded via β-oxidation.

Part II Historical Indications of Hydrocarbons in the Bowen and Surat basins

4 Assessment of Groundwater Hydrocarbon Records from the UQ CCSG Queensland Water Atlas

4.1 Introduction

Because of a relatively long history of petroleum, including CSG, exploration and development as well as agricultural use of groundwater, the Bowen and Surat basins provide a significant amount of water quality data, bore/well data as well as detailed geological models (Hunter et al., 2016). In Australia, groundwater monitoring is employed to establish trends in water quality before, during and after mining and CSG activities. The Water Act 2000 establishes responsibilities for Queensland petroleum tenure holders to monitor, assess, and minimize the risks that CSG operators pose to aquifer water quality (DNRM, 2016). Furthermore, if multiple adjacent gas fields are present, impacts of water extraction on groundwater pressure can overlap and a cumulative approach is needed for the effective assessment and management of groundwater pressure impacts. In Queensland, the Surat Cumulative Management Area (CMA) has been established in 2011 where the Office of Groundwater Impact Assessment is responsible for assessing impacts and establishing integrated management arrangements in an Underground Water Impact Report (e.g., DNRM, 2016) updated every three years. The primary use of groundwater from the Cumulative Management area is for consumptive purposes including agriculture, industry, power stations, urban, stock and domestic usages. A total amount of some 215,000 megalitres per year is extracted for these purposes with 55,000 megalitres originating from the Condamine Alluvium and about 85,000 megalitres per year from other Great Artesian Basin aquifers. The remainder is extracted from volcanic sediments and deeper formations beneath the Great Artesian Basin (DNRM, 2016).

In this study, we investigated a large chemical dataset of company-derived and public water samples that was submitted to the UG CCSG Water Atlas, a web-based system enabling the integration, analysis, and 3D sub-surface visualization of groundwater monitoring data and geological models (Hunter et al., 2016). This atlas was established to 1) improved data collation across multiple organizations and monitoring programs; 2) establish more streamlined quality assurance and quality control procedures; 3) and provide readily accessible easy-to-use tools for evaluating changes in chemistry due to analytical, environmental, or geological factors (Hunter et al., 2016)

4.2 Sampling area

Due to the impacts of multiple CSG fields adjacent to each other, the Surat CMA was established in 2011 to provide a system to assess and manage the cumulative underground water impacts from multiple petroleum tenures. It covers the area of CSG development in the Surat Basin and the southern Bowen Basin. The extent of the Surat CMA is shown in Figure 1B.

4.3 Sampling and analysis

Water samples were collected from baseline, monitoring and CSG wells penetrating horizons in the Surat CMA by the following companies: APLNG; Arrow Energy; Origin Energy; QGC; and Santos. This water chemistry dataset was collected from between 2009 and 2014, containing a comprehensive list of hydrocarbons and other organic compounds and covers important aquifers in the Surat CMA. Sample collection, transportation and storage complied with Australia/New Zealand standards, AS/NZS 5667.1:1998 (AS/NZS, 1998), (Water Sampling Guidelines—Part 11 Guidance on sampling groundwaters) and Monitoring and Sampling Manual 2009, Environmental Protection (Water) Policy (DEHP, 2009).

Results were submitted to the Centre for Coal Seam Gas, University of Queensland, for incorporation into the UQ CCSG Water Atlas. It should be noted that the results submitted and discussed in this report is patchy and does not represent a continuous span of data for specific locations over several years. Furthermore, we can only discuss the detection of various hydrocarbons and other organic compounds relative to their limit of reporting. These caveats needs to be taken into account when interpreting the results discussed herein. Future studies involving a more continuous dataset for specific locations over an extensive period of several may alter or corroborate the conclusions that can be drawn here.

4.4 Results and discussion

Overall occurrences of hydrocarbons and other organic compounds in the Surat CMA

Tables 3 and 4 show the range of hydrocarbons and other organic compounds that have been analysed and their concentrations relative to detection limits. As can be seen from these tables, relatively few compounds have concentrations above the limit of reporting. Based on these results, it appears that the occurrences of hydrocarbons and other organic compounds in the CMA groundwater is limited. These results also compare with a previous literature survey of hydrocarbon and other compounds in groundwater from coal-bearing Australian basins in Queensland and New South Wales (Schinteie et al., 2015). However, it should be noted that the data does not represent a continuous span for specific locations over several years. Furthermore, there is no supporting information such as drilling/hydrofraccing activity, history of any spillages, location of petroleum storage tanks etc.

Of those compounds that yielded values above their detection limits, the majority belonged to the Total Recoverable Hydrocarbons (TRHC) or, simply stated, Total Petroleum Hydrocarbons (TPH). TPH is defined as the measurable amount of petroleum-based hydrocarbons in an environmental medium (e.g. Schinteie et al., 2015). Since there are over several hundred chemical compounds that are defined as petroleum-based, it is not practical to measure each one separately. However, it is useful to measure the total amount of TPH at a site. TPH is a mixture of chemicals comprising aliphatic hydrocarbons, cycloalkanes, monoaromatics, alkanes and polar aliphatics and aromatics (containing N, O or S). TPH can be divided into groups of petroleum hydrocarbons that act alike in soil or water (hydrocarbon fractions) but may contain many individual chemicals (e.g. Schinteie et al., 2015). TPH is typically divided into the following groups (Although variations, such as C15-C28, occur):

- C6-C10 (excluding BTEX)

- >C10-C16

- >C16-C34

- >C34-C40.

Due to the importance of BTEX compounds, these are typically separately discussed. Likewise, PAHs are also separately discussed.

Isolated TPH occurrences > LOR were noted in the:

- Bandana Coal Measures between 1/09/2009 and 15/09/2009 (C10-C14, ≤1.02 ppb; C15-C28, ≤1.8 ppb; C29-C36, ≤0.39);

- Hutton Sandstone in 5/12/2014 (C6-C10, ≤0.01 ppb; C10-C14, ≤0.17 ppb; C10-C16, ≤0.16; C16-C34, ≤0.25 ppb; C15-C28, ≤0.18 ppb; C29-C36, ≤0.09 ppb; C34-C40, ≤0.05 ppb; C10-C40, 0.41 ppb; C10-C36, ≤0.44 ppb);

- Kumbarilla Beds in 8/06/2011 (C6-C10, 0.02 ppb);

- Springbok Sandstone between 28/06/2014 and 5/12/2014 (C10-C14, ≤3.51 ppb; C10-C16, ≤3.47 ppb; C16-C34, ≤8.52 ppb; C15-C28, ≤7.87 ppb; C29-C36, ≤1.03 ppb; C34-C40, ≤0.55 ppb; C10-C40, ≤9.64 ppb; C10-C36, ≤9.42 ppb);

- Precipice Sandstone between 18/11/2011 and 22/11/2013 (C10-C14, ≤0.08 ppb; >C16-C34. ≤0.34 ppb; C15-C28, ≤0.31 ppb);

- Mooga Sandstone between 25/10/2012 and 30/01/2014 (>C10-C16, ≤0.28 ppb; >C16-C34, ≤0.36 ppb; C15-C28, ≤0.39 ppb; C29-C36, ≤0.28; >C34-C40, ≤0.18).

Isolated occurrences of BTEX compounds > LOR were noted in the:

- Condamine River Alluvium in 18/11/2013 (toluene, 23 ppb);

- Hutton Sandstone 18/03/2014 (toluene, 2 ppb).

The toluene concentration levels in these units are well below drinking water guidelines imposed by the Queensland Public Health Regulation (800 ppb; QPHR 2005), Australian Drinking Water Guidelines (800 ppb; NHMRC 2004), World Health Organisation Drinking Water Guidelines (700 ppb, WHO 2008), and the United States National Primary Drinking Water Standards (1000 ppb; US-EPA 2003).

TPH and BTEX compounds were also detected in the Gubberamunda Sandstone and the Walloon Coal Measures. Due to a larger available dataset, these two sedimentary units will be discussed in more detail below.

Table 3 Hydrocarbons analysed in baseline assessments and water quality monitoring in the Surat basin. NA = number of water samples not analysed for hydrocarbons; LOR = number of water samples with hydrocarbons reported at or below limit of reporting; >LOR = number of water samples with hydrocarbons reported above detection. Yellow highlight shows most often detected hydrocarbons.

Parameter	NA	LOR	>LOR	Parameter	NA	LOR	>LOR
C6-C10 fraction	778	152	10	Propane	888	52	0
C6-C10 fraction minus BTEX	816	117	7	Propene	888	52	0
C6-C9 fraction	219	708	13	Butane	888	52	0
C10-C14 fraction	219	693	28	Butene	888	52	0
C10-C16 fraction	923	14	3	Styrene	855	85	0
C10-C36 fraction	766	133	41	Anthracene	232	708	0
C10-C40 fraction	923	12	5	Benz(a)anthracene	232	707	1
C15-C28 fraction	219	658	63	Benzo(a)pyrene TEQ WHO	384	555	1
C16-C34 fraction	923	12	5	Benzo(b)fluoranthene	232	707	1
C29-C36 fraction	219	671	50	Benzo(g.h.i)perylene	232	708	0
C34-C40 fraction	923	15	2	Benzo(k)fluoranthene	232	707	1
Total C6-C36	472	446	22	Benzo(a) pyrene	615	325	0
SGC10-C14 fraction	894	46	0	Acenaphthene	305	635	0
SGC15 - C28 Fraction	894	42	4	Acenapthylene	305	635	0
SGC29-C36 fraction	894	40	6	Fluorene	399	541	0
SGC10-C36 fraction (sum)	894	39	7	3-Methylcholanthrene	472	468	0
>C10-C16 fraction	795	141	4	7,12-Dimethylbenz(a)anthracene	472	468	0
>C10-C40 fraction	801	110	29	diben(a.h)anthraceneC22H14	232	708	0
>C16-C34 fraction	795	128	17	1.3.5-Trimethylbenzene	876	64	0
>C34-C40 fraction	801	135	4	1.2.4-trimethylbenzene	876	64	0
SG>C16-C34 fraction	894	42	4	Chrysene	232	707	1
SG>C34-C40 fraction	894	43	3	Fluoranthene	232	708	0
SG>C10-C40 fraction (sum)	888	48	4	Indeno(1.2.3cd)pyrene	253	687	0
TPH C6-C9 fraction	882	57	1	Meta & para –Cresol	472	466	2
TRPH C10-C16 fraction	915	25	0	Meta & para-Xylene	188	752	0
TRPH C16-C34 fraction	915	24	1	n-Butylbenzene	855	85	0
TRPH C34-C40 fraction	915	24	1	n-Propylbenze	932	8	0
Benzene	17	922	1	Napthalene	67	870	3
Ethylbenzene	17	923	0	o-Cresol	472	468	0
Toluene	17	910	13	p-Isopropyltoluene	855	85	0
Xylenes total	613	327	0	Phenanthrene	74	862	4
Sum of BTEX	784	146	10	Pyrene	232	706	2
Ortho-xylene	188	752	0	sec-Butylbenzene	855	85	0
				Tert-Butylbenzene	888	52	0
				Sum of polycyclic aromatic hydrocarbons	791	149	0

Elevated hydrocarbon occurrences in the Gubberamunda Sandstone

The results from a total of 52 individual water samples were made available by the companies and represent a timespan from 31/05/2011 to 18/03/2014. Out of these 52 water samples, nine yielded hydrocarbons > LOR. These hydrocarbons consisted of toluene and a suite of C_6 to C_{10} compounds (excluding BTEX). Benzene concentration levels were at or below the limit of reporting for the very same sample that displayed relatively high toluene levels. No information was available on ethylbenzene and xylenes levels.

