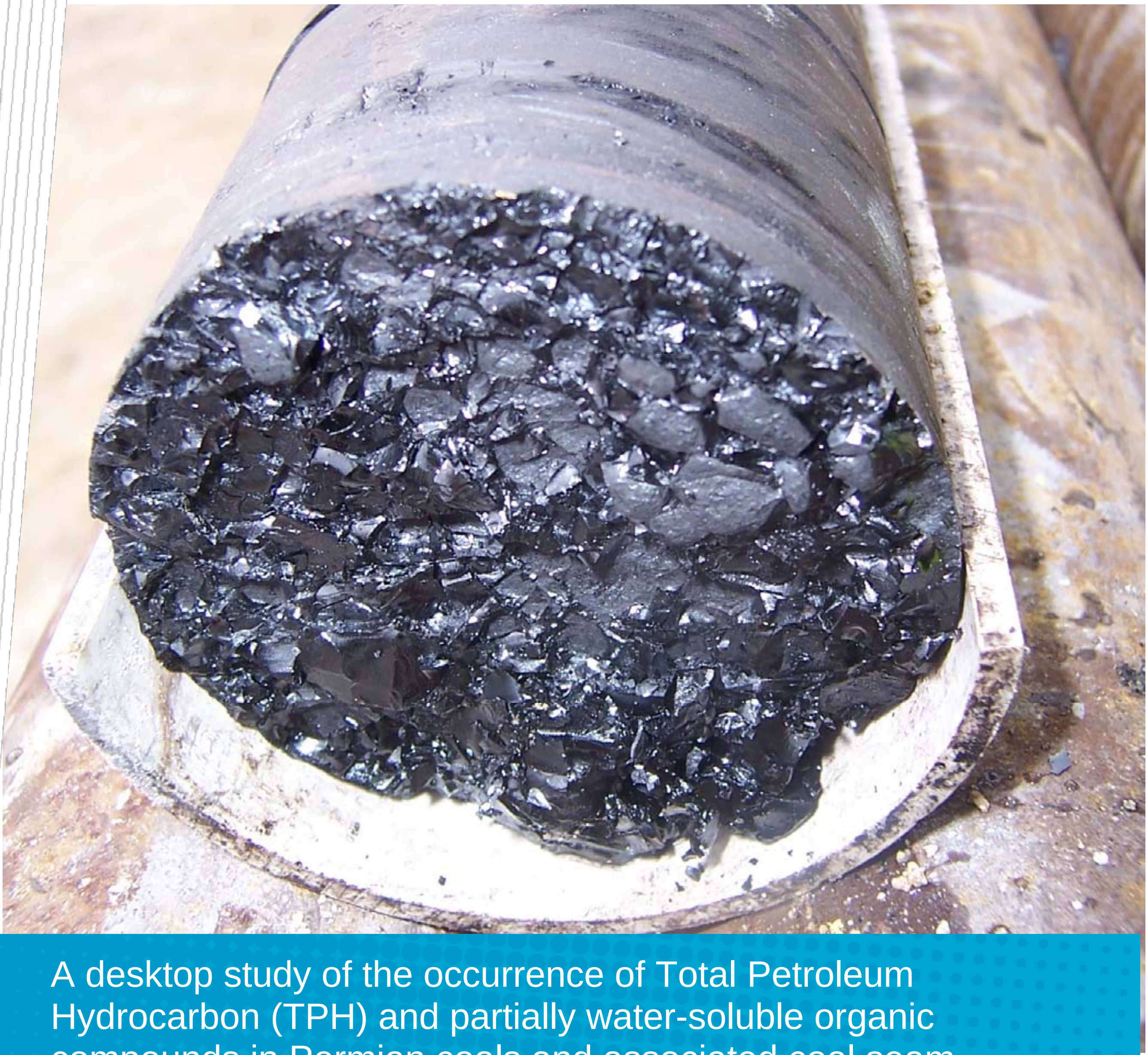

A desktop study of the occurrence of Total Petroleum Hydrocarbon (TPH) and partially water-soluble organic compounds in Permian coals and associated coal seam groundwater

Petroleum & Geothermal Research Portfolio

Open File Report EP-13-09-11-11

A report to AGL Energy

Herbert Volk[1], Kaydy Pinetown[1], Colin Johnston[3] and Wendy McLean[3]

1) CSIRO Earth Science and Resource Engineering
2) CSIRO Land and Water
3) Parsons Brinckerhoff

Enquiries should be addressed to:

Dr. Herbert Volk
Organic Geochemistry Team Leader, Petroleum & Geothermal Research Portfolio
P.O. Box 136, North Ryde, Sydney, NSW 1670, AUSTRALIA
Phone: + 61 2 9490 8954
Email: Herbert.Volk@csiro.au

or

Dr. Neil Sherwood
Stream Leader Unconventional Gas
NSW 1670, AUSTRALIA
P.O. Box 136, North Ryde, Sydney, NSW 1670, AUSTRALIA
Phone: + 61 2 9490 89576
Email: Neil.Sherwood@csiro.au

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EXECUTIVE SUMMARY

The increased exploitation of coal seam gas (CSG) has raised concerns over the possible presence of dissolved hydrocarbons in produced groundwater as well as the release of these compounds in groundwater systems hosting the coal measures. An extensive search has been conducted for information on the occurrence of Total Petroleum Hydrocarbon (TPH) and partially water-soluble organic compounds (e.g. benzene, toluene, ethylbenzene and xylenes (BTEX), phenols) in Permian coals and associated coal seam groundwater. The Permian coals have been a particular target for exploiting CSG in Australia. The search incorporated peer-reviewed literature and text books identified in scientific literature databases, information from state and federal geological surveys, and open file reports identified through internet searches or available in the archives of CSIRO and Parsons Brinckerhoff. An extensive review of Permian coal basins across Australia has also been included in this desktop study.

Numerous occurrences of oil shows are associated with Permian coals, and it is conceivable that these oil shows may lead to the occurrence of TPH in formation water. However, very few records are available on naturally elevated TPH in groundwater produced from Permian coal basins. Where petroleum occurrences have been analysed in detail it proved to be difficult to associate these occurrences to specific coal measures, or even distinguish oils from Permian versus younger coals. The most thorough documented studies on the use of geochemistry to make such distinctions have been conducted for the Cooper-Eromanga and Bowen Basins.

The majority of organic matter in coal is derived from lignin, a largely aromatic biopolymer. Water-soluble constituents of coal are largely aromatic hydrocarbons and heterocyclics, and they may be produced by the cleavage of the aromatic structures within the coal matrix. Water-soluble compounds from coals and petroleum may include a wide variety of oxygen-bearing aromatic compounds (e.g. phenols, aldehydes, ketones, and various carboxy-, hydroxyl- and methoxy- bearing compounds), nitrogen-bearing compounds (pyridines and amines), and monoaromatic hydrocarbons such as BTEX, and to some extent polycyclic aromatic hydrocarbons (PAHs) and low molecular weight aliphatic hydrocarbons. Many of these organics have adverse health effects and some of them are known carcinogens.

Despite the aromatic nature of coals, reports on BTEX and other organics associated with CSG are sparse. Many of the reports of organics in groundwater were linked to underground coal gasification (UCG) operations in QLD, which is fundamentally different to CSG production. In March 2005, Sydney Gas reported BTEX below the laboratory limit of reporting (LOR) in their gas exploration well, Jilliby 1 at Wyong intersecting the Newcastle Coal Measures. AGL reported that BTEX concentrations were below LOR in their gas exploration well HB01 penetrating the Wittingham Coal Measures in the Hunter Valley. In November 2010 Arrow Energy announced that traces of benzene (1

to 3 ppb) were detected in three wells in its developments in the northern Bowen Basin. Investigations are currently under way to determine if benzene is naturally occurring at this site or is elevated due to resource development activities. TPH data are available for Permian coal seams in the Bowen Basin at the Middlemount Mine. TPH were also identified in waters associated with the Permian Wittingham and Newcastle Coal Measures in the Yarramalong and Hunter valleys (AGL and Sydney Gas). APLNG published a table of average amounts of organic compounds from forty seven wells in the Talinga gas field. While many of the compounds may have been naturally released from coals, other such as nitrophenol and chlorophenols have no known biological origin and hence are not of coal origin.

Although it is recognised that dissolved organic compounds may be present in some CSG produced waters, an extensive study issued by the Committee on Management and Effects of Coalbed Methane Development and Produced Water in the Western United States (2010) highlights that in the USA these compounds are neither well documented nor well researched. Through the course of this desktop study it became clear that organics in water associated with Permian coals in Australia have also not been researched in a comprehensive manner. Where organic compounds have been found, these were often difficult to trace to their origin. Some of the detected compounds such as halogenated phenols clearly have no natural origin from coal. Others such as BTEX and PAH may be derived from coal.

Additional baseline data, together with periodic checks of organic compound concentrations throughout the production life of a gas well would assist in building a suitable database and understanding the occurrence and distribution of these compounds in deep groundwater systems. Fingerprinting of aromatic compounds in coals and how these translate into fingerprints leached into groundwater may offer a way to trace organics in future studies.

1. INTRODUCTION

This desktop study completed on behalf of AGL Energy (AGL) summarises the results of a literature review on the occurrence of Total Petroleum Hydrocarbon (TPH) and partially water-soluble organic compounds such as the aromatic hydrocarbons benzene, toluene, ethylbenzene and xylenes (BTEX) in Permian coals and associated coal seam groundwater. Australia has vast Permian coal resources, and coal seam gas (CSG) from the Sydney-Gunnedah-Bowen Basin is the foundation of a burgeoning multi-billion dollar energy export industry in Queensland. However, concerns over environmental impacts of this expanding industry on water resources have led to significant public resistance. One of those concerns is the concentration of organics in water.

2. SCOPE

The project brief from AGL for this literature review was to:

- Identify Permian Coal basins across Australia
- Undertake a literature study that focuses on:
    - The organic chemistry of Permian coals
    - The organic hydrochemistry of associated coal seam groundwaters
- Report on the conclusions of the most relevant studies, focusing on the natural occurrence of TPH/BTEX compounds

To address the issue of organics in coal seam groundwaters, it is important to document the current stage of knowledge on this issue. The purpose of this report is to document that current state of knowledge from both Australian and overseas coal basins. The focus is on older Carboniferous and Permian coal basins where possible because it is these basins where AGL is focusing most of its CSG production and exploration activities. This study is based on published information, internet searches and open file information and research.

3. APPROACH AND METHODOLOGY

The following sources of information were used to compile this literature review:

3.1 Information from scientific literature databases

3.1.1 Information from Herbert Volk's literature

22 of 3253 references from Herbert Volk's literature database were selected and included in this literature review.

3.1.2 Information from EAOG member database

The European Association of Organic Geochemists (EAOG) compiles monthly databases on a range of topics concerning organic geochemists, and provides this information to its members as searchable EndNote databases. Databases from 2005 - May 2011 were searched for the terms Permian&Coal&Water, and Permian&Coal&Australia. Each year contains between 3000-5000 references which were searched.