Relatively high toluene concentration levels (> LOR) were detected in groundwater samples on the following collection dates: 15/11/2011; 12/09/2012; 15/09/2012; 13/04/2013; 13/05/2013; 27/06/2013; 23/07/2013; 29/09/13; 01/10/13; and 15/12/2013. Toluene concentrations during these periods ranged from 89 ppb to 203 ppb (Figure 18).

In addition, relatively high C6-C10 (minus BTEX compounds) TPH concentration levels (> LOR) were detected in groundwater samples on the following collection dates: 12/09/2012; 13/04/2013; 13/05/2013; 27/06/2013; 23/07/2013; and 01/10/13. C6-C10 (minus BTEX compounds) TPH concentrations during these periods ranged from 0.04 ppb to 0.12 ppb (Figure 19).

As can be seen by comparing Figures 18 and 19, occurrences of high concentrations of toluene and the TPHs (>LOR) do not necessarily coincide.

Table 4 Organic compounds reported to OGIA and number of detects. NA = not analysed; NA = number of water samples not analysed for organic compounds; LOR = number of water samples with organic compounds reported at or below limit of reporting; >LOR = number of water samples with organic compounds reported above detection.

| Parameter	NA	LOR	>LOR	Parameter	NA	LOR	>LOR
1.1.-Dichloropropylene	898	42	0	1.3-dichloropropane	876	64	0
1.1.1.2-Tetrachloroethane	877	63	0	Diethylene glycol	929	11	0
1.1.2-Thrichloroethane	876	64	0	2.4.6-trichlorophenol	399	541	0
1.1.2.2-Tetrachloroethane	876	64	0	Bromobenzene	855	85	0
1.2-Dichloroethane	876	64	0	Chlorobenzene	855	85	0
1.2-Dichlorobenzene	876	64	0	2-chlorophenol	378	562	0
1.2-Dichloropropylene	876	64	0	2-nitrophenol	378	562	0
1.2.3-Trichlorobenzene	876	64	0	4-Nitrophenol	472	468	0
1.2.4-Trichlorobenzene	876	64	0	2,4-Dinitrophenol	472	468	0
1.3-Dichlorobenzene	876	64	0	Phenol	378	559	3
1.4Dichlorobenzene	876	64	0	2.4.5-trichlorophenol	399	541	0
2-Chlorotoluene	855	85	0	Pentachlorophenol	378	562	0
2.4-Dichlorophenol	399	541	0	2,3,4,6-Tetrachlorophenol	472	468	0
2.4-Dimethylphenol	399	541	0	2-Methyl-4,6-dinitrophenol	472	468	0
2.6-Dichlorophenol	455	485	0	4-chloro-3-methyphenol	378	562	0
4-Chlorotoluene	855	85	0	2-methylphenol	922	18	0
2-Butoxyethanol	929	11	0	Dichlorodifluoromethane	855	85	0
Dinoseb	472	468	0	Trichloroflouromethane	855	85	0
Aroclor 1016	884	56	0	Carbon tetrachloride	855	85	0
Aroclor 1221	884	56	0	Dibromomethane	855	85	0
Aroclor 1232	884	56	0	Formaldehyde	863	77	
Aroclor 1242	884	56	0	Bromomethane	855	85	
Aroclor 1248	884	56	0	3&4 methyphenol	922	18	
Aroclor 1254	884	56	0	Chloromethane	855	85	
Aroclor 1260	884	56	0	Dibromochloromethane	855	85	0
Aroclor 1262	884	56	0	Bromoform	932	8	0
Total Polychlorinated Biphenyls	884	56	0	bromodichloromethane2	855	85	0
Hexachlorophene	472	468	0	Chloroform	932	8	0
Tetrachloroethene	855	85	0	Cis-1.3-dichloroprophylene	932	8	0
1.1-dichloroethene	876	64	0	cis-1.2-dichloroethane	876	64	0
Vinyl chloride	855	85	0	1.2-dibromo-3-chloropropane	899	41	0
1.1.1-trichloroethane	877	63	0	Ethanol	693	247	0
1.2-dibromoethane	932	8	0	Isopropanol	929	11	0
1.1-dichloroethane	876	64	0	Trans-1.3-dichloropropylene	932	8	0
Acetaldehyde	855	85	0	Tr-1.2-dichloroethene	877	63	0
Ethylene glycol	929	11	0				
Trichloroethene	855	85	0				
1.2.3-trichloropropane	876	64	0				
2.2-dichloropropane	876	64	0				
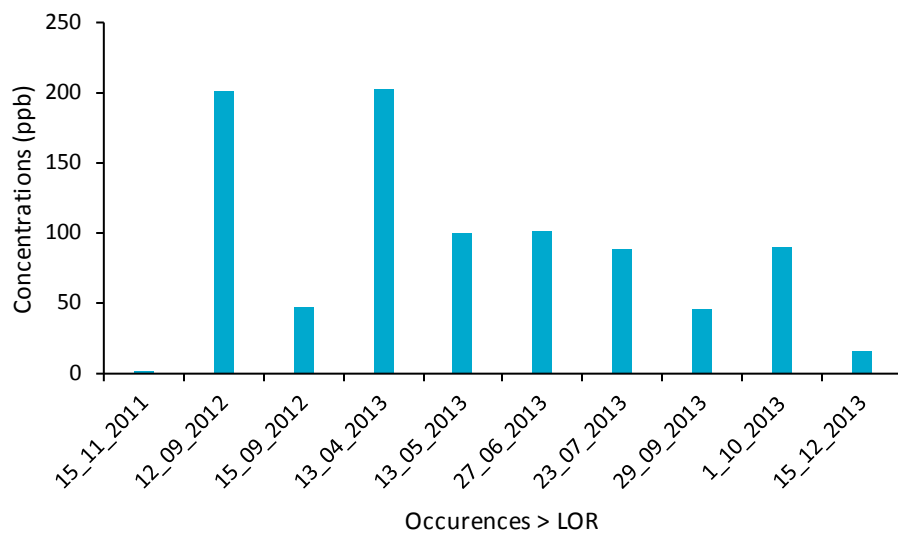
Figure 18 Concentrations (ppb) of dissolved toluene from water samples in the Gubberamunda Sandstone
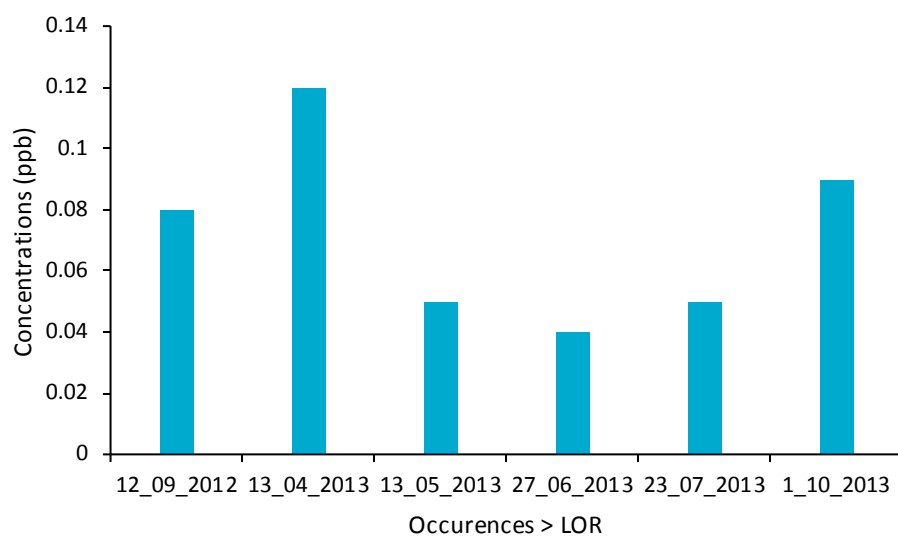

Figure 19 Concentrations (ppb) of dissolved C6-C10 (minus BTEX) TPHs from water samples in the Gubberamunda Sandstone
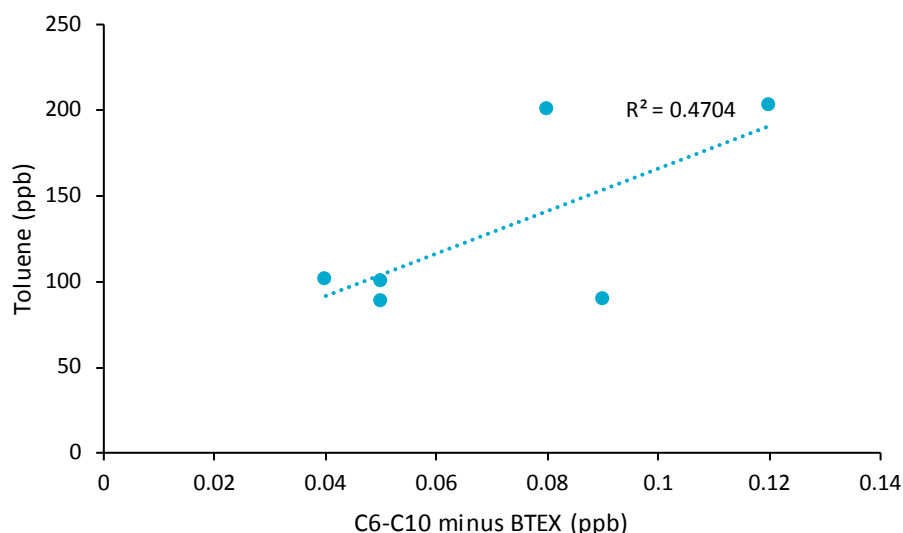
Figure 20 Relationship between toluene and C6-C10 (minus BTEX) TPH concentrations in the Gubberamunda Sandstone

The toluene concentration levels in the Gubberamunda Sandstone are well below drinking water guidelines imposed by the Queensland Public Health Regulation (800 ppb; QPHR 2005), Australian Drinking Water Guidelines (800 ppb; NHMRC 2004), World Health Organisation Drinking Water Guidelines (700 ppb, WHO 2008), and the United States National Primary Drinking Water Standards (1000 ppb; US-EPA 2003).

Toluene can be formed naturally through the aromatization of organic matter (including coal and petroleum formation as well as during forest fires), or artificially through catalytic conversion of fuels, chemical spills and discharges of industrial effluents (e.g., Government of Canada, 2012). The source of the toluene in the Gubberamunda Sandstone cannot be ascertained with the information at hand. For example, no information was made available of any spillage incidences, or information regarding proximity to facilities petrol stations, industrial sites etc. Furthermore, no further information is available regarding the extent of these hydrocarbon concentrations over a much longer period of time. However, it is of note that benzene concentration levels were at or below the limit of reporting for the very same samples that displayed relatively high toluene levels. One explanation could be human-induced spillage of chemicals. Industrial grade toluene is 98% pure and may contain up to 2% xylene and benzene (e.g., Barberes et al., 2018 and references therein). Furthermore, elevated co-occurrences of other light C6-C10 compounds may indicate spillage/release of hydrocarbons in the gasoline range, which range from C6-C12 (e.g., API, 2001). A weak positive correlation (R^2 = 0.47) was observed between the toluene and the C6-C10 (minus BTEX) concentration levels (Figure 20), possibly indicating a potential spill/release of gasoline range hydrocarbons from a refined fuel. However, as mentioned above, high relative concentrations of toluene were not always accompanied by elevated concentrations of TPHs. Differences in the rates of biodegradation between compounds may also have a role to play. Some experimental studies have demonstrated faster microbial degradation of benzene than toluene (e.g. Wolicka et al., 2009; Mukherjee and Bordoloi et al., 2012). Therefore, Other BTEX compounds have been originally present.

A natural source of these hydrocarbons can also not be discounted. As described in Part I of this report, lighter hydrocarbons have a higher propensity to disorpe from organic-rich hydrophobic

substances such as coal and crude oil than their heavier counterparts and may have become dissolved in groundwater of the Gubberamunda Sandstone. However, this sandstone unit is not associated with any extensive coal layers that may explain such natural occurrences. Migrated petroleum is another potential source

Elevated hydrocarbon occurrences in the Walloon Coal Measures

The results from a total of 106 individual water samples from the Walloon Coal Measures (WCM) were made available by the companies and represent a timespan from 22/09/2009 to 15/01/2013. Out of these 106 water samples, 46 yielded hydrocarbons > LOR. These hydrocarbons largely consisted of a suite of TPHs from C6 to C40 and range in concentrations from 0.04 ppb to 3.6 ppb. A limited positive correlation between TPH groups (C15-C28 vs. C29-C36) > LOR could be noticed if their concentrations were ~ < 2 ppb (Figure 21). In other TPH groups, correlations could not be discerned (Figure 222).

Toluene concentrations > LOR were detected in 6 samples (2.5 ppb, 30/06/2010, 2 x different wells; 2.5 ppb, 2/07/2010 2x different wells; 3 ppb, 16/08/2012; 2 ppb, 15/01/2013). Benzene concentration levels were at or below the limit of reporting for the very same sample that displayed relatively high toluene levels. No information was available on ethylbenzene and xylenes levels. No correlations were discerned between toluene and TPH concentrations.

See detailed discussion above regarding the occurrence and biodegradation of toluene and other BTEX compounds in the natural environment. The occurrence of toluene in the WCM is not surprising as it is a natural constituent of coal. Regardless, toluene concentrations ≤3 ppb show that it does not appear to exist in coal-associated groundwater at significantly higher levels where it would exceed government imposed water quality guidelines. Nevertheless, it must be restated that data presented in this study does not represent a continuous span for specific locations over several years. In future studies, groundwater chemistry data that was more frequently sampled over a long continuous time-span may either confirm the results presented herein or provide a different insight.
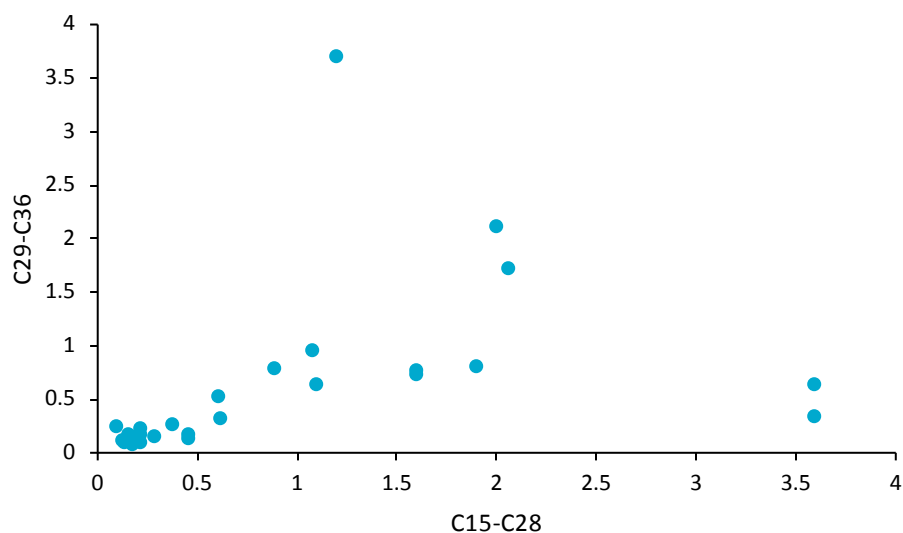
Figure 21 Relationship between C29-C36 and C15-C28 TPH concentrations in the Walloon Coal Measures.
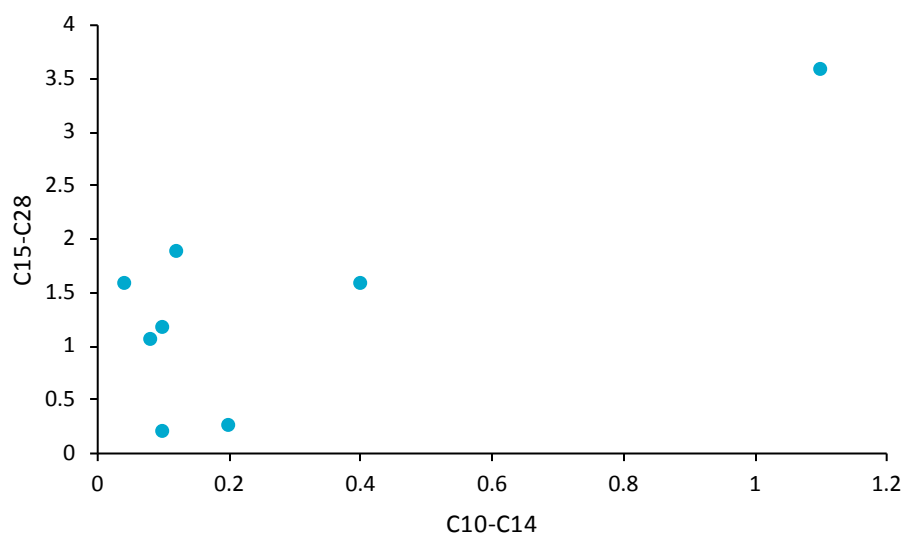
Figure 22 Relationship between C15-C28 and C10-C14 TPH concentrations in the Walloon Coal Measures.

4.5 Conclusions

Relatively few hydrocarbons and other organic compounds were found to have concentrations above the limit of reporting in the Surat CMA. Of those that were reported, the concentrations were well below common drinking water guidelines. Based on these results, it appears that the occurrences of hydrocarbons and other organic compounds in the CMA groundwater is limited in frequency and in concentration. These results also compare with a previous literary survey of hydrocarbon and other compounds in groundwater from coal-bearing Australian basins in Queensland and New South Wales (Schinteie et al., 2015).

Groundwater chemistry data presented here show relatively low concentrations of various hydrocarbons in the Surat CMA. Concentration levels of detected compounds were ≤9.64 ppb for

TPH compounds and ≤203 ppb BTEX compounds (mostly toluene). Such values were well below drinking water guidelines for BTEX compounds imposed by various government agencies.

In conclusion, while sources for these detected hydrocarbons in the Surat CMA can be suggested, concrete evidence is lacking. Furthermore, due to the lack of any supporting data and no information in regards to hydrocarbon occurrences in over a longer period of time, any interpretations on the sources of these hydrocarbons need to be treated with caution.

5 Applicability of oil and gas mud logs in discerning historical hydrocarbon gas distributions

5.1 Introduction

The success and rapid development in CSG activities in Australia over the past 10 years has led to increased scrutiny over the environmental impact of drilling activities required for gas production development. One aspect of public concern relates to the risk of stray or "fugitive" gas migration into groundwater sources. For example, there has been ongoing media attention triggering government and industry investigation into alleged changes in gas seep flows to the Condamine River and its associated alluvial aquifer (Iverach et al., 2017; Lafleur and Sandiford, 2017). Although recognized to be a gas seep prior to CSG development, debate on this issue has focused on whether subsurface resource development has increased the methane flux in these areas as well as induced additional migratory pathways. Such debate is important, as Australian coal-bearing sedimentary basins are also host to local and regional groundwater sources that are important to environmental, community, agricultural and industrial interests. In Queensland, for example, the Surat Basin hosts aquifers that form part of the Great Artesian Basin, one of the largest freshwater artesian basins in the world (e.g. Habermehl, 1980).

Previous scientific studies and historical observations demonstrate a range of natural hydrocarbon occurrences in both the Bowen and Surat basins (e.g. Underschultz et al., 2016). However, in order to assess whether increased CSG extraction is likely to exacerbate the flux of hydrocarbon gases in the Bowen and Surat basins, it is necessary to establish a historical record against which current data can be assessed. Such records, together with periodic assessment of current gas compositions throughout the production life of a gas well, would assist in understanding the occurrence and distribution of these compounds in deep groundwater systems.

In this study, we investigate the applicability of using historical mud log data as a first step to in establishing historical hydrocarbon gas occurrences in the Bowen and Surat basins. We gathered and digitized publicly available mud log gas detector data, allocated them to stratigraphic horizons and mapped their distributions. Trends in gas characteristics and their spatial distribution could then be analysed against the regional, formation-scale stratigraphic framework. We show that data obtained from mud-logs could provide a readily-available, low-cost source of information for environmental agencies wanting to gain insights into the broad distribution of historical hydrocarbon occurrences.

5.2 Material and methods

5.2.1 Data extraction from mud logs

Gas data was extracted from chromatologs (mud logs) of open-file well completion reports in scanned document file (e.g., pdf) and image file (e.g., tiff, jpg) formats obtained from the Queensland Digital Exploration Reports System (QDEX; Geological Survey of Queensland, 2017a). Locations of these wells are shown in Figure 23. Files Records of gas readings were digitized by either manually extracting data or using the G3data Graph Analyzer version 1.5.3 (GNU General Public License). Collected data consists of recorded values of background gases and gas shows, which varies in magnitude or composition. Data points from background gases and gas shows were extracted and interpreted with values transposed into a spreadsheet with associated metadata (e.g. geographic coordinates, well name). The data set discussed here consists of recorded hydrocarbon gases (methane, ethane, propane, butane), as well as higher molecular weight homologues (pentane, and hexane), from mud logs in parts per million (ppm), and hydrocarbon ratios (e.g., gas dryness, wetness, character, balance) derived from these gas readings.

5.2.2 Data mapping

Geographic information system (GIS) data layers, including fault lines and fold axes, outcrops, stratigraphic distributions, as well as structural tops and thicknesses were obtained from the Queensland Spatial Catalogue (QSpatial; Geological Survey of Queensland, 2017b). Data was mapped using QGIS (GNU General Public License; QGIS Development Team, 2017), an open-source desktop GIS application.