3.1.3 Web of Knowledge

Web of Science is a multidisciplinary index, with searchable author abstracts, covering the journal literature of the sciences (Science Citation Index Expanded), social sciences (Social Sciences Citation Index) and arts and humanities (Arts and Humanities Citation Index). It was our main source of information from scientific literature databases available for subscribers. The following Booleans and Field Tags are available for customising search results:

Booleans (not case sensitive):
AND, OR, NOT, SAME, NEAR

Field Tags (not case sensitive):
TS= Topic, TI= Title, AU= Author [Select terms from the index], RID= ResearcherID, GP= Group Author [Select terms from the index], ED= Editor, SO= Publication Name [Select terms from the index], DO= DOI, PY= Year Published, CF= Conference, AD= Address, OG= Organization, , SG= Suborganization, SA= Street Address, CI= City, PS= Province/State, CU= Country, ZP= Zip/Postal Code, FO= Funding Agency, FG= Grant Number, FT= Funding Text,

The following search terms were applied:
ts=Permian and ts=water and ts=Australia and ts=coal, 21 hits, 2 pertinent
ts=Permian and ts=organic and ts=Australia, 72 hits, 17 pertinent
ts=Permian and og=curtin and ts=coal, 6 hits, 1 pertinent
ts=permian and au=alexander and ci=perth, 10 hits, 6 pertinent
ts=water and ts=gas and ts=organic and ts=coal, 200 hits, 4 pertinent

3.1.4 American Geophysical Union AGU Digital Library

Browse, search content, and access full-text articles for the following AGU titles: Journal of Geophysical Research, Water Resources Research, Reviews of Geophysics, Geophysical Research Letters, Radio Science, Tectonics, Paleonoceanography, Global Biogeochemical Cycles, Geochemistry, Geophysics, Geosystems, and Space Weather.

Searches yielded information that was already discovered in Web of Science, and hence was not considered in more detail in this study.

3.1.5 Energy Citations Database

The Energy Citations Database (ECD) provides free access to over 2.4 million science research citations with continued growth through regular updates. There are over 267,000 electronic documents, primarily from 1943 forward, available via the database. Citations and documents are made publicly available by the U.S. Department of Energy (DOE). Many of the search results are linked to a PDF file that can be downloaded free of charge.

Copyrighted, peer-reviewed articles and book chapters do not show up in the search results. The relevance of the articles was found to be low. A search for coal "permian water australia" yielded 155 matches, and a search for "Permian organic Australia" yielded 190 matches. Several of the search results were duplicated from Web of Knowledge, and no new relevant references were found. A search for "Permian Curtin coal" yielded 5 matches (all irrelevant), a search for "permian alexander perth" yielded 7 results (irrelevant or duplicated). A search for "water gas organic coal" yielded 10854 hits, most of them irrelevant and in sheer number not a meaningful search result.

3.1.6 Environmental Sciences & Pollution Management on ProQuest

This multidisciplinary database provides unparalleled and comprehensive coverage of the environmental sciences. Abstracts and citations are drawn from over 6000 serials including scientific journals, conference proceedings, reports, monographs, books and government publications.

Searches in this information source can be highly customised. A search for (((Permian) AND water) AND australia) AND coal returned 7 results, but these were either irrelevant or duplications of previous search results. A search for ((Permian) and organic) and Australia yielded 19 search results, and included some books and conference abstracts in addition to peer-reviewed articles, the latter being duplicated form Web of Knowledge database searches. ((Permian) AND alexander) AND perth found 0 results, while (((water) and gas) and organic) and coal returned 519 search results. Many of the search results were on the partitioning of organic matter from coal tar particles and hence not the subject of this review.

3.1.7 GeoRef on ProQuest

The GeoRef database, established by the American Geological Institute (AGI) in 1966, provides access to the geoscience literature of the world. GeoRef is the most comprehensive AGI database in the geosciences and continues to grow by more than 80,000 references a year. The database contains over 3 million references to geoscience journal articles, books, maps, conference papers, reports and theses. The GeoRef database covers the geology of North America from 1693 to the present and the geology of the rest of the world from 1933 to the present. The database includes references to all publications of the U.S. Geological Survey. Masters theses and doctoral dissertations from US and Canadian universities are also covered. To maintain the database, GeoRef editor/indexers regularly scan more than 3,500 journals in 40 languages as well as new books, maps, and reports. They record the bibliographic data for each document and assign index terms to describe it. Each month between 4,000 and 7,000 new references are added to the database.

The search interface of Georef on ProQuest is very similar to that of Environmental Sciences & Pollution Management on ProQuest. A search for (((Permian) AND water) AND australia) AND coal returned 116 results, of which 7 pertinent references were selected.

A search for ((Permian) and organic) and Australia yielded 881 search results, which yielded results from the following dominant sources; Queensland Government Mining Journal (62) Abstracts - Geological Society of Australia (47) Organic Geochemistry (39) International Journal of Coal Geology (38) Advances in the Study of the Sydney Basin: Proceedings of the Symposium (32) Bulletin - Australia, Bureau of Mineral Resources, Geology and Geophysics (30) Proceedings - Australasian Institute of Mining and Metallurgy (20) Abstracts with Programs - Geological Society of America (20) Geochimica et Cosmochimica Acta (18) AAPG Bulletin (17) Quarterly Notes - Geological Survey of New South Wales (16) The APEA Journal (14) Annual Meeting Expanded Abstracts - American Association of Petroleum Geologists (14) Australian Coal Geology (12) Report - Geological Survey of Queensland (12) Palaeogeography, Palaeoclimatology, Palaeoecology (12) Australian Journal of Earth Sciences (10). While many interesting papers were included on Permian coal geology in Australia, the search results were too wide for being scrutinised in detail.

A search for ((Permian) AND alexander) AND perth found 22 results which were largely already covered from a search in the Web of Knowledge. A search for (((water) and gas) and organic) and coal returned 920 search results. This generic search was difficult to distil down to relevant articles. Many of interesting articles were already found in previous searches. This was also true for a search using the term "((Permian) and organic) and Australia" (881 results), and for a search for (((water) and gas) and organic) and coal (920 search). A search for ((Permian) AND alexander) AND perth found 22 results, of which 4 additional references were selected.

3.1.8 GeoScienceWorld

GeoScienceWorld (GSW) includes peer-reviewed articles and other materials with linked reference lists from 30 high-impact journals in a broad range of geoscience areas. The digital collection is updated continuously with the most current journal issues. A primary strength of GSW is the ability to search full text in a linked collection, but GSW is also integrated with GeoRef, the premier abstracting and indexing database in the field, hence a separate search in GeoScienceWorld did not yield information that was not found by GeoRef.

3.2 Information from State and Federal Geological Surveys

3.2.1 Geological Survey of New South Wales

Geoscience information, open file and confidential company reports and well completion reports are accessible via the NSW Department of Primary Industries Digitally Imaging of Geological System (DIGS) database. The database is searchable for fields such as, for example, ‘keyword’, ‘location’ and ‘subject’, and search results are downloadable in portable document format (pdf). Searches conducted for this review on Permian coal basins in NSW have produced 47 publically available documents that are attached to this review.

3.2.2 Geological Survey of Queensland

The Geological Survey of Queensland maintains the Queensland Digital Exploration (QDEX) reports system, which is a similar database to that of the NSW Department of Primary Industries. Various search fields are provided, although a preset list of keywords is accepted for certain search fields. It is a requirement that users register to access this database, although information (up to 50MB of data) can be downloaded free of charge once found. Search results are also downloadable in pdf format. A variation of keywords searches produced numerous documents related to coal and petroleum in general, but none specifically related to the focus of this review.

3.2.3 Geological Survey of Western Australia

Similar to the Geological Survey of Queensland, the Geological Survey of Western Australia maintains a very comprehensive information management system (WA Petroleum and Geothermal Information Management System, WAPIMS), archiving predominantly open file and confidential company reports, comprehensive well completion reports and maps. Users are also required to register to access this database and information can be download free of charge in various formats (xls, pdf, LAS) once found. Given the size of the database, which contains information for more than 3000 wells, a thorough search of the database was outside the scope of this review.

3.2.4 Department of Primary Industries and Resources South Australia, Mineral Resources Tasmania and Geoscience Australia

Geoscience information (geology and resources) were obtained from the Department of Primary Industries and Resources South Australia, Mineral Resources Tasmania and Geoscience Australia websites for basins located in South Australia and Tasmania, as well as for general information on Australia’s coal and petroleum resources.

Key references used to summarise the geology of Australian coal-bearing basins in this review include Harrington *et al.* (1989) and Ward *et al.* (1995), amongst others.

4. PERMIAN COAL BASINS ACROSS AUSTRALIA

4.1 Coal and petroleum production in Australia

Australia produced 497 Mt of raw coal in 2008. Its recoverable economic demonstrated resources (EDR) of black coal amounted to 39.2 Gt at the end of 2008, with 56% of this resource located in Queensland and 40% in NSW, of which 35% are contained within the Sydney Basin and 34% within the Bowen Basin (GA and ABARE, 2010).

Gas production in 2008 was around 1,832 PJ. This includes production from conventional and unconventional sources. Economic and sub-economic conventional gas resources are estimated to be 180,400 PJ, of which 92% are in the Bonaparte, Browse and Carnarvon Basins. Economic demonstrated CSG resources were estimated to be 16,590 PJ, 95% of which is located in Queensland, with a total identified resource of 168,600 PJ. Tight gas resources are estimated to be 22,000 PJ (GA and ABARE, 2010).

Australia is a significant producer of fossil energy for domestic and export purposes. In 2008, Australia produced 1,059 PJ of crude oil, condensate and liquefied petroleum gas (LPG), predominantly from basins located offshore of Western Australia (GA and ABARE, 2010). As at January 2009 Australian crude oil resources were estimated to be around 8,414PJ (identified oil resources of 30,794 PJ), with crude oil representing 27%, condensate 53%, and naturally occurring LPG 20%, of liquid petroleum resources. Most of the oil resources are contained within the Carnarvon, Bonaparte, Gippsland, Browse, Perth and Bass Basins offshore, and within the Cooper-Eromanga, Bowen-Surat and Amadeus Basins onshore. Condensate resources are found in ten basins, but the Bonaparte, Browse and Carnarvon Basins contain 92% of the resource. Similarly, naturally-occurring LPG resources are identified in eight basins with the majority (85%) of this resource contained within the Carnarvon, Browse and Bonaparte Basins. Australian's shale oil resources were estimated to be around 131,600 PJ in 2009 with most of it located in Queensland (GA and ABARE, 2010).

4.2 Basins (mainly) in NSW

4.2.1 Ashford Coal Field

Geological setting

The Ashford Coalfield crops out as a discontinuous belt, located between Bonshaw and Ashford on the New South Wales (NSW)/Queensland border (Figure 1; Flood, 1995). The coal measures occur over a distance of 80 km (NEC, 2011a). The coal measures were formed within a west-slipping subduction complex and deposited on metamorphosed Carboniferous mudstone, chert, tuff and quartzite. A major reverse fault, the Severn Thrust, forms the western margin of the deposit and strata dips steeply towards the northwest into the thrust fault (Flood, 1995). It is suggested that the Ashford Coal Measures are remnants of Early Permian deposits on the New England Block (O'Brien, 1989a), and have been correlated with the Greta Coal Measures in the northern Sydney Basin (Flood, 1995). The two main seams containing coal and carbonaceous shale, the Ashford and Bonshaw seams are present within the 300 m of mudstone, sandstone and conglomerate comprising the coal measure sequence (O'Brien, 1989a).

Coal and petroleum resources

The Ashford seam is the most economic seam. It varies between <2 and >15 m and occurs between 10 to 30 m above the Carboniferous/Permian unconformity (NEC, 2011a). The coal is vitrinite-rich and classified as high rank with a mean maximum vitrinite reflectance (VR) of 1.02%, as reported by Flood (1995), and 1.14% as found by Northern Energy Corporation (NEC, 2011b). It has a low sulphur content (0.45%) and moderately low ash yield (Flood, 1995). The minor Bonshaw seam is around 2 m thick and situated 50m above the Ashford seam (NEC, 2011a).