5.3 Results and discussion

5.3.1   Limitations in using mud logs to obtain gas concentrations

Recorded gas concentrations in mud logs are affected by a multitude of variables originating from in-situ geological factors as well as drilling activities and well bore conditions. Geological variables include rock porosity, relative permeability, gas saturation, temperature, pressure, solubility, and compressibility. Well drilling variables include flushing to bring heavy sediment to the surface, drill rate, pump rate, mud density and viscosity, hole size, gas detector efficiency, accessible rock and gas volume, differential pressure and temperature, phase changes, and surface losses of the gases (Hashimov, 2015). Due to multiple variables affecting mud log gas concentration readings, it is almost impossible to normalise these readings and with the current mud logging technology at hand, accurate quantification of gas shows is considered unattainable (Hashimov, 2015). For these reasons, there are significant uncertainties in the quantitative data presented in this study and recoded values of gas (ppm) should be considered minimum values of what might actually be occurring in the rock formation at that location and depth. Therefore, to help avoid inconsistencies between the wells, we only took maximum values into account and clustered quantitative data into groups (e.g., 0-1000 ppm, 1000-2000 ppm).

Another limitation of the data set is the location of the wells and their associated mud logs. Wells were drilled for commercial purposes are not evenly distributed throughout the study areas. This limitation is a problem when the data is interpolated on a map, resulting in significant uncertainties in areas where wells do not exist and extrapolation is required. Furthermore, not all wells have associated mud log data available or record information on specific hydrocarbon gases (i.e. only recorded total hydrocarbon gas). Finally, the examination of mud log data for gas content is manually intensive and not easily automated. An initial pilot study was conducted by Underschultz et al. (2016) and this study has now added more wells to the previously assembled data set. However, there are insufficient resources to examine all wells with mud logs so a selection process was used to examine a geographically representative sub-set of wells where mud log data exists.

In this study, however, we demonstrate that despite numerous limitations, a mud log-derived data set can still provide important information when quantitative data is plotted spatially. During digitalisation of the data, we observed that gas shows in the wells showed similarities when the mud logs were produced by, for example, the same drilling rigs, same gas trap/detector system, or similar mud types. This was especially the case in mud logs produced by the same company, or companies sharing the same drilling rig. Mud logs within a time frame of < 10 years also showed significant similarities.
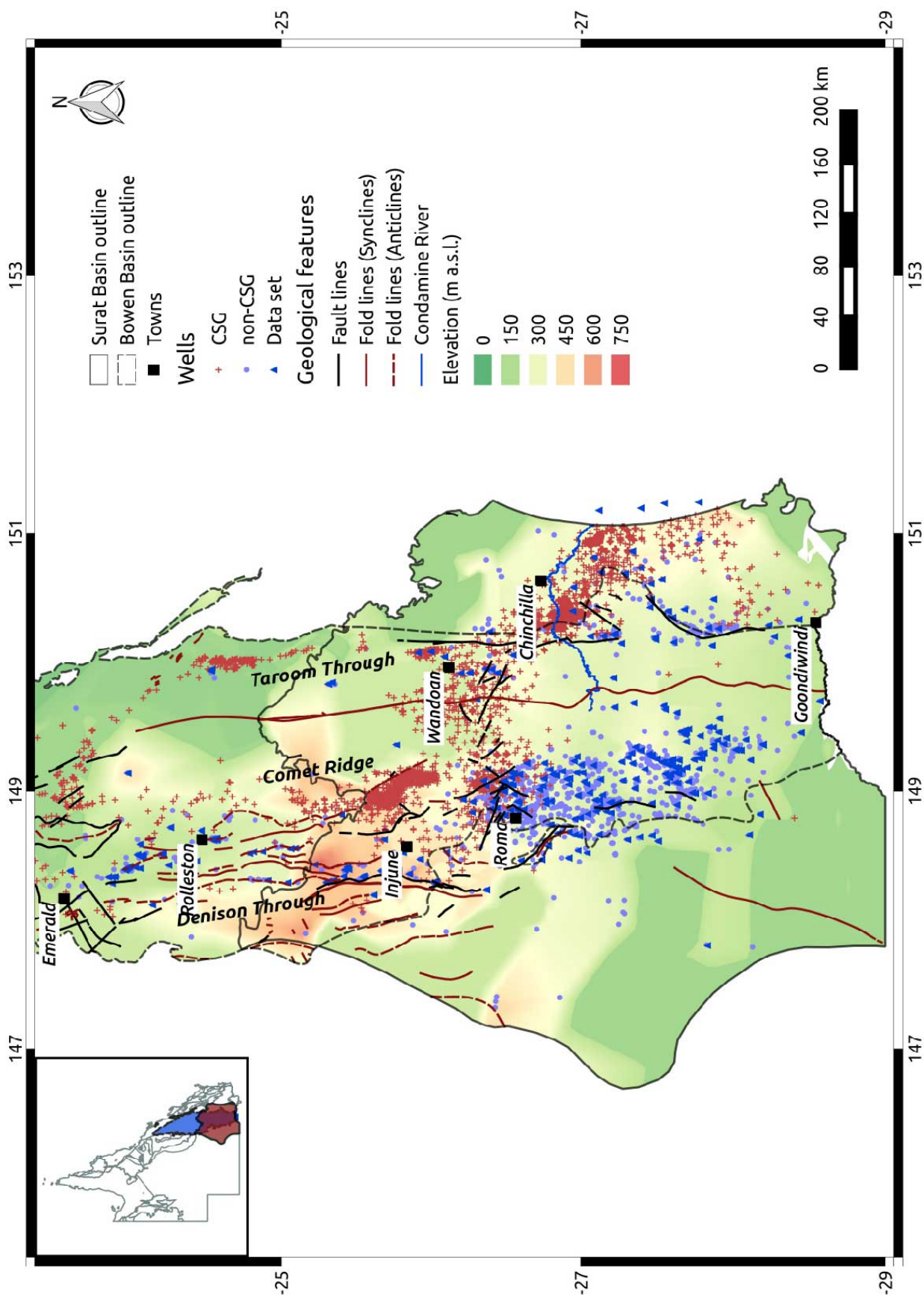
Figure 23 Overview of CSG and non-CSG wells in the Bowen and Surat basins. Mud log data for this study originated from non-CSG wells categorized as "Data set". Inset on the upper left show the locations of the Bowen (blue/dark red) and the overlying Surat (light red) basins.

5.3.2 Estimations of gas concentrations and quality

Gas concentrations in ppm were estimated for several stratigraphic horizons in the Bowen and Surat basins (Figure 24). Estimates for each horizon were derived from multiple wells, providing a statistical range. As shown in Figure 24, hydrocarbon gas concentrations in the Bowen Basin generally increase up to the Blackwater Group followed by an overall decline in progressively younger sequences of the Bowen and Surat basins. This overall trend is punctuated by gas-rich intervals that represent source rocks such as the Walloon Coal Measures (WCM). These trends are corroborated with previous studies where these gas-rich stratigraphic horizons are described.

In the Bowen Basin, the bulk of the generated hydrocarbons originate the Moolayember Formation, Baralaba Coal Measures, Burunga Formation, Banana Formation, Flat Top to Buffel formations and the Reids Dome beds (Boreham et al., 1996; Carmichael and Boreham, 1997). The Permian Baralaba Coal Measures and Burunga Formation were suggested to be the most productive units, forming more than 90% of the oil and ~65% of the thermogenic gas within both the Bowen and Surat basins (Shaw et al., 2000). CSG is contained primarily within the seams of the WCM of the Surat Basin. The Walloon Subgroup CSG consists almost entirely of methane (>98%; air-free basis), with only minor amounts of carbon dioxide and nitrogen, and very low levels of ethane (<1%; Hamilton et al., 2012). It should be noted that the estimated concentration ranges reported here encompass the entirety of each stratigraphic horizon. However, it is well known that significant variations in gas concentrations can occur within particular stratigraphic horizons. The Walloon Coal Measures in the Surat Basin, for example, contains multiple, heterogeneous coal measures with variable gas content (Scott et al., 2007; Ryan et al., 2012).

The hydrocarbon gas compositions determined in this study are consistent with previous findings from Australia and worldwide; methane is the dominant component of coal seam gas with secondary amounts of higher molecular weight hydrocarbons. As summarized by Clayton (1998), the relative proportions of methane and higher carbon-number hydrocarbons depends mainly on: (1) biogenic versus thermogenic gas generation; (2) elemental composition of coal macerals (e.g., Rice et al., 1989); thermal maturity of the coal; and (4) retention capacity of hydrocarbon gases in the coal matrix at low thermal maturities (Rigby and Smith, 1982).

Hydrocarbon gases in coal seams are derived either through microbial degradation of coal or by thermal breakdown of kerogen (e.g. Clayton, 1998). Biogenic coal seam methane forms via demethylation of organic molecules or carbon dioxide reduction and requires a concerted, synthrophic activity of microorganisms to degrade the complex and heterogenous organic matter of coal (e.g., Clayton, 1998; Faiz and Hendry, 2006; Midgley et al., 2010; Strąpoć et al., 2011). Gas formation is proposed to occur at the early peat and lignite stages as well as over geologic time through the incursion of nutrient-carrying meteoric water in coal beds (e.g., Rice and Claypool, 1981; Clayton, 1998; Faiz et al., 2003; Faiz and Hendry, 2006; Flores, 2014). Thermogenic gas, by contrast, is generated by thermocatalytic reactions of coal and other sedimentary rocks (e.g., shale) at higher temperatures. The generation of thermogenic gas begins at a coal rank approximately equivalent to vitrinite reflectance (% Ro) of ~0.6 (~110°C) with significant gas generation occurring between 1.0%

and 3% Ro (Higgs, 1986; Scott, 2002). While the source and thermal maturity have a primary control on gas wetness (Tissot and Welte, 1984), biodegradation (Boreham et al., 2001; Head et al., 2003; James and Burns, 1984; Milkov, 2011; Pallasser, 2000), expulsion and migration fractionation (Lorant et al., 1998; Prinzhofer and Huc, 1995) and absorption/desorption (Snowdon, 2001; Xia and Tang, 2012) can have varying influence on molecular and isotopic compositions.