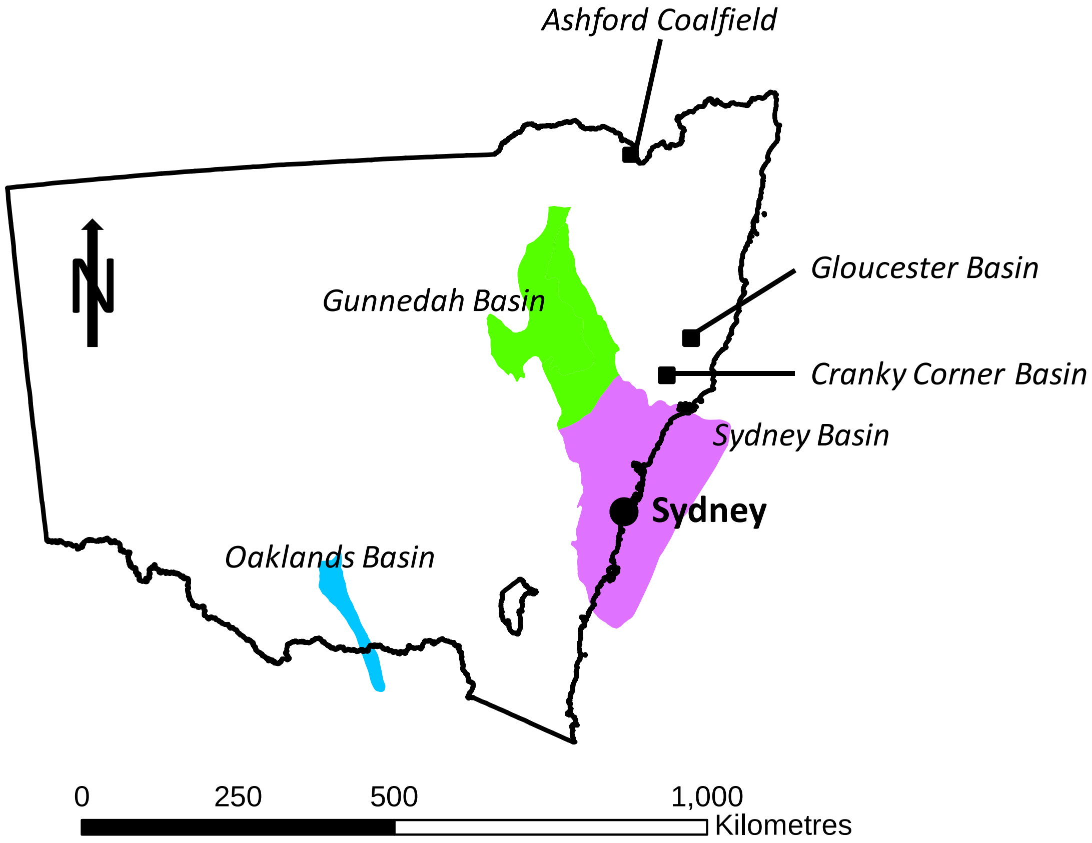


Figure 1: Location of Permian sedimentary basins in New South Wales.

4.2.2 Cranky Comer Basin

Geological setting

The Cranky Corner Basin is located northwest of Newcastle and is a synclinal structure composed predominantly of Late Carboniferous and Permian rocks (Figure 1). The axis of the structure strikes approximately northeast to southwest (Stevenson, 2003). Carboniferous sediments of the Seaham Formation form the base lowermost stratigraphic unit of the basin and are overlain by Late Carboniferous to Early Permian rocks of the Dalwood Group. Sediments within the Dalwood Group vary from volcanic conglomerates and felsic tuffs of the Tamby Creek Formation at the base, to bioturbated sandstones and siltstones of the Billy Brook Formation at the top of the Dalwood Group (Stevenson, 2003). The two formations located between these are the Beckers Formation and Cranky Corner Sandstone, consisting of bioturbated shoreface sandstones and siltstones, and very fine- to medium-grained upwards-coarsening fossiliferous sandstone, respectively (Stevenson, 2003). Within the Greta Coal Measures which overlie the Dalwood Group, three significant coal horizons are present, namely the Stanhope, Eui and Tangorin seams (Stevenson, 2003). The Stanhope seam appears to be of great interest. The Big Table Top Formation of the Maitland Group overlies the Greta Coal Measures.

Coal and petroleum resources

A conglomerate of around 1.2 m thickness divides the 3m thick Stanhope seam in an upper and a lower split. The upper spilt consists of banded lithotypes with dull coal horizons and pyrite lenses. The seam has a moderate (10%) ash yield and high (5%) sulphur content (Stevenson, 2003). The lower spilt comprises banded dull and bright coal with carbonaceous siltstone and claystone towards the base. It has a sulphur content of 5% and ash yield of 15% (Stevenson, 2003). The Stanhope seam is predominantly vitrinite-rich with a mean random VR of 0.58% reported by Diessel and Gammidge (2003) for the lower split of the seam. The highest mean random VR in the basin of 0.75% is reported for the Beckers Formation (Diessel and Gammidge, 2003). Studies by Boreham and Korsch (2003) on the source potential of rocks in the Cranky Corner Basin suggest that considerable gas and oil potential exists in the Type II/III organic matter of the Seaham Formation and Greta Coal Measures. Hydrogen-rich Type I organic matter in the Greta Coal Measures and the Billy Brook Formation also shows excellent source rock potential (Boreham and Korsch, 2003).

4.2.3 Gloucester Basin

Geological setting

The Gloucester Basin is a remnant inter-arch basin located approximately 100 km north of Newcastle (Figure 1). It is 40 km long and 10 km wide. The north-south trending synclinal nature of the basin is the result of collision between the East Australian and Pacific Plates, forming associated magmatic

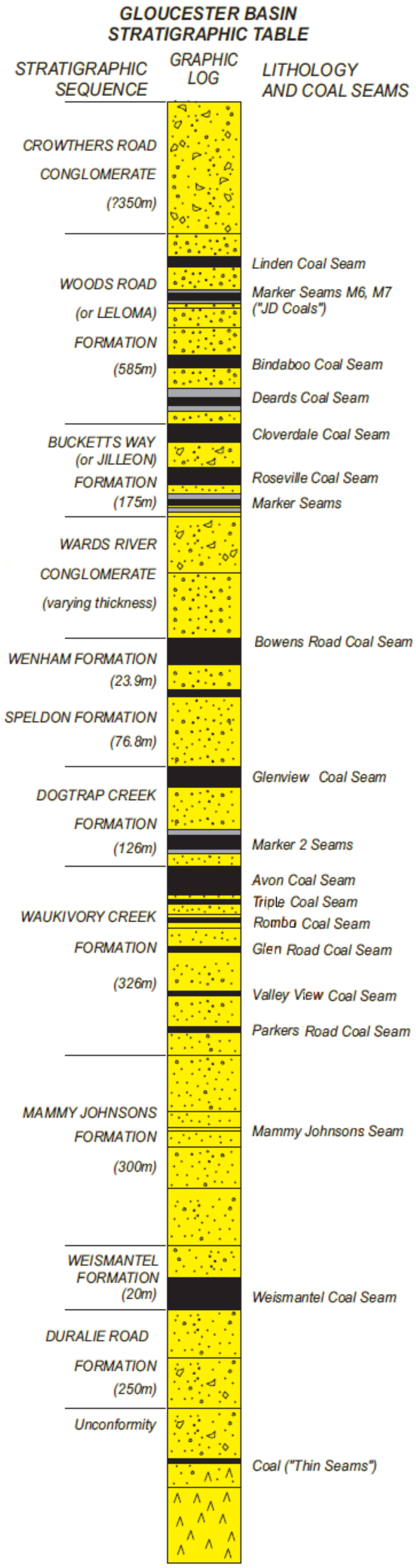


Figure 2: Stratigraphy of the Gloucester Basin (from Gloucester Coal, 2011).

arch and sedimentary basins. The basin has been exposed to periods of normal and reverse faulting, with major tilting associated with late stage compressional movements towards the end of the Permian, dividing the basin into three major structural units (Hughes, 1995). The Permian aged volcanic sequence of the Stroud Group is the lowermost formation and appears to be continuous with the Dalwood Group of the Sydney Basin. It underlies the Permian marine sediments of the Dewrang Group and the Permian non-marine sediments of the Gloucester Coal Measures. The Weismantel seam is the best developed coal seam within the Weismantel Formation (Figure 2) of the Dewrang Group (Brakel, 1989a). The main coal deposits in the basin are contained within the Avon and Craven Subgroups of the Gloucester Coal Measures. These deposits are separated by the Speldon Formation which was deposited by a marine transgression (Hughes, 1995).

Coal and petroleum resources

There are numerous coal seams within the Avon and Craven Subgroups. The main coal seams are Weismantel, Avon, Glenview, Bowens Road and Cloverdale seams. The Weismantel seam is the thickest uniform seam in the basin and contains a moderately high (1.80%) sulphur content. It is not considered an economic target on the northern, western and eastern margins of the basin. The Avon seam varies between 5 and 20 m in thickness, with one predominantly clean coal ply at the top of the seam, giving it the most potential for economic development (Hughes, 1995). Similar to the Weismantel seam, the Glenview seam has a fairly high sulphur content ranging between 0.7 and 7.5%. It has a maximum thickness of 3 m. The Bowens Road seam consists predominantly of dull coal, and varies between <1 and 12 m. Coals below this seam generally contain a high proportion of inherent mineral matter, whereas those above are mainly lower ash coals after washing. The Cloverdale seam varies between 5 and 10 m in thickness and consists of variable coal and stone bands. Coals in the Gloucester Basin can be classified as medium to high volatile bituminous, with high raw ash values. Vitrinite contents vary between 65 and 75% for washed products of all except the Weismantel seam, which is around 45 to 50%. Vitrinite reflectance values are also variable ranging from 0.71% for the Weismantel seam to 1.20% for the Parkers Road seam (Hughes, 1995). Oil and gaseous hydrocarbons (mainly methane) have been identified in the basin during coal exploration drilling programs (Thornton, 1982). Numerous oil occurrences have been reported in the Durallie Road and Speldon Formations (Hughes, 1995). The Gloucester Basin CSG Project which is currently underway has reported 3P reserves of 360 Bcf of gas (Gloucester Project, 2011).

4.2.4 Gunnedah Basin

Geological setting

The Gunnedah Basin is a foreland basin which links the Sydney Basin in the south and Bowen Basin in the north (Figure 3). Major structural features include the Boggabri Ridge in the east, which separates the Maules Creek Sub-basin from the Mullaley Sub-basin, and the Rocky Glen Ridge in the west, which separates the Mullaley Sub-basin from the Gilgandra Sub-basin (Tadros, 1995a). The basin has rocks of Permian and Triassic age, with younger sediments of the Surat Basin portion of the Great Australian Basin (Hamilton *et al.*, 1989). Numerous sills, dykes and plugs have intruded the Permian and Triassic strata of the basin. The Early Permian Leard and Goonbri formations (Figure 3) overlying the basal Boggabri volcanic rocks consist of kaolinised pelletoidal claystone and lacustrine lithic sandstone and siltstone, respectively. The Maules Creek Formation is a thick unit in the Maules Creek Sub-basin but thinner in the Gilgandra Sub-basin and consists of lithic conglomerate, sandstone, siltstone, claystone and coal seams of up to 8 m thick. This was followed by deposition of the marine Porcupine Formation and shallow marine Watermark Formation (Tadros, 1995a), comprising sandstone, conglomerate and subordinate shale and limestone, and siltstone, sandstone, claystone and laminite, respectively (Hamilton *et al.*, 1989). Initial deposition of the Late Permian Black Jack Formation started with inundation followed with the return of marine conditions. This resulted in the formation of the Arkarula Sandstone Member. This was shortly followed by regression depositing fluvial sediments to the delta environment in the main portion of the basin, and then by the formation of the Hoskissons Coal Member due to widespread peat development. The uppermost Permian sediments of the Gunnedah Basin were deposited in an alluvial system with the end of Permian sedimentation marked by compression (Tadros, 1995a).

Coal and petroleum resources

The Maules Creek and the Black Jack Formations contain the majority of economic coal deposits in the Gunnedah Basin. Coal seams in the Maules Creek Formation vary between 1.5 and 3.5 m in thickness with frequent splitting. The Brown Seam is known for it good quality with a raw ash yield between 11.8 and 27.3%. The most important seams within the Black Jack Formation are the Hoskissons and Melvilles seams, ranging between 2.5 and 3.5 m, and >1 and 17 m, respectively. The Hoskissons seam is a medium ash, high volatile bituminous coal. Vitrinite reflectance in the basin varies between 0.5 and 0.9% (Tadros, 1995a). The seams within both formations contain prospective coal seam methane deposits as well as potential conventional gas plays as indicated by recent exploration activities (NSW DPI, 2011a). The Arkarula Sandstone Member and the Watermark Formation are considered to have the best potential for sources of petroleum since both are marine and liptinite rich. Permian reservoir units are included within the Black Jack Group and Watermark Formation. Numerous gas shows and some oil shows have been recorded in the Gunnedah Basin (NSW DPI, 2011a).

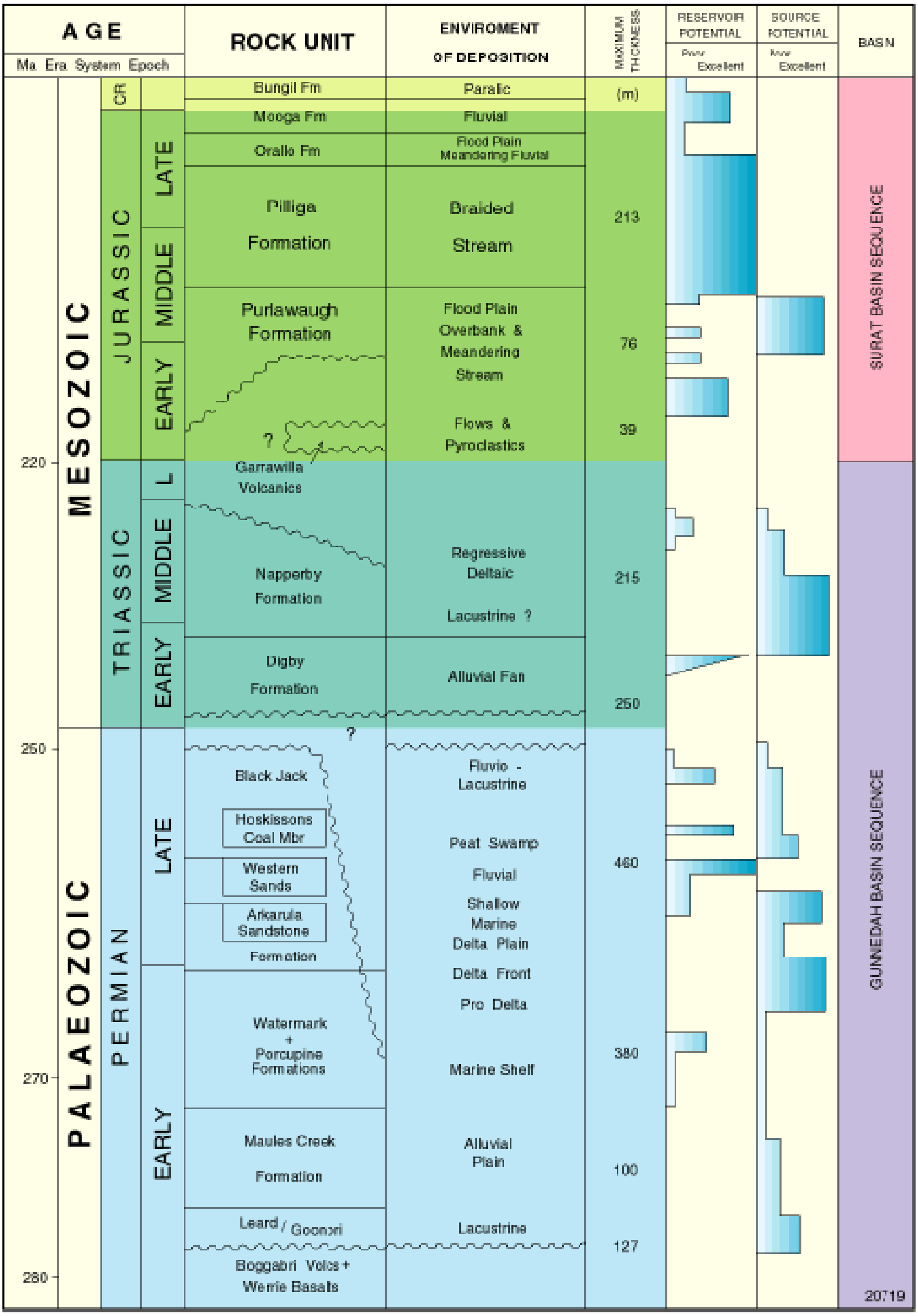


Figure 3: Stratigraphy of the Gunnedah Basin (NSW DPI, 2011a)

4.2.5 Oaklands Basin

Geological setting

The Oaklands Basin, which extends across the border between NSW and Victoria (Figure 1), is a Permo-Triassic basin completely concealed by Cainozoic sediments of the Murray Basin (Yoo, 1995). The basin orientation is dominated by the northwest-southeast trending Ovens Valley Graben (O’Brien, 1989a). Sediments of the basin are divided into the Early Permian Urana Formation, the Late Permian Coorabin Coal Measures and the Triassic Jerilderie Formation (Yoo, 1995). Marine mudstone, siltstone, sandstone, diamictite and conglomerate of the Urana Formation overlie metamorphosed sediments and Devonian granites. Three formations are recognised in the Coorabin Coal Measures, namely, the Narrow Plain, Loughmore, and Nowranie Creek Formations. The Narrow Plain Formation is a basal point bar sequence comprising micaceous sandstone with conglomerate bands and carbonaceous fragments, along with the Lane Shaft Coal Member (the main coal seam in the basin) at the top of the formation. The middle point bar deposits of the Loughmore Formation consist of sandstone, siltstone, claystone and carbonaceous claystone with the Coreen Creek Coal Member at the top. The Nowranie Creek Formation is only present in a small area and consists of claystone, carbonaceous claystone and abundant coal partings (Yoo, 1995).

Coal and petroleum resources

The Lane Shaft Coal Member is a low-volatile sub-bituminous coal varying in thickness between 4 and 18 m. It generally contains high proportions of inertinite and liptinite. The Coreen Creek Coal Member is poorly developed and generally <1.5 m thick although a 4. 8 m section of the seam has been intersected (Yoo, 1995).

4.2.6 Sydney Basin

Geological setting

The Sydney Basin forms part of the composite Permo-Triassic Sydney-Gunnedah-Bowen Basin system, and is located between the New England Fold Belt in the northeast and the Lachlan Fold Belt in the west (Figure 1; Scheibner, 1999). It covers about 44,000 km^2 onshore and 5,000 km^2 offshore, extending to the edge of the continental shelf (Stewart and Alder, 1995). It is a transitional tectonic foreland basin formed during Late Carboniferous to Early Permian continental rifting. Volcanics of the Dalwood Group are considered to be the lowermost stratigraphic unit of the basin (Figure 4), with the rest of the onshore region comprising Permo-Triassic sediments. Fluvial, coastal plain and marine sediments form the earliest Permian deposits in the basin were followed by a widespread marine transgression. Coal measure sedimentation began in the Early Permian and was terminated towards the end of the Permian due to major uplift and basin tilting (Tadros, 1995b). The northern parts of the basin are overlain by Jurassic and Cainozoic basalts (Stewart and Alder, 1995). The basin is divided into five coalfields, namely the Hunter, Newcastle, Central, Southern and Western Coalfields. The main lithostratigraphic units of the basin can be well correlated across these coalfields, particularly across the Hunter and Newcastle Coalfields and the Southern, Central and Western Coalfields. Three coal measure sequences are present in the Hunter, Newcastle, Central and Southern Coalfields. Coal in the Western Coalfield is contained within the Illawarra Coal Measures (Figure 4; Tadros, 1995b).

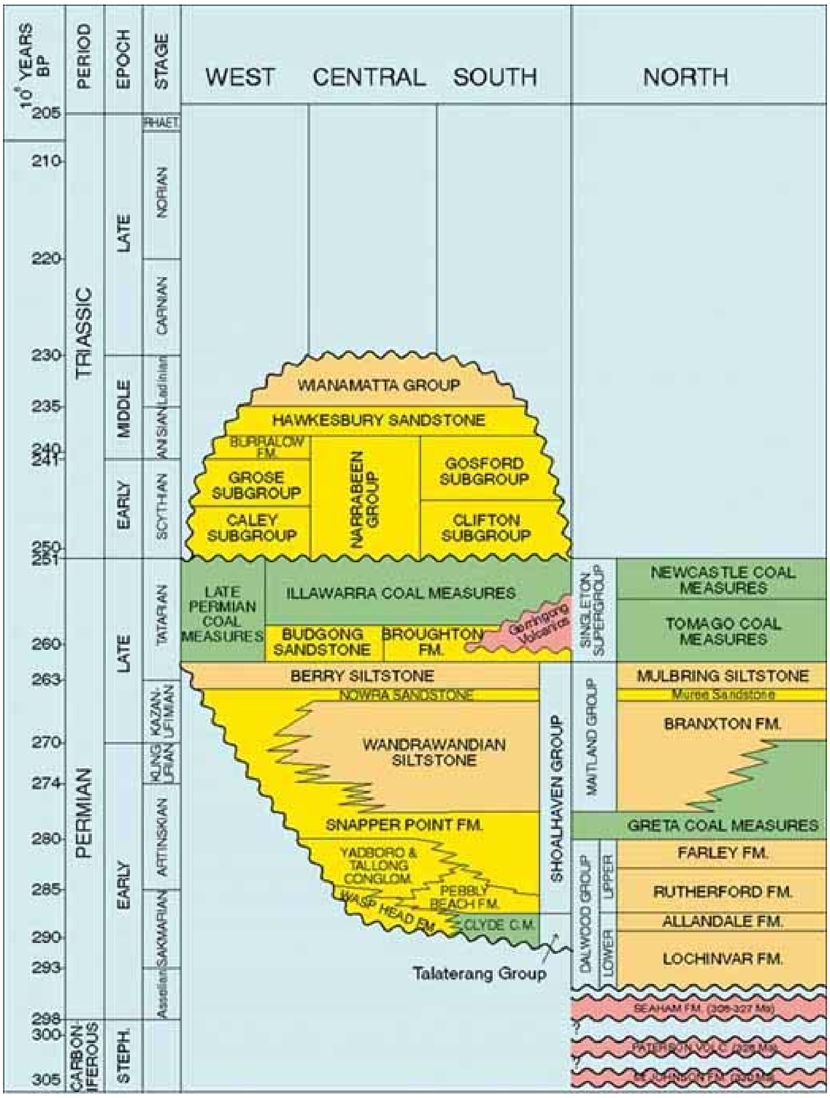


Figure 4: Stratigraphy of the Sydney Basin (NSW DPI, 2011b).

Coal and petroleum resources

The Sydney and Gunnedah Basins host the majority of coal resources in NSW. Numerous identifiable coal seams are contained within each coal measure sequence in each coalfield. Vitrinite reflectances vary between 0.60 - 0.80% for coals in the Wittingham Coal Measures of the Hunter Coalfield in the northern extent of the basin (Pinetown *et al.*, 2008), to 0.91 - 1.31% for the Bulli seam of the Illawarra Coal Measures of the Southern Coalfield (Armstrong *et al.*, 1995). Well-developed coal seams are well over 2 m in thickness and have been mined for both thermal and coking coal purposes (Tadros, 1995b). Oil occurrences have been noted in the coal measure sequences as well as the marine sediments of the basin (Stewart and Alder, 1995). Analysis of dispersed organic matter and pyrolysis data has shown that the Mulbring Siltstone, Denman Formation and Wollombi Coal Measures have good oil and gas potential. Although vitrinite reflectances indicate that the deeper central parts of the basin are overmature, the remainder of the basin is mature for oil (NSW DPI, 2011b). The coal measure sequences in the Sydney Basin are thermally mature to be within the gas generation window. Hence some enormous reservoirs of CSG are present throughout the basin (NSW DPI, 2011b). Gas contents in many areas are in excess of 18 m^3/t, and the gas consists predominantly of methane (up to 95% in some areas), along with ethane concentrations of up to 5% in deeper regions (NSW DPI, 2011b). High concentrations of the carbon dioxide have also been observed (Faiz and Hutton, 1995; Pinetown *et al.*, 2008).