In this study, we broadly attempt to distinguish between biogenic and thermogenic gas distributions. Biogenic hydrocarbon gas is usually compositionally and isotopically distinct from its thermogenic counterpart (e.g., Whiticar et al., 1986). However, in the absence of isotopic data (not included in the well completion reports), we can only rely on calculated ratios of hydrocarbon gases and their depth distributions to make inferences on their genetic (i.e. biogenic versus thermogenic) origin. We employed two ratios to determine the degree of gas dryness recorded in our mud log dataset: (1) the gas dryness ratio $C_1/(C_1+C_2+C_3+C_4+C_5+C_6)$; and (2) the $C_1/(C_2+C_3)$ ratio. The gas dryness ratio describes the quantity of wet gases present relative to methane (e.g., ratio of 0.8 indicates 80% methane and 20% wet gases). This ratio works well in the absence of any wet gases since a ratio of 1 indicates 100% methane. The $C_1/(C_2+C_3)$ ratio is used to distinguish whether a gas is either microbial, thermogenic, or mixed in origin (Claypool and Kvenvolden, 1983); values above 100 indicate a microbial origin, values below are 50 indicative of a thermogenic origin, while values between 50 and 100 are considered to be of mixed origin. However, this ratio needs to be carefully interpreted. While biogenic hydrocarbon gas is considered 'dry' as it is composed solely of methane, thermal cracking of wet gases can also produce a very dry gas composition (e.g., Clayton, 1998). A further limitation in using this ratio is caused by the absence of data. In some sedimentary horizons from this study, usually shallow formations where methane is the predominant gas, not many data points could be generated as ethane and propane were absent and it is not clear if this absence is due to the higher order gases not being measured or not being present. Therefore, since this ratio can only be interpreted in the presence of a complete data set and is not further discussed here.

The mud log data from this study indicates variability in gas dryness in the Bowen and to a lesser extent in the Surat basins. This variability in gas wetness is a consequence of the complex geological circumstances of these basins. Only the Bowen Basin has experienced maximum thermogenic gas generation (Draper and Boreham, 2006). While a small portion of hydrocarbon gases in the Surat Basin have been speculated be thermogenic in origin, the vast majority is regarded as biogenic; most thermogenic gas in the Surat Basin is regarded to have migrated from the underlying Bowen Basin (Draper and Boreham, 2006). Mixing of both thermogenic and biogenic gases in both basins have been noted isotopically (Draper and Boreham, 2006)

Previous isotopic studies have shown that the vast majority of gas in the WCM are biogenic rather than thermogenic in origin. Nevertheless, remnant thermogenic gas has been isotopically detected (Golding et al., 2013; Hamilton et al., 2014, 2015) and this conforms to the presence of a small degree of gas wetness from the mud log data presented here. Since the WCM are only of a sub-bituminous rank, it is believed that thermogenic gas may have migrated into this stratigraphic horizon from further below at some locations. The quantity of thermogenic gas migration remains unclear (Towler et al., 2016).
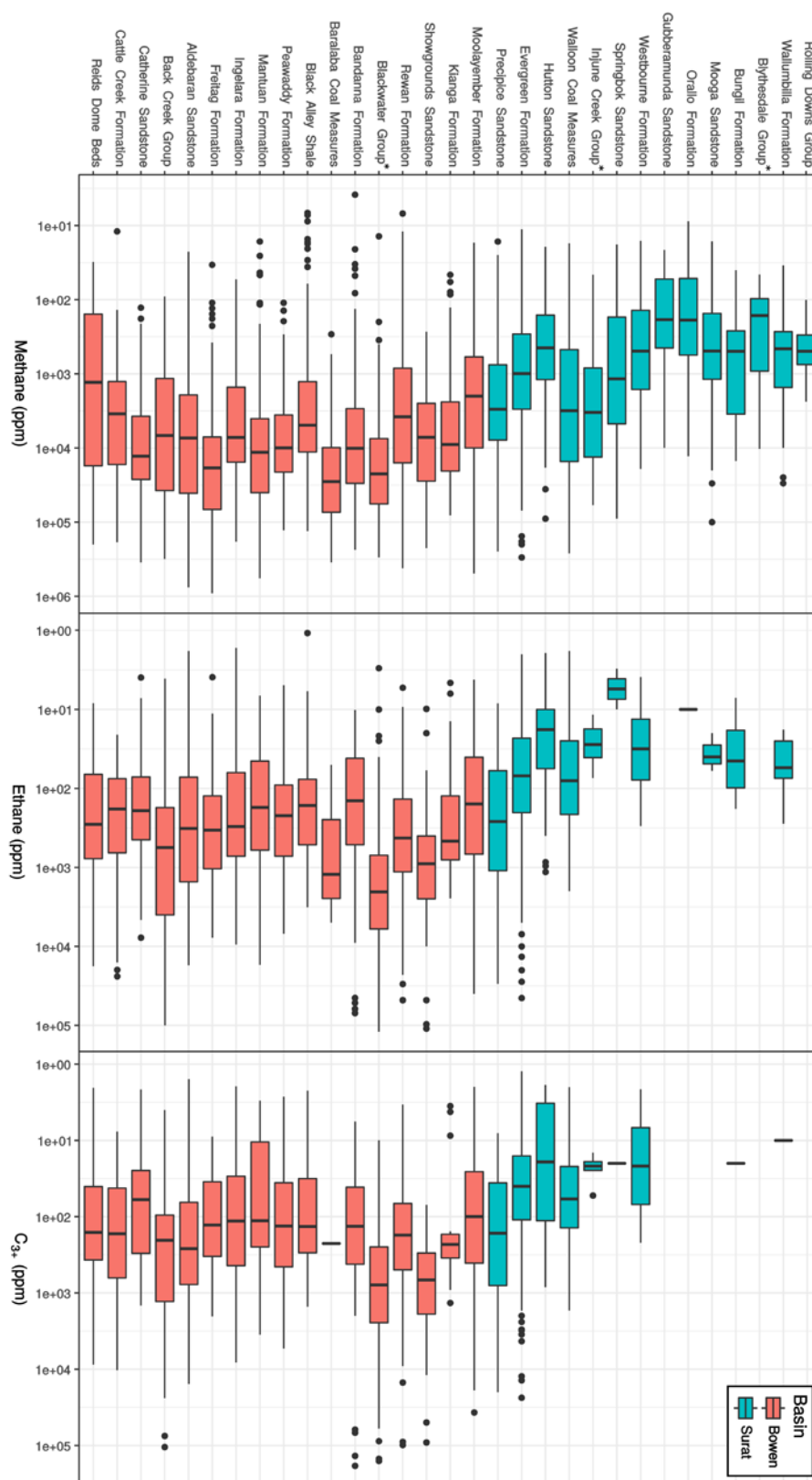
Figure 24 Formation-specific ranges of absolute and non-corrected gas concentrations. Boxes show the interquartile ranges (IQR) between 25% (Q1) and 75% (Q3), respectively, and 50% (median) is represented by the solid black lines. Whiskers show values in the ranges of 1.5*Q1 and 1.5*Q3, respectively. Black dots are outliers that are statistically situated outside these ranges. * Denotes groups which include geologic formations additionally plotted in this figure (e.g., Injune Creek Group partly includes the Walloon Coal Measures) but were not differentiated within the mud logs.

5.3.3 Spatial distribution of hydrocarbon gases in the Walloon Coal Measures

The Walloon Subgroup comprises six formations, which, from oldest to youngest, are the Durabilla Formation, Taroom Coal Measures, Tangalooma Sandstone, Lower Juandah Coal Measures, Juandah Sandstone and Upper Juandah Coal Measures. CSG recovery occurs generally at depths of 200 to 600 m, originating from seams of the Taroom and Juandah coal measures (Papendick et al., 2011). This trend is reflected in Figures 25 and 26, with the highest methane concentrations being generally recorded ≤ 600 m and located at sites where currently active CSG-extraction is taking place. A shallow nature of CSG has been previously shown in a range of different basins worldwide and relates, among other factors, to the ideal depth occurrences for microbial activity producing biogenic methane and a common trend of decreasing permeability with depth (e.g., Tao et al., 2005; Faiz and Hendry, 2006; Pashin, 2007; Penner et al., 2010).

While CH_4 in the Walloon Coal Measures in mainly of biogenic origin (Papendick et al., 2011), carbon isotopic values also indicate potentially thermogenic or mixed gas ($\delta^{13}C$ −58.5‰ to −45.3‰) signatures, with $\delta^{13}C$ values for CH_4 becoming more thermogenic from the top of the Juandah Coal Measures to the base of the Tangalooma Sandstone (Hamilton et al., 2014b). In the Taroom Coal Measures, the $\delta^{13}C$ values for CH_4 decrease with increasing depth. Based on stable carbon isotopes alone Hamilton et al. (2014b, 2015) interpret this pattern as a transition from microbially- to thermogenically-sourced CH_4 in the central coal seams; based on the other data such as $\delta^{13}C$ values for CH_4 and δD values for CH_4, Hamilton et al. (2014, 2015) concludes that microbial CO_2 reduction is the primary source of Walloon Subgroup CH_4, and that stratigraphic variations in gas content mainly reflect the extent of microbial methanogenesis.

Wet gases, as well as *n*-alkane homologues up to hexane, have also been detected in this study in mud-logs of the WCM (Figures 27-30) and provide further confirmation on the distribution of thermogenic gas in these strata. While thermogenic gas concentrations are dwarfed by those of methane, wet gases have been detected in both shallow and deeper sections of the WCM, with wet gas concentrations progressively increase in deeper sections. This mud log-derived data therefore corroborates with the isotopic data by Hamilton et al. (2014b, 2015) mentioned above. Since thermogenic gas in the WCM is regarded to originate from a stratigraphically distant Permian source, and many intervening units have sealing capacity, a viable migration path associated with for example fault leakage is required (e.g., Hamilton et al., 2012; Garnett et al., 2013; Underschultz et al., 2016). Areas not associated with faulting, in turn, could serve as seals separating the WCM from underlying or overlying aquifers and this could isolate certain parts of the WCM from upwards thermogenic gas migration, or assist in gas retention respectively. For example, the Tangalooma Sandstone, a unit interbedded within the WCM, has been suggested to act as a regional seal, forming a barrier to the upwards migration of thermogenic gas (Hamilton et al., 2012). Such an interpretation is supported by increased ethane concentrations just below this sandstone unit (Hamilton et al., 2012). Steeply dipping (60–80°) normal faults are the most common fault structures present within the Surat Basin (e.g., DNRM, 2016), which could act as conduits for the upward migration of wet gases into the WCM.

Figure 25 Mud log-derived methane concentrations (ppm) in relation to the structural tops (meters before Kelly Bushing, m KB) of the Walloon Coal Measures

Figure 26 Mud log-derived methane concentrations (ppm) in relation to the structural thickness (m) of the Walloon Coal Measures
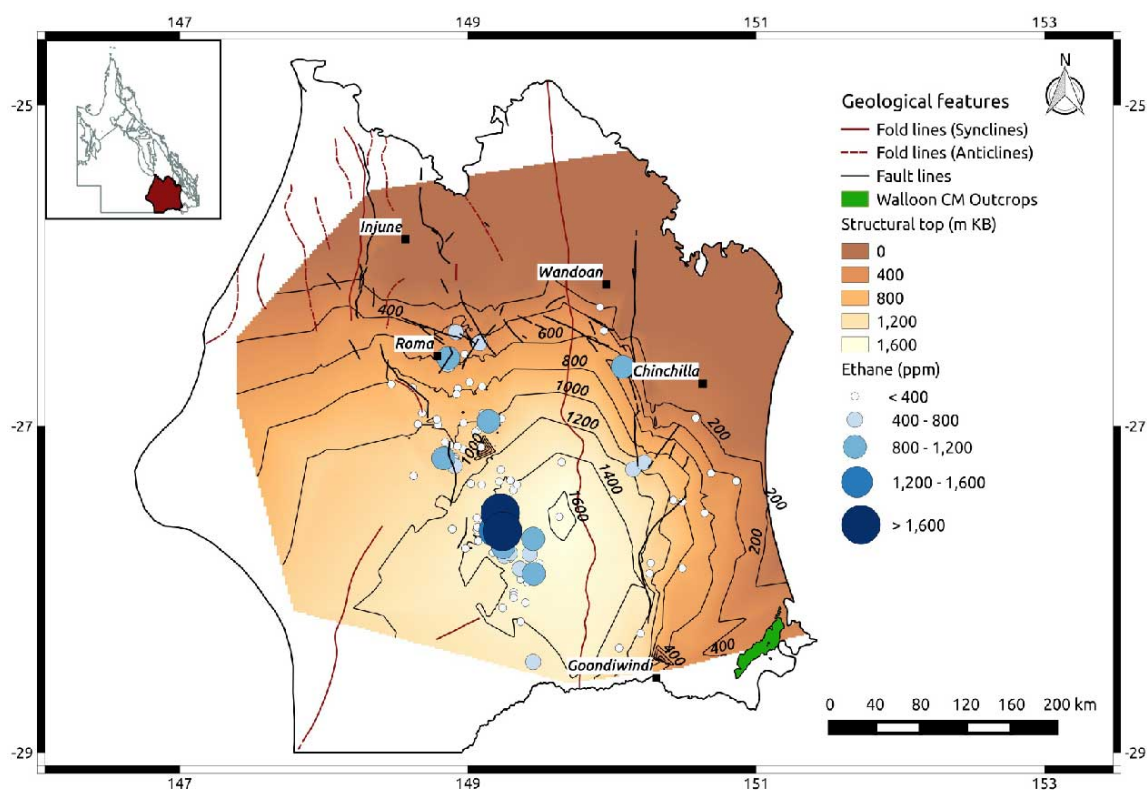
Figure 27   Mud log-derived ethane concentrations (ppm) in relation to the structural tops (meters before Kelly Bushing, m KB) of the Walloon Coal Measures
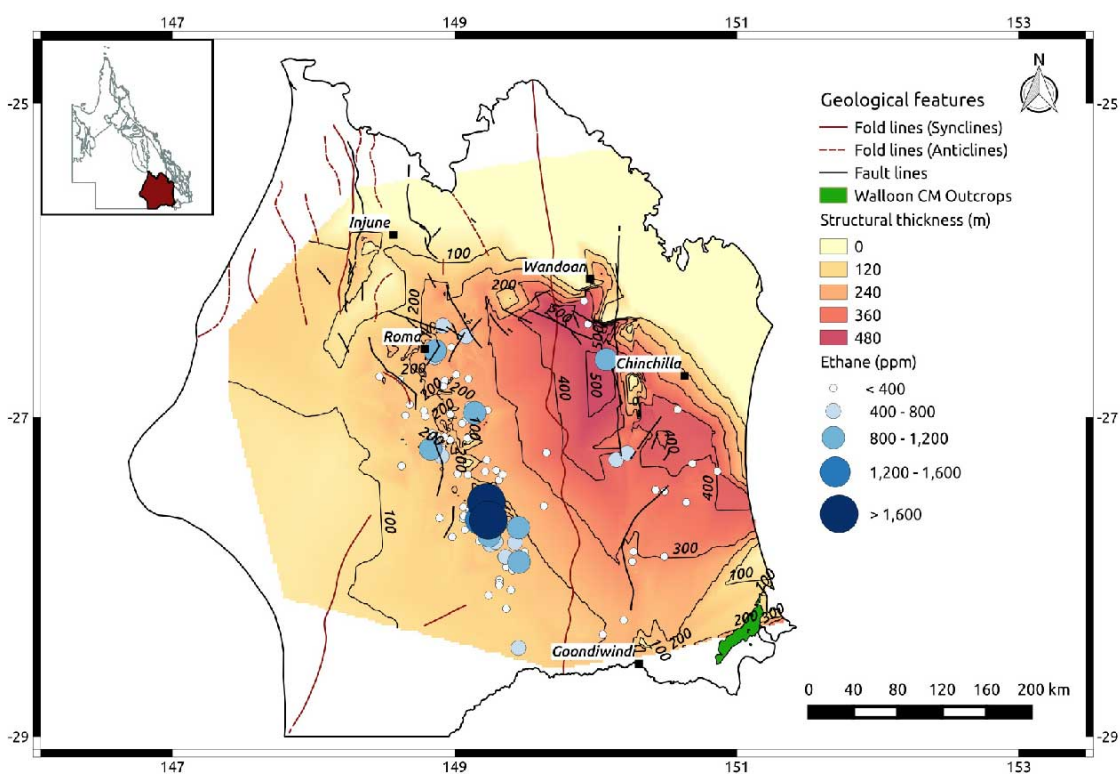
Figure 28   Mud log-derived ethane concentrations (ppm) in relation to the structural thickness (m) of the Walloon Coal Measures
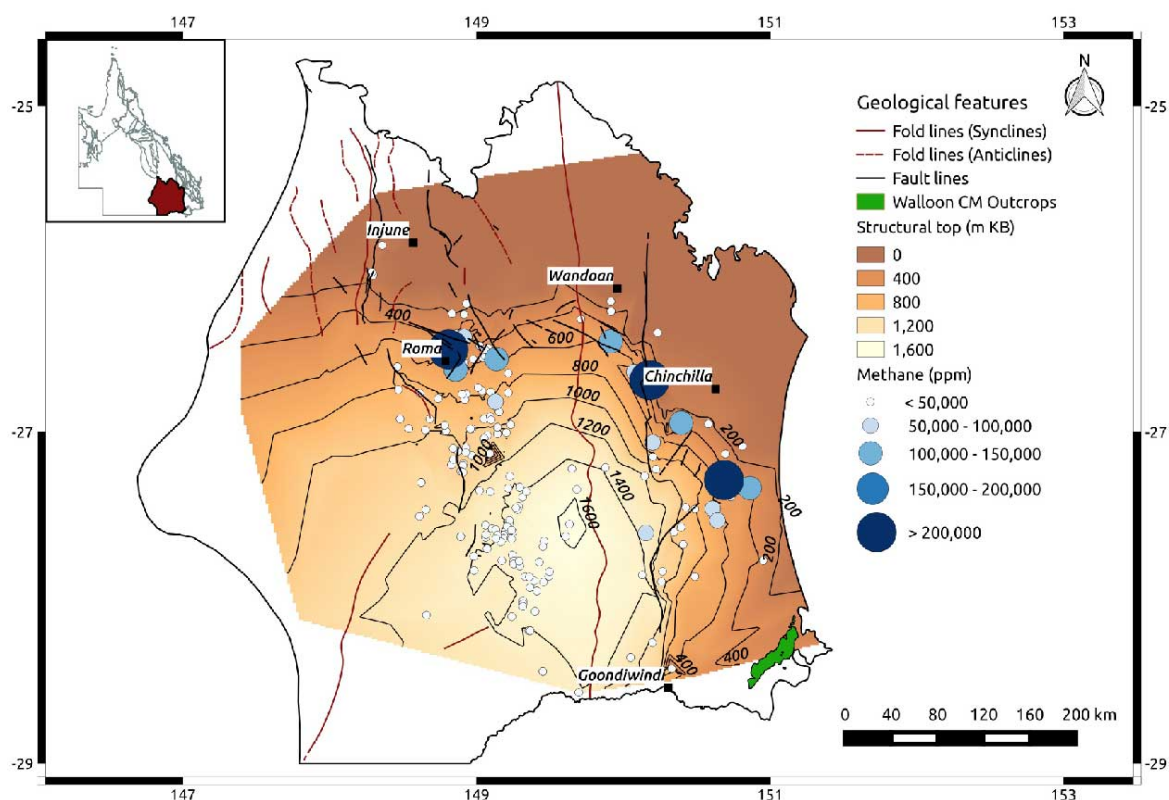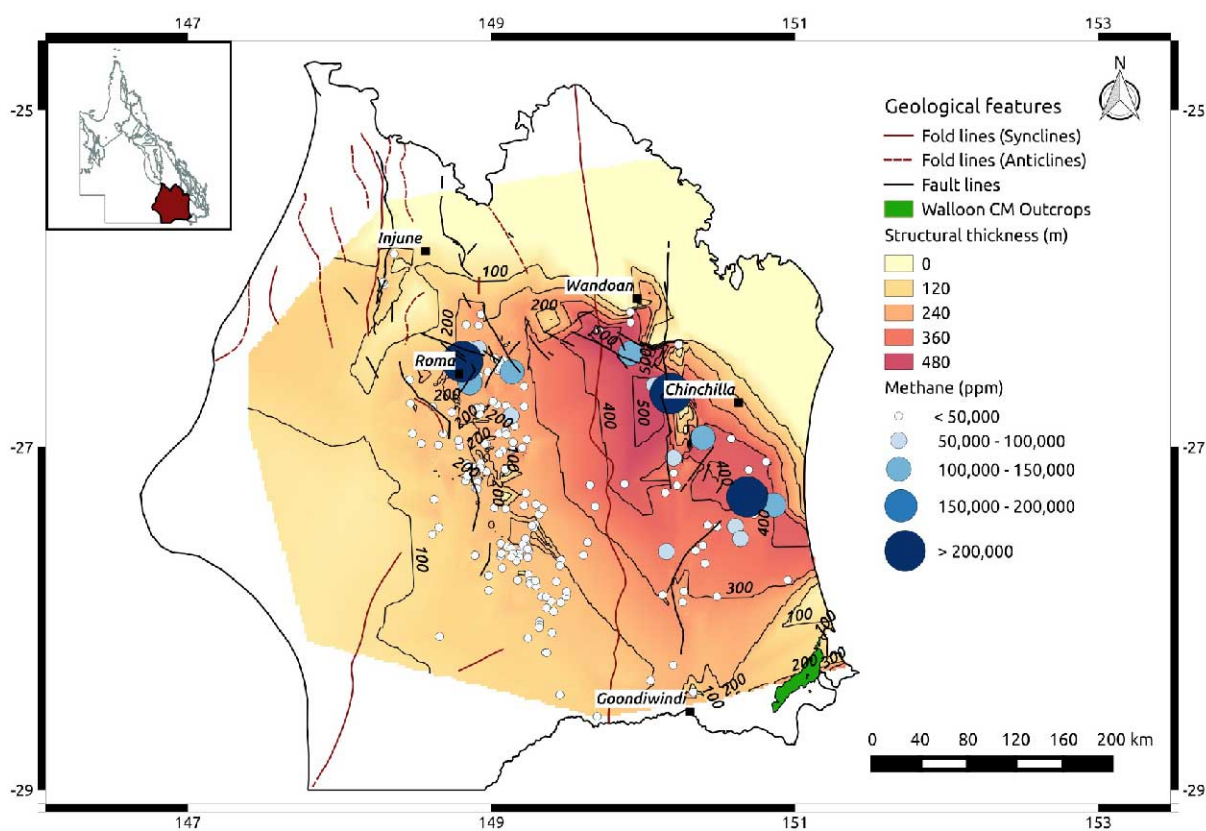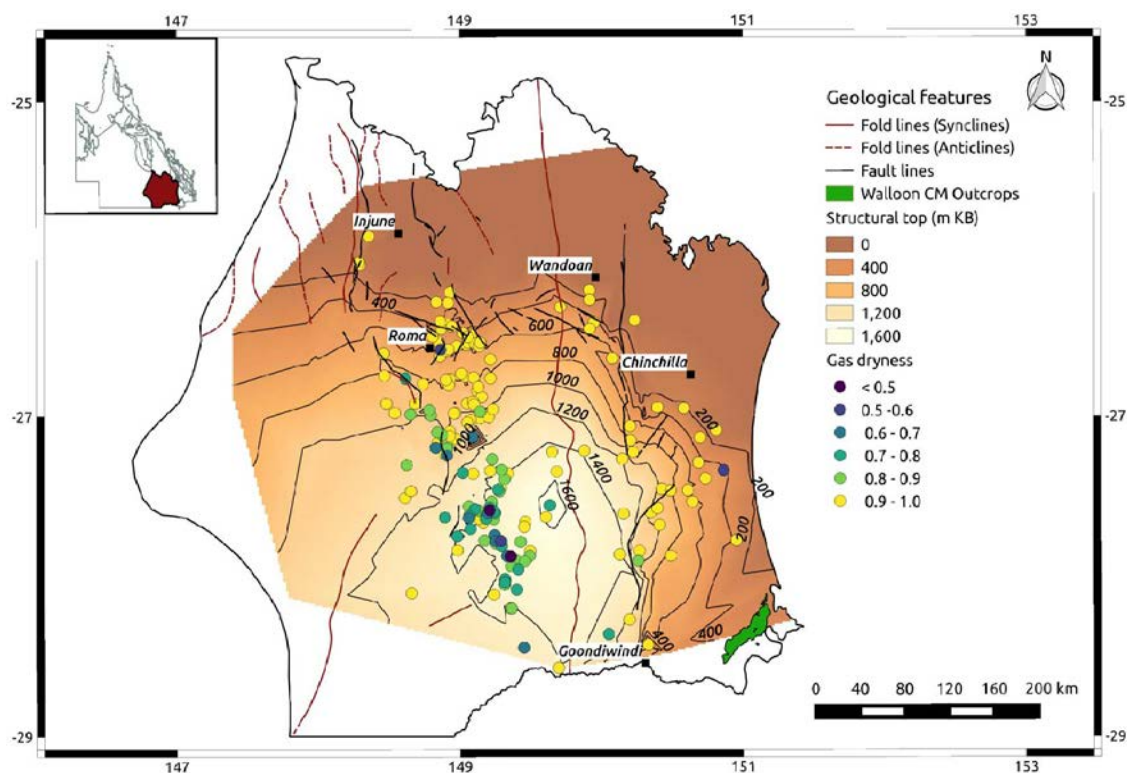
Figure 29 Mud log-derived gas dryness states in relation to the structural tops (meters before Kelly Bushing, m KB) of the Walloon Coal Measures
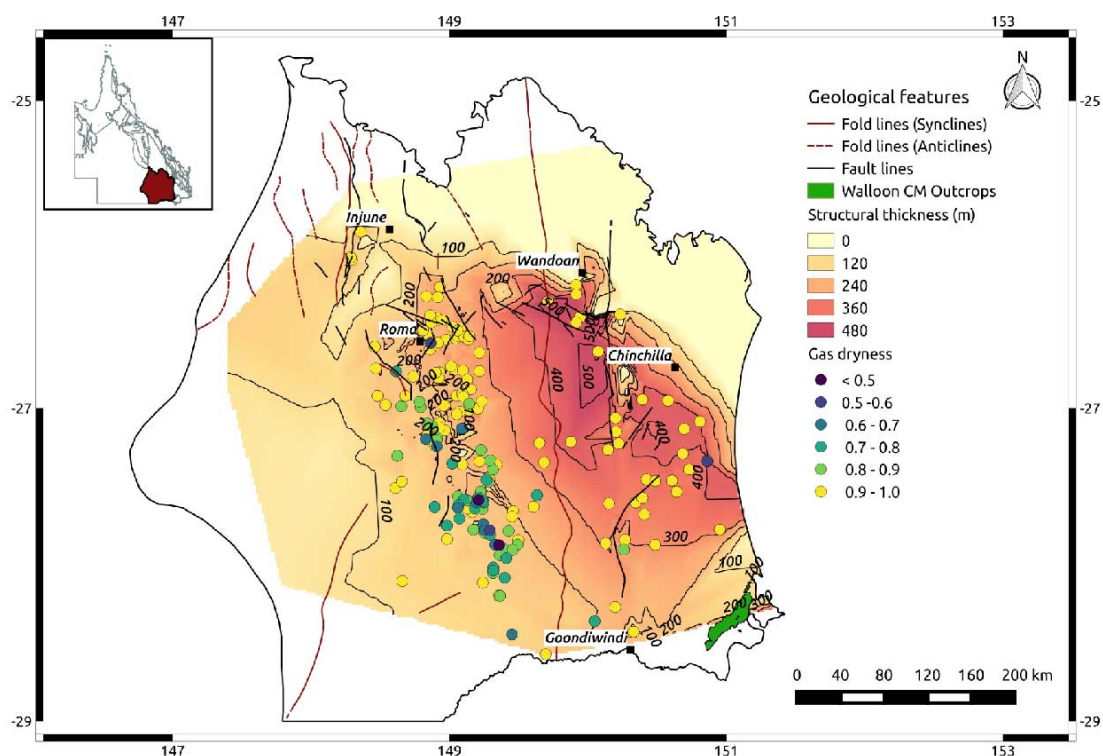
Figure 30 Mud log-gas dryness states in relation to the structural thickness (m) of the Walloon Coal Measures