Oil shows have been noted in the Sydney Basin for many years and have been encountered in every major stratigraphic unit ranging from Carboniferous volcanic rocks to the Middle Triassic Hawkesbury Sandstone and in the form of oil slicks in the offshore Sydney Basin (Herbert, 1984; Alder *et al.*, 1998). Ahmed *et al.* (2009) presented a detailed study on molecular and isotopic characteristics of 6 oils shows and seeps from the Southern Coalfield, and indicated the Permian coals as the most likely source of these petroleum occurrences.

4.3 Basins (mainly) in QLD

4.3.1 Blair Athol

Geological setting

The Blair Athol Basin is a northeast-southwest orientated cratonic basin approximately 8 km long and 6 km wide developed on the western margin of the Bowen Basin (Figure 5) during the Early to Middle Permian (Mallett *et al.*, 1995). It appears that contemporaneous basement subsidence controlled sediment accumulation. The Blair Athol Coal Measures unconformably overlie the Anakie Metamorphic Group. The coal measure sequence has a maximum thickness of 250 m and was initially deposited in a high energy regime. The sequence includes a lower conglomeratic section up to 150 m thick with conglomerate, sandstone, carbonaceous shale and minor coal seams. The upper section is up to 100 m thick and consists mainly of sandstone, siltstone and coal (Mallett *et al.*, 1995).

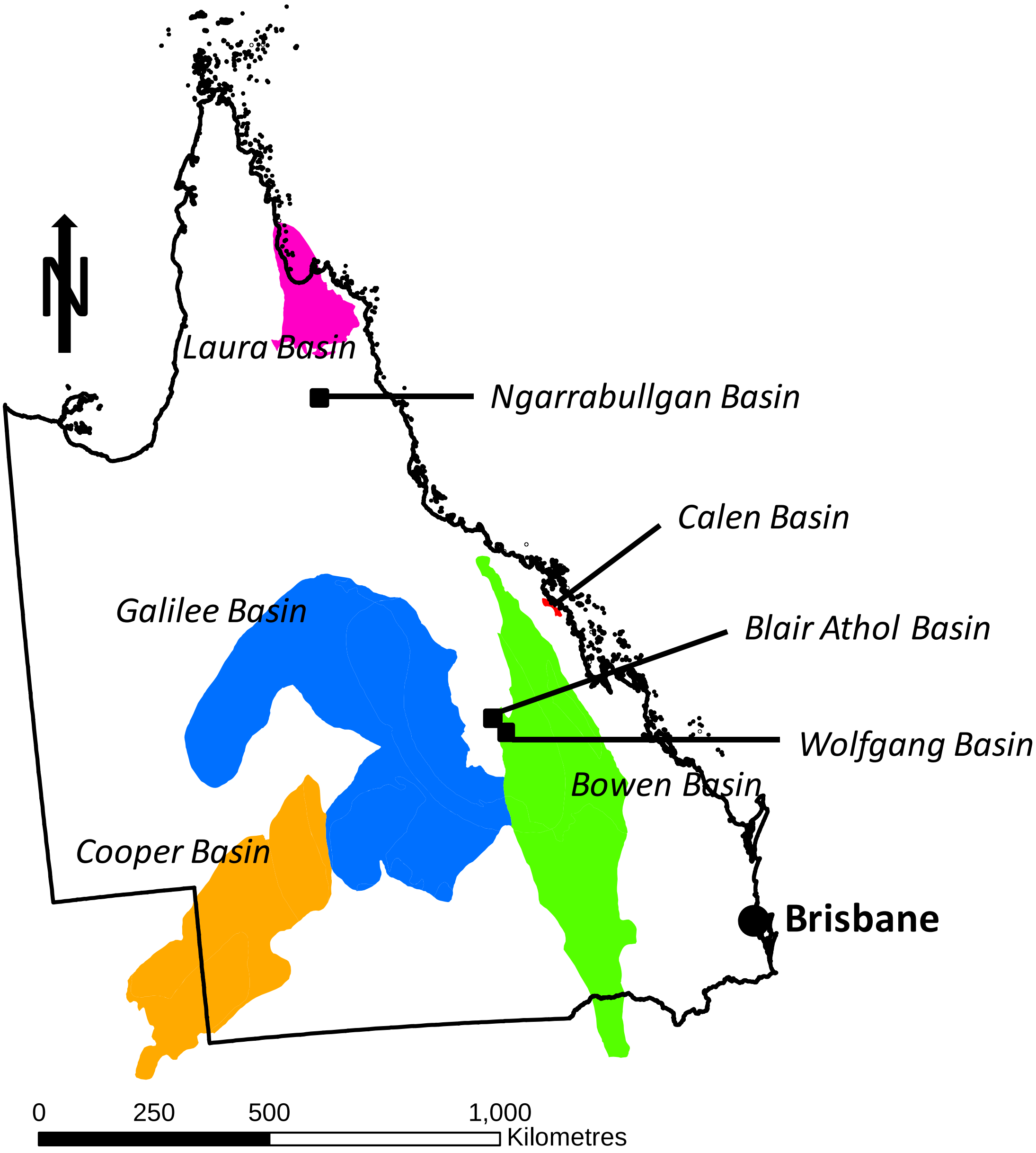


Figure 5: Location of Permian sedimentary basins in Queensland.

Coal and petroleum resources

Four major coal seams have been identified with the oldest, the No. 4 seam, having the widest distribution. It forms a single seam of up to 5 m in the southeast and has an average ash yield of 16.6%. The No.3 seam is economically the most important with an average thickness of 29 m. It is classified as high volatile C bituminous coal with low mineral matter content (Mallett *et al.*, 1995). Although the coal is dull and massive, relatively brighter sections are found near the top and at the base. The No. 2 seam varies in thickness between 0.3 and 2.3 m, and the No. 1 seam is only preserved in two isolated locations with a thickness of up to 8.9 m (Mallett *et al.*, 1995).

4.3.2 Bowen Basin

Geological setting

The Bowen Basin is the northern basin of the Bowen-Gunnedah-Sydney Basin system (Figure 5) and one of the major coal basins of the world. It is composed of a series of troughs and highs developed after extensional and compressive events. The main morphotectonic units of the basin trend north-northwest-south-southeast and include, from west to east, the Springsure Shelf, the Denison Trough, the Comet Ridge and Collinsville Shelf, the Taroom Trough, the Connors and Auburn Arches, and the Marlborough Trough (Mallett *et al.*, 1995). The extensional phase during the Early Permian resulted in the deposition of coals in the west (fluviodeltaic Reids Dome beds deposited in the Denison Trough, Figure 6) and volcanics in the east. This was followed by a period of thermal sag in the Early to Middle Permian. During this period shallow and marginal marine sediments accumulated along with local coal measure sequences (Collinsville Coal Measures and Blair Athol Coal Measures) in a series of depositional environments, ranging from fluvial to paralic. The basin underwent an extensive period of marine transgression during the Late Permian with no known terrestrial deposits. This was then followed by the deposition of extensive marginal marine to deltaic peat sediments forming important coal measures such as the Moranbah, the Fort Cooper, Rangal and Baralaba Coal Measures. The Permian coal bearing units are overlain by the Triassic Rewan Formation (Mallett *et al.*, 1995).

Coal and petroleum resources

Coal Measures in the Bowen Basin are divided into four groups, numbered I to IV. Group I Coal Measures include the Reids Dome Beds, and those interbedded with the Lizzie Creek Volcanics. Group II Coal Measures can be found in marginal areas of the basin, such as the Collinsville Coal Measures and those in the Clermont District (Blair Athol Coal Measures, Wolfgang Basin and Rugby Deposit). Group III and IV Coal Measures include the coal-bearing units from the Moranbah Coal Measures to the top of the Rangal Coal Measures, where most of Queensland’s economic coal resources are contained (Mallett *et al.*, 1995). The coals in the Bowen Basin are rich in vitrinite (60-80%) (Hunt, 1989) and coal rank ranges from high volatile bituminous to anthracite (Middleton, 1989). Group III coals are generally vitrinite-rich, have a low (<10%) washed ash yield, and have vitrinite reflectances varying between 0.98 and 1.60%. Group IV coals contain similar proportions of vitrinite and inertinite. Vitrinite reflectances have a wider range, varying between 0.58 and 2.59% (Mallett *et al.*, 1995). The extensive coal deposits of the basin are also reservoirs to its vast CSG resources, fuelling rapid growth of this industry in recent years. The Bowen Basin contains around 34% of Australia’s CSG resources (GA and ABARE, 2010).

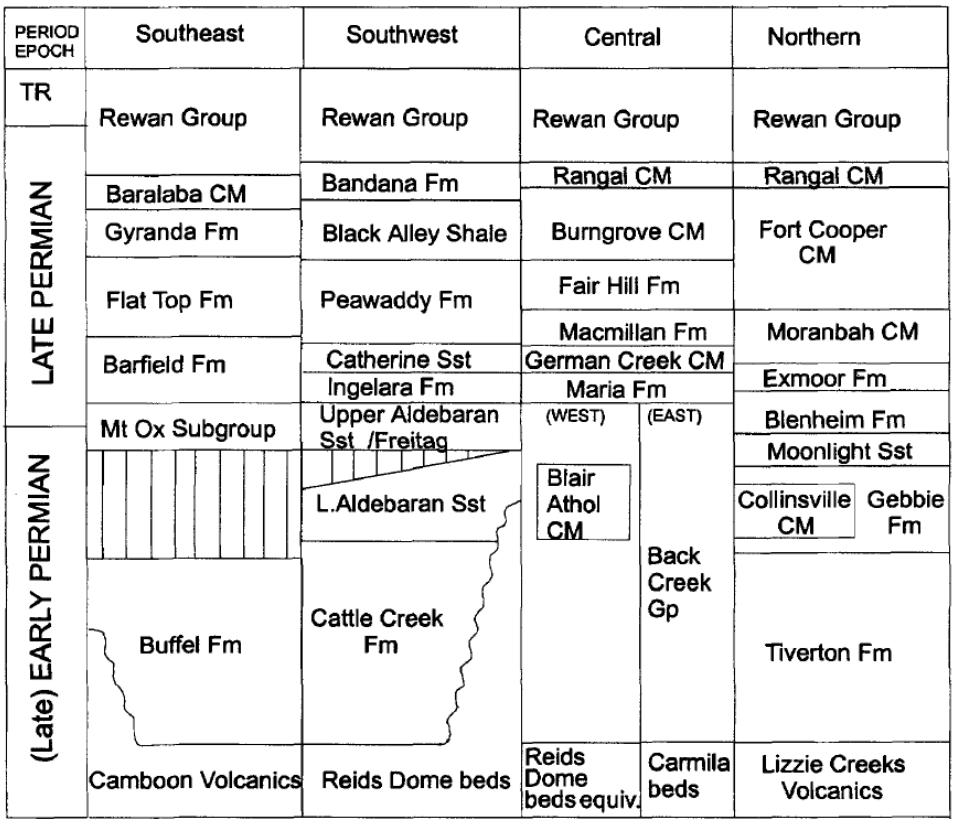


Figure 6: Stratigraphy of the Bowen Basin (from Uysal et al.*, 2000).*

4.3.3 Calen Basin

Geological setting

The Calen Basin is considered to be an extensional northwest-trending graben located northwest of Mackay (Figure 5). It outcrops over 240 km^2. The coal measures have been folded into a broad syncline with dips almost near-vertical as a result of local faulting and folding. The northern region of the basin is structurally more complex compared to the south (Brakel, 1995). Late Permian- to Cretaceous-aged intrusions have been emplaced in the Calen Coal Measures in the form of two large plugs of rhyolite, a sill of microgranite, a large body of porphyritic dolerite, and numerous dykes and sills (Brakel, 1995). The formation hosting the Calen Coal Measures is between 350 and 400 m thick (Brakel, 1995). It forms the current ground surface and overlies the Lizzie Creek Volcanics and the Carmilla beds (Brakel, 1989b). The contact with the Lizzie Creek Volcanics is unconformable. The Calen Coal Measures were mainly deposited in a lower delta-plain environment with brief switches to upper delta-plain and fluvial regimes (Brakel, 1995). Sediments are mainly coarse quartz sandstone, thin pebble conglomerate, sandstone/siltstone laminite, siltstone, claystone, carbonaceous shale and coal (Brakel, 1989b).