5.4 Conclusions

In this study, we investigate the applicability of historical mud log data to estimate hydrocarbon gas concentrations and their distributions in the Bowen and Surat basins - two economically important coal-bearing basins. The hydrocarbon gas distributions, compositions and production potentials in the Bowen and Surat basins have previously been well studied and provided ideal test cases for the applicability mud-logs as an environmental tool.

The resulting data set, consisting of recorded hydrocarbon gases (methane, ethane, propane, butane) and higher *n*-alkane homologues (pentane and hexane) in parts per million (ppm), was allocated to stratigraphic horizons and mapped. While mud log gas data suffers from a range of limitations, broad distribution and concentration trends were discernible. These trends were in agreement with previous geochemical and isotopic work in the Bowen and Surat basins on the occurrences of hydrocarbon gases. In particular, the distribution of wet gases in the thermally less mature WCM indicate significant upward migration of thermogenic gases.

The approach and results presented in this study can multiple applications, it can serve as useful, low cost exploration tool for the search of economic hydrocarbon gas reserves in frontier basins. Provided mud logs are publically available for such basins, their digitization and interpretation can provide useful information on the composition, relative quantity and distribution of potentially exploitable methane and wet gases.

Part III Conceptual Model

Modelling the fate of hydrocarbons and other organic compounds in groundwater in Queensland's coal-bearing sedimentary basins is a complex task that involves the interaction of numerous sedimentary/mineral assemblages, aqueous and gas phases as well as the biosphere. Such systems are characterized by complexity seldom encountered in the laboratory. As in many other scientific disciplines, any attempts to gain insights into complex systems necessitates comparisons to idealized counterparts from the complexity of nature (e.g. Stumm and Morgan, 1996). In this section, we discuss and conceptually model physico-chemical processes occurring at broad lithosphere-hydrosphere-atmosphere interfaces.

Natural sources of groundwater quality degradation by organic compounds in the Bowen and Surat basins are many and varied. Provided a transport mechanism is available (e.g., flowing water and buoyancy), an introduced hydrocarbon/organic compound will spread within the soil-rock-groundwater system (e.g., Tikhomirov, 2016). However, in this system, a natural hydrocarbon compound will also be affected by geological, physico-chemical and biological influences (e.g., Jackson, 1980). These processes rarely act in isolation but are related to each other or interact.

Dissolved hydrocarbon/organic compounds are carried by advection through moving groundwater, traveling at the same rate as the average linear velocity of the waterbody. If a free hydrocarbon phase is migrating, it will not only be affected by the groundwater flow but also by buoyancy forces Dispersion of a hydrocarbon/organic compound will increase with increasing groundwater velocity and aquifer heterogeneity (e.g., Tikhomirov, 2016). Groundwater in geologic formations flows through pores and fractures in formations from areas with a greater water level/head towards areas where it is lower. This difference in water levels over a geographic distance in the aquifer is generally referred to as the hydraulic gradient (e.g., Brassington, 2007). Groundwater in coal formations such as the Walloons and other GAB aquifers is often deemed to be 'confined' (i.e. with an overlying aquitard). Therefore, the flow rate is controlled by permeability, hydraulic gradient, and storativity, which act as the two primary hydraulic parameters (e.g. Flores, 2014). Permeability is a measure of the ease with which a fluid can move through an aquifer, while storativity is refers to the capacity of an aquifer to store or release water in response to pressure changes. Geologic formations consisting of material with a high permeability are known as aquifers. Formations with lower permeability, by contrast, are referred to as aquitards (e.g., Brassington, 2007). Within geologic formations, water generally encounters greater permeability along horizontal bedding planes than vertically across them. In the GAB, recharged groundwater within confined aquifers flows slowly (~1–5 metres per year; Habermehl, 1980) along bedding planes and fractures.

Detailed geophysical logging revealed that aquifers have complex lithologies where even main aquifers contain significant proportions of low permeability siltstone and mudstone. Aquitards, by contrast, can contain some high permeability lithologies such as sandstones that can harbour reasonable quantities of water (e.g., Brassington, 2007). The Walloon Coal Measures, for example, contains thin permeable coal seams with inter burden of low permeability siltstone that can harbour

significant quantities of water, particularly in areas at shallow depth where it is more readily recharged (DNRM, 2016).

The GAB is a hydrogeological basin comprised of geologic sequences from several different basins. Main aquifers within the GAB, are the Precipice Sandstone, Hutton Sandstone, Springbok Sandstone, Gubberamunda Sandstone, Mooga Sandstone, Bungil Formation, and their equivalents (DNRM, 2016). Simplistically, however, the GAB can be described as alternating layers of laterally continuous permeable sandstone aquifers and lower-permeability siltstone and mudstone aquitards, which generally dip in a south-westerly direction. The majority of recharge in the GAB is the result of rainfall, directly infiltrating outcrop areas or indirectly from streams or overlying aquifers in the north, north-west, north-east and east along the Great Dividing Range (e.g. Kellett et al., 2003). However, due lateral and vertical variability in the lithology, variations in groundwater recharge and the length of time the water resided in the formation, water quality is spatially variable (DNRM, 2016).