Coal and petroleum resources

The widespread igneous intrusions have resulted in localised coking of the coal, although mining during 1932 to 1939 has produced some good quality high rank thermal coal from an exploited seam of around 2.6 m thick (Brakel, 1995). The coal is of low volatile bituminous rank with ash and volatile contents both varying between of 16.2 to 17.3% (Brakel, 1995).

4.3.4 Cooper Basin

Geological setting

The Cooper Basin is a north easterly trending intracratonic basin located in the north-east part of South Australia extending north-east into Queensland (Figure 7). No part of the basin is exposed (Wells and O'Brien, 1989). In South Australia the basin covers an approximate area of 35,000 km^2 (PIRSA, 2011b). The total area exceeds 130,000 km^2. The basin rests on older Palaeozoic rocks and is unconformably overlain by the Jurassic rocks of the Eromanga Basin (Wells and O'Brien, 1989). The major tectonic elements are three major northeast-southwest trending troughs (the Patchawarra, Nappamerri and Tenappera Troughs) in the South Australian part of the basin. These are separated by two structural ridges (Gidgealpa–Merrimelia–Innamincka (GMI) and Murteree) (PIRSA, 2011b). The Arrabury and Windorah Troughs are located in the northern region of the basin in Queensland. The oldest units are the Late Carboniferous to Early Permian glacial sediments of the Merrimelia Formation and Tirrawarra Sandstone. This is overlain by the peat swamp and floodplain facies of the Patchawarra Formation. Permian coals in the basin are hosted by the Patchawarra and Toolachee Formations (Beeston, 1995). At its deepest in the central areas of the Nappamerri Trough, the Patchawarra Formation may be up to 900 m in thickness (Wells and O'Brien, 1989). Two thin (100 m) lacustrine shale units (Murteree and Roseneath shales; Figure 7) with intervening fluvio-deltaic sediments (Epsilon and Daralingie Formations) overlie the Patchawarra Formation (PIRSA, 2011b).

Coal and petroleum resources

Coal is widespread in the Permian Cooper Basin, the major accumulations of which are found in the Patchawarra and Toolachee Formations (Wells and O'Brien, 1989). The Patchawarra Formation is typically located at depths in excess of 2000 m where the cumulative thickness of coal is up to 50 m and in one seam alone up to 25 m (Wells and O'Brien, 1989). In the deeper (2500 m) Toolachee Formation, the black bituminous coals have a cumulative thickness of 13 m, the thickest individual seam being 5 m (Wells and O'Brien, 1989). The rank of these inertinite-rich coals range from medium volatile bituminous to anthracite with vitrinite reflectance ranging from 0.8 to >4.0% (Middleton, 1989). Deep burial coal in the basin resulted in source rock maturation and substantial oil and gas production. The Patchawarra Trough contains vast oil and wet gas reserves (PIRSA, 2011b). The Nappamerri Trough is over-mature and contains mainly dry gas. The principal hydrocarbon source rocks are the Permian coal measures and shales, these are dominated by Type III kerogens derived from higher plant assemblages (PIRSA, 2011b). Locally the Late Permian Toolachee Formation is the richest source unit along with the lowermost shales and coals of the Early Permian Patchawarra Formation (PIRSA, 2011b). Most oils contain significant dissolved gas and are typically medium to light and paraffinic, with low to high wax contents (PIRSA, 2011b). The Roseneath Shale is currently being investigated by Beach Energy for its shale gas potential.

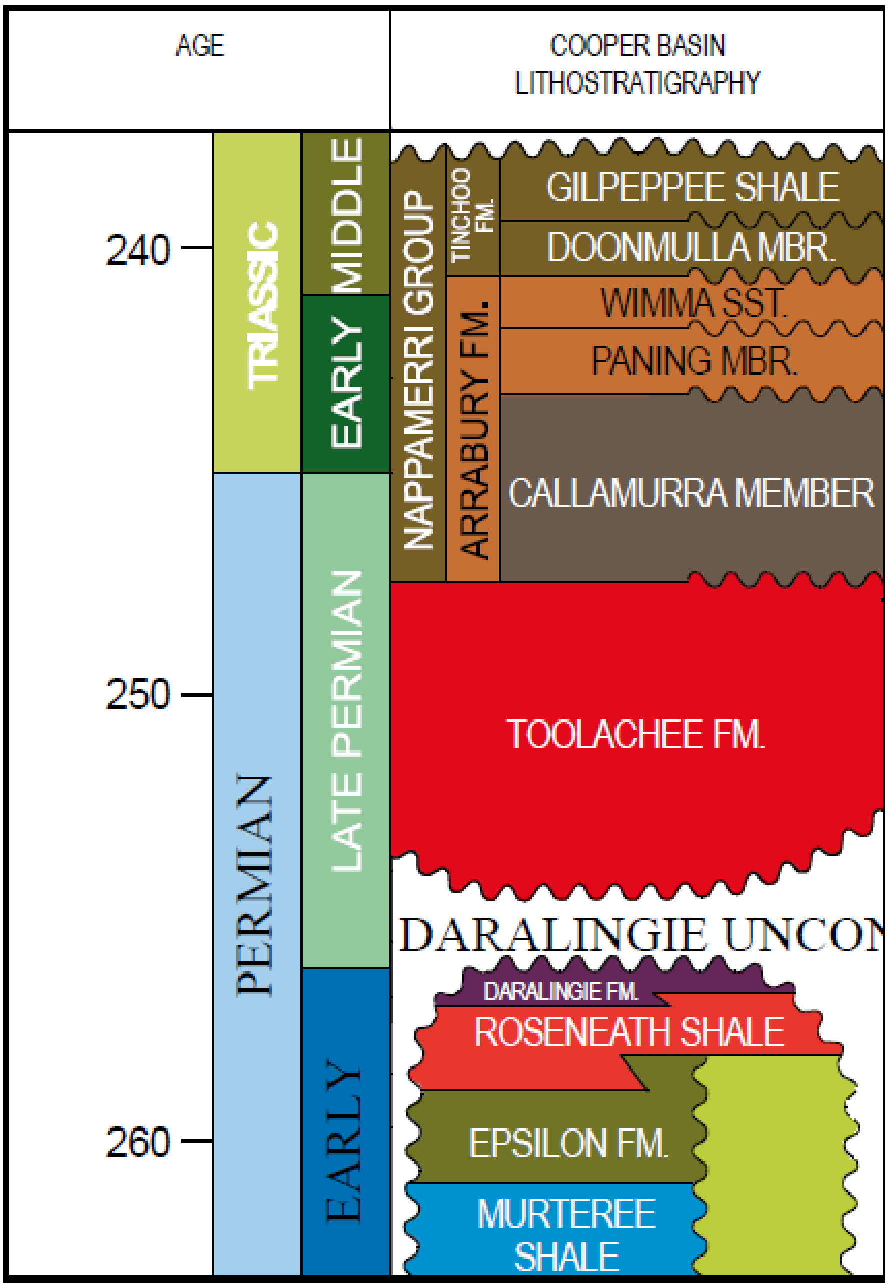


Figure 7: Stratigraphy of the Cooper Basin (from Krawczynski, 2004).

4.3.5 Galilee Basin

Geological setting

The Galilee Basin in central Queensland (Figure 5) is an intracratonic basin filled with Late Carboniferous to Middle Triassic sediments and unconformably overlain by the Eromanga Basin (Wells, 1989a). Permo-Triassic rocks are only exposed along the eastern margin of the basin. The basin is divided into northern and southern regions by the east-west trending Barcaldine Ridge (Scott *et al.*, 1995). The Galilee Basin hosts the Permian-aged Aramac Coal Measures, an equivalent of the Reids Dome beds in the Bowen Basin, as well as the younger coal-bearing Bandanna Formation and Colinlea Sandstone of the Betts Creek beds. These are overlain by the Triassic Rewan Formation. These formations have equivalents in other areas of the basin, but are considered to be the major coal-bearing sequences. The fluvially deposited sediments of the Aramac Coal Measures and are separated from the Late Permian Betts Creek beds by a disconformity (Wells, 1989a; Scott *et al.*, 1995). The coal measures are divided into a lower interval with sandstone and minor mudstone and coal, and an upper interval of sandstone and subordinate coal. Rocks of the Betts Creek beds comprise sandstone, interbedded siltstone, shale and coal which were deposited under delta and alluvial plain environments (Wells, 1989a). Three areas of maximum coal development within the Betts Creek beds are recognised along the Lovelle Depression, the western margin of the Koburra Trough and within the Koburra Trough (Scott *et al.*, 1995).

Coal and petroleum resources

Aggregated coal thickness in the Aramac Coal Measures is up to 60 m along the Lovelle Depression and around 29 m in the Koburra Trough. The coal is predominantly dull with a low vitrinite reflectance. Limited data show that these coals have ash yields of 0.8% and volatile matter of 39%. Although there appears to be little potential for mining, the coal measures are considered a major source for CSG (Scott *et al.*, 1995). Coals of the Betts Creek beds vary in thickness between 0.15 and 20 m with an aggregate of 45 m. A typical coal has an average ash yield of 15.3% and volatile matter of 29.4%. Along the eastern margin of the Koburra Trough, these coals are of low rank (Scott *et al.*, 1995) with mean vitrinite reflectance ranging between 0.40 and 0.80% (Wells, 1989c). Apart from the most recent interests from the coal seam methane industry, the Upper Permian coals of the Galilee Basin also appear to have potential for oil production from shales (Scott *et al.*, 1995).

4.3.6 Laura Basin

Geological setting

The intracratonic Laura Basin in northern Queensland (Figure 5) covers 18,000 km^2 onshore and extends over 16,000 km^2 offshore, probably to the edge of the continental shelf. It is separated from the Carpentaria Basin in the west by the Peninsula Ridge, and in the north it is separated from the Torres Shelf by the Grenville High. The basin overlies the Carboniferous to Devonian rocks of the Hodgkinson Basin. The thick Permian sediments of the Sub-Laura Basin, as described by Wells (1989b), comprise the Little River Coal Measures and the Normanby Formation. The coal measures are intensely folded and faulted and poorly exposed, consisting mainly of feldspathic and lithic sandstones, silty shales, impure limestones and coals. It is interpreted that the Upper Permian sediments were deposited in a continental-lacustrine setting. The impure poor quality coals are between 7 and 30 m thick (Wells, 1989b).

Coal and petroleum resources

Little is known about these coals and exploration during 1979 showed that the coals were of poor quality. No commercial deposits were found. The Permian rocks are thought to be supermature, although not due to deep burial, but more likely the result a high geothermal gradient (Wells, 1989b).

4.3.7 Ngarrabullan Basin

Geological setting

The Ngarrabullgan Basin is a flat-bottomed, broad asymmetrical syncline trending northwest (Figure 5; (Matheson, 1995). The basin margins are faulted to the east and west and warping of the Late Permian strata has produced a monoclinal flexure in the northwest and a syncline further east along the axis of the basin (Matheson, 1995). The basin unconformably overlies the Devonian Hodgkinson Formation and part of the Featherbed Volcanics, and underlies about 300 m of conglomerate and sandstone of the Pepper Pot Sandstone (Matheson, 1995). The area is commonly known as Mount Mulligan. The Mount Mulligan Coal Measures are up to 149 m thick and comprise conglomerate, sandstone, shale, mudstone and coal (Wells, 1989c). The coal measure sequence was divided into three units, namely, a basal unit with up to 60 m of shale, siltstone and minor sandstone, a massive cobble and pebble conglomerate succession, and an upper unit of siltstone, lithic sandstone and up to four coal seams (Matheson, 1995).

Coal and petroleum resources

The Mount Mulligan Coal Measures were exploited on a small scale for the first half of the 20th century but resources remain poorly constrained. The coals are of high volatile bituminous rank with a mean vitrinite reflectance of 0.75% (Matheson, 1995). With a raw ash yield of 15 to 23% it is unsuitable for coking (Wells, 1989c). The four main identified seams vary in thickness from 0.4 to 1.7 m with only the No. 3 seam that has been extensively worked for its clean coal. Estimated coal resources range from 45-90 Mt (Matheson, 1995).

4.3.8 Wolfang Basin

Geological setting

Similar to the Blair Athol Basin, the Wolfgang Basin is a small cratonic basin which forms part of the larger Bowen Basin complex. It is situated around 12 km southeast of Blair Athol (Figure 5; Mallett *et al.*, 1995). The basin is fault controlled to the west. Its coal measure sequence is underlain by older coal measures comprising sandstone, mudstone and thin coals which can be correlated with the Reids Dome beds. Its main coal measure section can be correlated with the top of the Cattle Creek Formation, above which 100 m of conglomerate and up to 165 m of coal measures have been deposited (Mallett *et al.*, 1995). Coal seam thicknesses are similar to those in the Blair Athol Basin, with some seams up to 2.5 m thick.

Coal and petroleum resources

The Wolfgang seam can be found over an area of 4 km^2. It is very clean and consists predominantly of dull coal. The medium to high volatile bituminous rank coal is has a mean maximum vitrinite reflectance of 0.72% and an average ash yield of 9.7% (Mallett *et al.*, 1995).

4.4 Basins (mainly) in SA

4.4.1 Arckaringa Basin

Geological setting

The Arckaringa Basin is a Permo-Carboniferous intracratonic basin extending over an area of 80,000 km^2 in central northern South Australia (Figure 8; Hibburt, 1984). Two key depocentres are formed from the north-west trending Boorthanna and Phillipson Troughs (PIRSA, 2011a). Further depocentres include the north-east trending Karkaro, Mt Furner and Walliras Troughs. Three formations are recognised, in ascending stratigraphic order, the Boorthanna, Stuart Range and Mt Toondina Formations. The Boorthanna Formation is a marine unit of glacial and post-glacial origin. The Stuart Range consists almost entirely of marine shale and the Mt Toondina Formation consists of an upper and lower siltstone separated by a thin layer of sandstone. The upper siltstone of the Mt Toondina contains interbedded carbonaceous shale and coal. The Permian sediments reach up to 900 m in thickness in the Boorthanna and Phillipson Troughs and 250 m in the Karkaro Trough (Hibburt, 1984).

Coal and petroleum resources

The upper siltstone of the Mt Toondina Formation contains seven deposits of lignite A/sub-bituminous C rank coal aggregating more than 20 Gt of measured, indicated and inferred resource (PIRSA, 2011a). Two coal deposits have been identified, the Lake Phillipson Deposit, which occurs in two shallow northwest trending troughs with individual thicknesses of up to 10 m and cumulative of up to 25 m (Hibburt, 1984). The Arckaringa Coalfield consists of four deposits with cumulative thicknesses of up to 25 m (Hibburt, 1984). The coals are not present throughout the entire basin due to erosion, non deposition and facies changes (Hibburt, 1984). In terms of hydrocarbon potential, source rock studies of the Permian sequence indicate that the basal Stuart Range Formation and Boorthanna Formation vary from immature to mature. The Boorthanna Formation TOC is generally <0.5% although one sample measured 1.8% (PIRSA, 2011a). While immature, the Mt Toondina Formation and much of the Stuart Range Formation have high TOC values indicating good oil-prone source potential at depth. TOC ranges from 0.45 to 2.7% in Stuart Range Formation, and is as high as 5.95% in Mt Toondina Formation. Permian sediments are most likely to be thermally mature in southern deep parts of the Boorthanna Trough. In the Phillipson Trough a higher heat flow event 150 million years ago may have boosted maturity of the Permian sequence (PIRSA, 2011a).

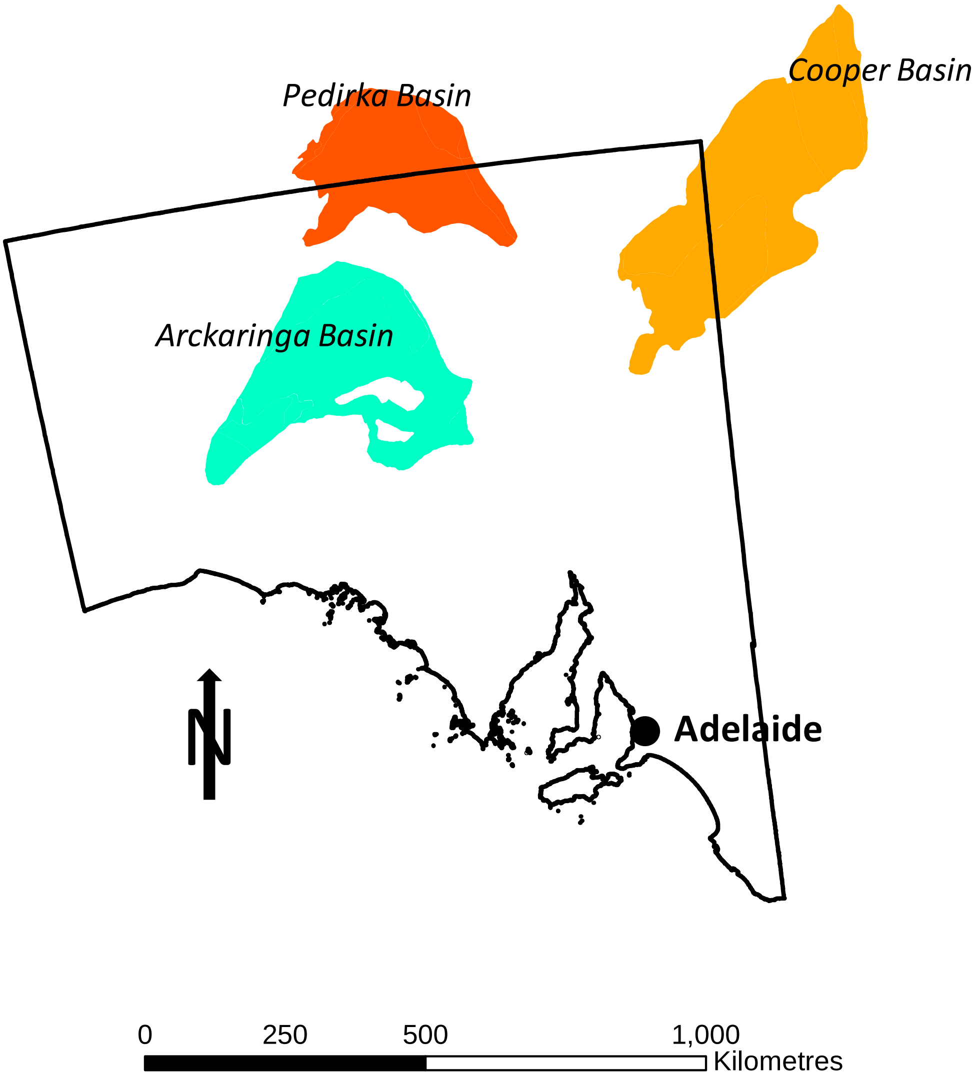


Figure 8: Location of Permian sedimentary basins in South Australia.

4.4.2 Pedirka Basin

Geological setting

The Pedirka Basin is an intracratonic basin of approximately 150,000 km^2. About 27,000 km^2 lies in SA and the remainder extends north into the Northern Territory (Figure 8; PIRSA, 2011c). Two Permo-Carboniferous formations are present - the lower Crown Point Formation and the uppermost Purni Formation (Figure 9). The Crown Point Formation consists of fluvioglacial and glacial lacustrine sediments while the Purni Formation consistes of sandstones, shales and coals. The Pedirka Basin correlates with the Permo-Carboniferous sediments of the productive Cooper Basin to the east and the Officer Basin to the southwest (Middleton *et al.*, 2007). The basin contains three major structural features trending north-south, the McDills anticlinal trend bounded to the east by the Madigan trough and to the west by the Eringa Trough (Middleton *et al.*, 2007). The deepest (in excess of 2000 m) and thickest (1000 m) sediments lie in the Madigan and Eringa Troughs.

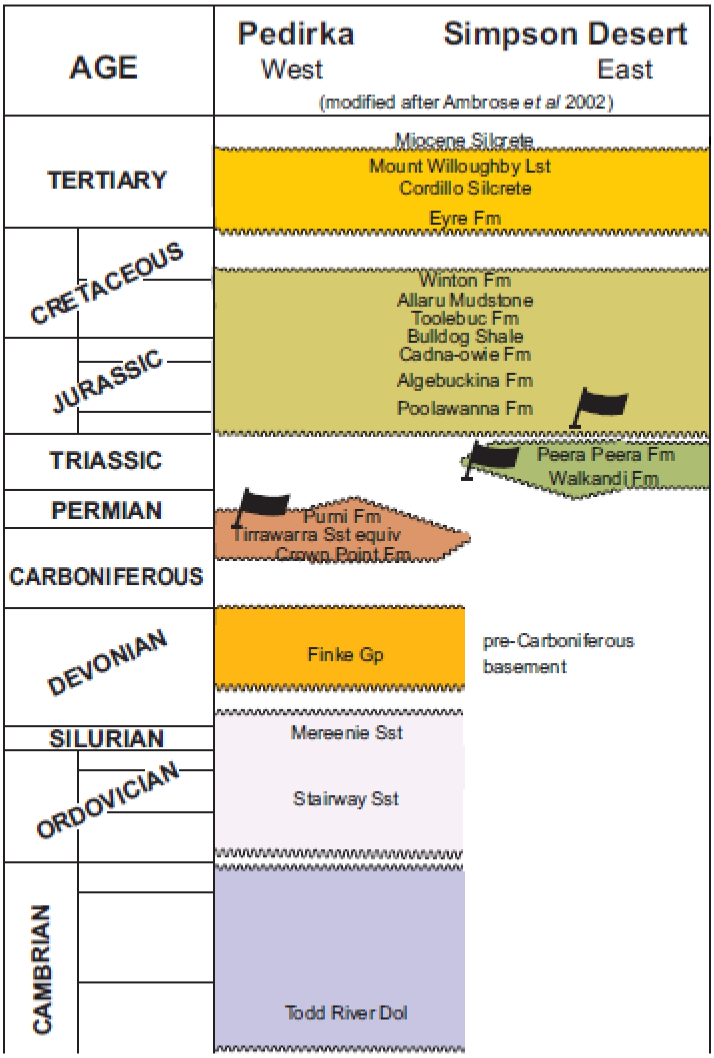


Figure 9: Stratigraphy of the Pedirka Basin (Gibson et al., 2011).