The Bowen and Surat basins have long and complex hydrocarbon generating histories, involving both thermogenic and biogenic hydrocarbon formation mechanisms. In the Bowen Basin, six source rock units have been recognized to account for the bulk of the generated hydrocarbons: Moolayember Formation, Baralaba Coal Measures, Burunga Formation, Banana Formation, Flat Top to Buffel formations and the Reids Dome beds (Boreham et al., 1996; Carmichael and Boreham, 1997). The Permian Baralaba Coal Measures and Burunga Formation were suggested to be the most productive units, forming more than 90% of the oil and ~65% of the thermogenic gas within both the Bowen and Surat basins (Shaw et al., 2000). CSG is contained primarily within the seams of the Walloon Coal Measures of the Surat Basin. The Walloon Subgroup CSG consists almost entirely of methane (>98%; air-free basis), with only minor amounts of carbon dioxide and nitrogen, and very low levels of ethane (<1%; Hamilton et al., 2012).

Both migrated petroleum as well as coal layers could, in principle, be major suppliers of natural hydrocarbons and other organic compounds. Crude oil, forming naturally underground, could also provide a range of hydrocarbons to groundwater. Since crude oil has the tendency to migrate to the surface by buoyancy, it would have an even greater capacity to come into contact with groundwater. Indeed, there is significant evidence for hydrocarbon migration in the Bowen/Surat basins. For example, since thermogenic gas in the WCM is regarded to originate from a stratigraphically distant Permian source, and many intervening units have sealing capacity, a viable migration path associated with for example fault leakage is required (e.g., Hamilton et al., 2012; Garnett et al., 2013; Underschultz et al., 2016). Using hydrocarbon migration indicators (mud logs, drill stem, wireline and production test sample analysis, and staining, fluorescence, and streaming hydrocarbon occurrences from drill cuttings and cores), Underschultz et al. (2016) noted that hydrocarbons are often clustered along lineations such as the Moonie-Goondiwindi and Burunga-Leichhardt fault systems. Atop the WCM, hydrocarbon migration indicators are clustered along the northeastern subcrop edge of the Surat Basin where muddy strata at the top are either thin or eroded suggesting vertical leakage occurred to the overlying Springbok Sandstone aquifer (Underschultz et al., 2016). Therefore, as a result of hydrocarbon migration, ample opportunity exists for hydrocarbons and other organic compounds to become incorporated within aquifer systems.

Groundwater quality associated with coal seams could also be degraded by various naturally occurring hydrocarbons and other organic compounds. Coal, can be thought of as a two-component system composed of a mobile phase (saturated and aromatic compounds) and a macromolecular network of higher molecular weight constituents (Given, 1984a,b; Given et al., 1986). The propensity of coal-derived aromatic hydrocarbons (and some saturated equivalents) to degrade aqueous solutions is not surprising. While solubilities of many hydrocarbons in water are extremely low, even in the range of temperature and pressure conditions encountered under geologic settings, gases and low molecular weight aromatics such as benzene, toluene and xylenes haven some propensity to enter groundwater (e.g. McAuliffe, 1966; Peake and Hodgson, 1966, 1967; Price, 1976).

The physico-chemical characteristics of hydrocarbons and other organic compounds is related to their various chemical structures. With respect to their release into groundwater, these hydrocarbons are typically placed into three groupings:

1) Aliphatic hydrocarbons, which are comprised of saturated straight-chain or branched-chain hydrocarbons;

2) Monocyclic aromatic hydrocarbons, which are comprised of benzene, toluene, ethylbenzene and the xylene isomers (BTEX);

3) Polyaromatic hydrocarbons, which refer to hydrocarbons containing to or more fused aromatic ring structures.

The specific molecular composition of hydrocarbons and other organic compounds in groundwater will principally depend on their depositional source(s). However, in general, lignite and anthracite coals contain much lower proportions of volatile organic matter <C_{10}) than their bituminous counterparts. Therefore, regional variations in the physical maturation conditions of coal needs to be taken into consideration (see Schinteie et al., 2015 and references therein).

The environmental fate of such compounds in the subsurface and their release into groundwater can at least partially be explained and predicted by their physical and chemical properties. Key hydrocarbon physico-chemical properties of concern are solubility, sorption, volatility, biodegradability, chemical stability, density, toxicity, and abiotic chemical reactions.

Importantly, any movement of hydrocarbon/organic compound may be retarded by adsorption onto naturally-occurring solids located either in the vadose zone or the aquifer. Indeed, solid-solution interfaces will be an important aspect in the fate of hydrocarbons and other organic compounds in groundwater. Sedimentary rocks in the subsurface and the surface are characterized by significantly high surface to volume ratios and would allow ample opportunities for any dissolved compound to interact with (Stumm and Morgan, 1996). In regards to hydrocarbons and other organic compounds, the hydrophobic effect is perhaps one of the most important factors leading to their sorption onto various surfaces. Porosity of coal is another property that affects hydrocarbon adsorption, since it affects the surface area onto which hydrocarbons can be sorbed. Therefore, organic-rich materials such as coals can significantly affect the concentrations of hydrophobic compounds in the environment. Indeed, previous absorption experiments by Taulis and Stearman (2015) showed that sub bituminous coal from the Surat Basin has the capacity to absorb benzene from aqueous solutions.

Importantly, microbes are able to degrade a host of different hydrocarbons in the Surat and Bowen Basins. The strategies used and the organisms involved varied by habitat. In oxic habitats, (outcrops, spoil piles etc) fungi are able to relatively rapidly depolymerase coal producing a range of smaller, more labile products (Bass and Richards, 2011). In these settings, bacteria too play important roles and are also able to cleave aromatic compounds from coal and cleave aromatic rings using similar enzymes to fungi (Seo et al., 2009). In anoxic environments, different processes, mostly undertaken by bacteria, drive degradation and mobilisation of hydrocarbons, though the exact process and identity of key taxa remain somewhat poorly characterised and would benefit from additional studies. The biodegradation of hydrocarbons can proceed at a relatively rapid scale, especially under oxidizing conditions. Barker et al. (1987), for example, observed the rate of degradation of ~7.6 mg/L BTX (benzene, toluene and xylene) compounds introduced below the water table to monitor the migration of hydrocarbon compounds through a sandy aquifer in Borden, Ontario. Within 434 days, essentially all the injected BTX mass was degraded, with compounds persisting longest in localized anoxic layers.

Dispersion will act to dilute and lower the concentration of a dissolved compound through hydrodynamic dispersion. Previous studies of hundreds of groundwater contamination sites throughout the U.S.A have provided significant insight into the fate and transport of petroleum hydrocarbons in the subsurface. Such work typically involved studies on, for example, leaking underground fuel tanks, petroleum storage tanks, and service station sites. Based on the observed trends, the studies grouped the plumes into four categories, assuming that the hydrocarbons originated from a point source in naturally flowing groundwater systems (Beck and Mann, 2010):

1)   Expanding Phase – occurring due to mass loading and resulting in the initiation of a plume.

2)   Stable Phase – resulting when continues expansion of the plume ceases due to balance occurring between mass loading and the rate of attenuation.

3)   Contraction Phase – occurring when the rate of attenuation exceeds mass flux of hydrocarbons, resulting in plume shrinkage.

4)   Depletion Phase – occurring when there is shrinkage of the hydrocarbon plume to the immediate vicinity of the source area.

More detailed guidelines for assessing the overall plume status are listed in Beck and Mann (2010). Measurements of concentration trends for plume analyses statistically-based trend analysis (e.g. Mann-Kendall, Mann-Whitney tests; Beck and Mann, 2010). Past and future plume behaviours are interpreted by describing them in both space (concentration vs. distance) and time (concentration vs. time). Therefore, it is necessary to collect long-term monitoring data from bores distributed throughout a plume. Uncertainties in calculating the rates of natural attenuation stems from factors such as monitoring network design, uncertainties in sampling methods and laboratory analyses, seasonal variations, as well as inherent heterogeneities in most groundwater plumes.

Case studies of groundwater quality degradation by hydrocarbons typically involve the oil spills from anthropogenic sources such as storage tanks and pipelines. From these studies, the distribution and concentrations of contaminants can be deduced. While anthropogenic point sources of contaminants may produce far greater amounts of hydrocarbons and other organics than natural systems, they prove valuable insights for inferring the groundwater distributions of natural counterparts (e.g. BTEX) over time and space.

In the groundwater water table directly affected by a 1979 pipeline rupture near Bemidji, Minnesota, for example, only 58% of the total dissolved organic carbon (TDOC) is comprised of non-volatile hydrocarbons with the majority of these compounds being aromatic compounds (mostly BTEX, alkylated benzenes, and polyaromatic hydrocarbons). Benzene was found to be the dominant (70%) volatile compound near the spilled oil followed by C1-4 alkylated benzenes (14%). Toluene and o-xylene decreased to below detection limits within 10 m of the source, while benzene and ethylbenzene travelled further downgradient. While the TDOC remained elevated (>10 mg/L) for a distance of ~75-80 m downgradient from the spill site, concentrations declined rapidly to below detection limit further away.

Organic compounds also have the propensity to volatilize in the vadose zone. These organic gases will subsequently migrate away from the source and may be either lost to the atmosphere, contaminate other water bodies, or accumulate in a bed of less permeable material. Some CSG wells in the Camden and Glaucester areas in NSW exhibited hydrocarbon profiles with VOCs composed of alkane class and straight chain, cyclic and branched alkanes through to C8 (Day et al., 2016). While alkenes were not detected in the hydrocarbon profile of the well gases, aromatic compounds were noted at low concentration with the highest aromatic content measured in samples from AGL operations at the Gloucester gas field (around 0.5ppmv benzene, 0.2ppmv toluene, 0.02ppmv xylenes). The occurrences of the larger (i.e. higher molecular weight) alkanes and aromatics correlated with those gases containing higher non-methane hydrocarbon concentration. Therefore, these components are believed to have originated from gas formation processes in the coal seam layers (Day et al., 2016). Aromatic compounds, for example, are generated under processes involved in its thermogenic and/or microbial formation; microbial fragmentation of coal can generate hydrocarbon intermediates including alkanes and related structures, benzene, toluene, ethylbenzene, xylenes and polycyclic aromatic hydrocarbons. These intermediates, in turn, can undergo anaerobic oxidation and fermentation to form methanogenic substrates that finally undergo methanogenesis to produce the methane dominant gas (Strąpoć et al., 2011). Since these compounds are detected in coal formation waters, it is possible that residual aromatic compounds can be found in coal seam gas.

Hydrocarbons may also enter the soil environment and exist either in the pore spaces in the free form or, in most of cases, become associated with sorbed organic matter or exist. The strength of this association will vary and depend on the nature of the hydrocarbon and the organic matter content of the soil (Connell and Miller, 1984; Sadler and Connell, 2003). Finally, if exposed to the surface, abiotic chemical reaction may also attenuate hydrocarbon and other organic compounds through the exposure to light. Aromatic hydrocarbons, in particular, are able to absorb both visible and ultraviolet light through their ring structures (van der Heul, 2009).

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