Coal and petroleum resources

Hydrocarbon shows and source discoveries have been made in this region (Middleton *et al.*, 2007). Excellent quality source rocks have been identified in the Purni Formation (Middleton *et al.*, 2007). The Purni Formation contains extensive coal-rich organic shale which appears to be both oil and gas-prone. The formation contains up to 4% dispersed organic matter (PIRSA, 2011c), with liptinite macerals in abundance (14-25%) in many coal samples and DOM in shale samples (Middleton *et al.* 2007). In South Australia, thermal maturity appears to increase from west to east with VR and is reported by PIRSA (2011c) as approaching 0.9% and by Middleton *et al.* (2007) as being in the range 0.7-1.0%, equivalent to peak oil generation. Rock-Eval Pyrolysis of ten coal and shale core samples from the basin revealed, when plotted on a pseudo van Krevelen diagram, two distinct fields, a type III kerogen gas prone zone and a mature type I/II kerogen zone (Middleton *et al.*, 2007). The Pedirka Basin is said to have good prospectivity in terms of the presence of good seal, trap and reservoir rocks (Guiliano, 1988).

4.5 Basins (mainly) in WA

4.5.1 Canning Basin

Geological setting

The Canning Basin is a large pericratonic basin in northern Western Australia (Figure 10). The basin is the largest onshore Permian basin in Australia and covers an area of 430,000 km^2 (Yeates *et al.*, 1984). Structurally the basin consists of two major northwest trending troughs (the Fitzroy Trough and Gregory sub-basin to the north and Kidson and Willara sub-basins to the south) separated by a central arch containing the Broome and Crossland Platforms (DMP, 2008). The Permian sediments of the Canning Basin can be separated into four key units. In ascending stratigraphic order they are:

1. The upper-Carboniferous-Permian glacial sediments of the Grant Group (laterally equivalent to the Paterson Formation in the south), approximately 300-800 m thick, and representing a period of rapid deposition (Mory, 2009; Figure 11).

2. The deltaic sediments of the Poole Sandstone form a potential reservoir for underlying oil bearing strata.

3. Overlying this is the marine shale-dominated Noonkanbah Formation, which reaches up to 640m in thickness and forms a potential seal for the underlying sandstones (Mory, 2009).

4. The Late Permian Liveringa Group represents a period of fluvio-deltaic deposition and includes deposits of thermal quality coal (Mory, 2009).

Coal and petroleum resources

The Fitzroy Trough is considered to be the most prospective area of the Canning Basin, and a range of oil shows were identified in the area (DMP, 2008). Exploration of the shales of the basal Noonkanbah Formation by Oil Basins Ltd. found them to be suitable for fracturing for the production of shale gas. These shales contain organic rich intervals which, in some areas, contain TOC values exceeding 9% (Meaney, 2010). The coals of the Liveringa Group are also considered to have potential for CSG drainage. In particular, the Lightjack Formation of the Liveringa Group is believed to contain Type II oil prone macerals, and could therefore serve as a source for conventional hydrocarbon accumulations (Meaney, 2010). The Lightjack Formation within the Liveringa Formation is the focus of coal exploration in the basin and has also been targeted for its CSG potential. Coal seam thickness within this formation ranges between 3 and 15 m.

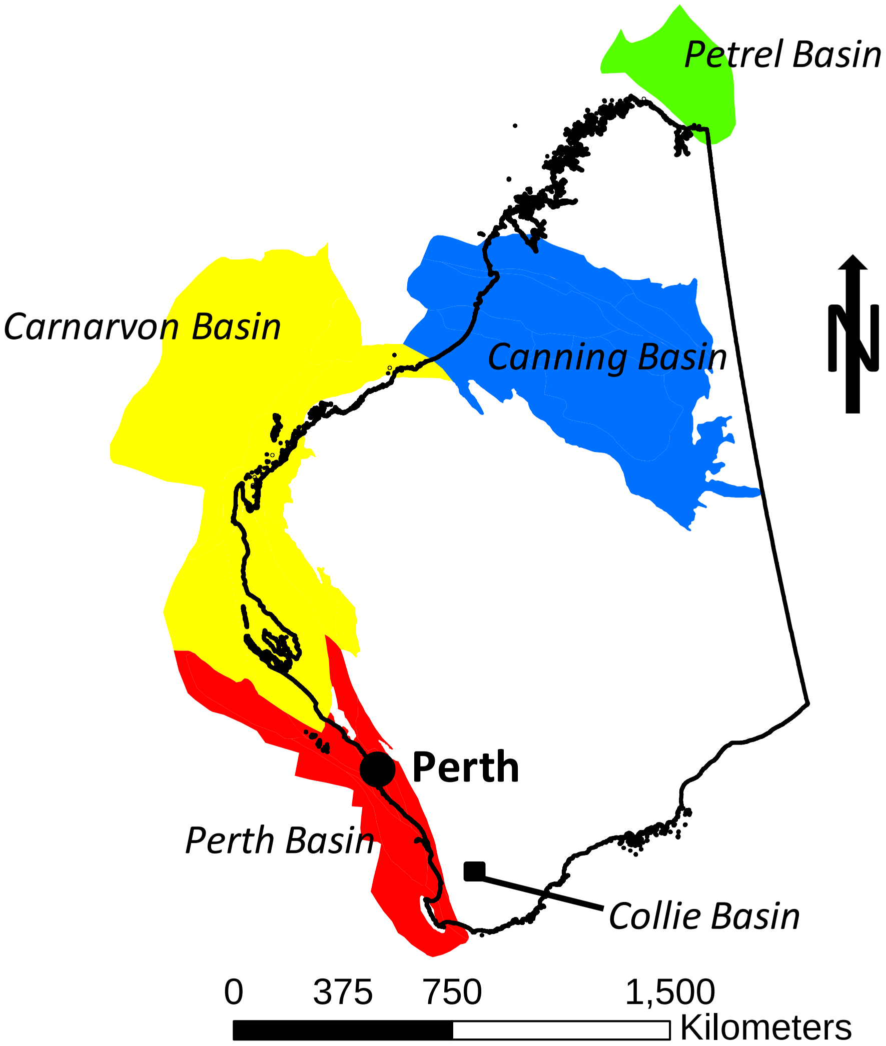


Figure 10: Location of Permian sedimentary basins in Western Australia

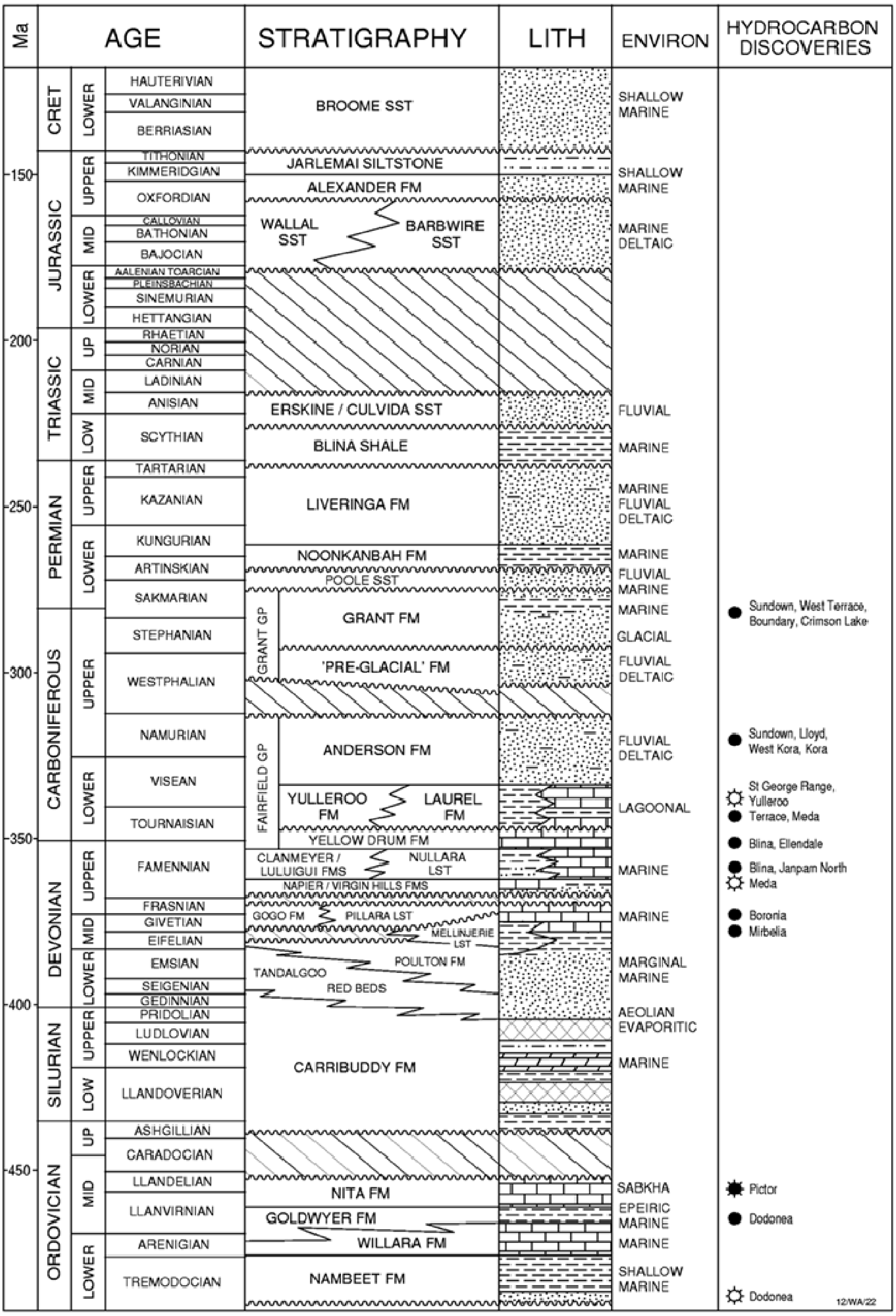


Figure 11: Stratigraphy of the Canning Basin (Cadman et al.*, 1993).*

4.5.2 Carnarvon Basin

Geological setting

The Carnarvon Basin is a northeast-southwest trending epicratonic basin which extends 1000 km along the western and northwestern coastline of Western Australia, covering 115,000 km² and 535,000 km² offshore (Mory and Backhouse, 1997; Figure 10). It is a transitional basin between the Perth and the Offshore Canning basins (Hocking, 1995). The basin is divided into the Southern Carnarvon Basin, comprising largely Palaeozoic sediments, and the Northern Carnarvon Basin, containing mainly Mesozoic sediments. Sub-basins of the Southern Carnarvon Basin include the Coolcalalalya Sub-basin, and the Byro, Bidgemia and Merlinleigh Sub-basins, which contain Late Carboniferous and Permian sediments, and the Gascoyne Sub-basin which contains primarily Silurian and Devonian sediments. The Coolcalalalya and Merlinleigh Sub-basins are separated from the Gascoyne Sub-basin by the Ajana and Wandagee-Yanrey Ridges (Hocking, 1995). The Mesozoic and Cainozoic sediments of the Northern Carnarvon Basin are contained within the Exmouth, Barrow and Dampier Sub-basins. The Peedamullah and Lambert Shelves are shallow offshore basement areas with onlapping Mesozoic and Cainozoic sediments (Hocking, 1995). Early Permian deposits of the glacigene Lyons Group and post-glacial Callytharra Formation (Figure 11) are together around 2,500 m thick. The Callytharra Formation is overlain by fluviodeltaic sediments of the Wooramel Group, which graded into siliciclastic, marine-shelf deposits forming the Byro and Kennedy Groups (Mory and Backhouse, 1997). Triassic sediments of the Locker Shale overlie the Kennedy Group on the offshore Peedamullah Shelf.

Coal and petroleum resources

The Wooramel Group is the only sequence in the Carnarvon Basin that appears prospective for coal. These units outcrop and have never been buried deeper, hence the potential for coal preservation and maturation is low (Hocking, 1995). The numerous oil and gas fields in the Northern Carnarvon Basin, however, demonstrates the petroleum potential of the region. The main source and reservoir rocks for accumulations in the Barrow Sub-basin are considered to be the Jurassic Dingo Claystone and the Cretaceous Barrow Group, respectively. On the sub-basin margins gas and condensate production has taken place within the Dampier Sub-basin with the Locker Shale considered to be the source rock for these accumulations (DMP, 2011a).

4.5.3 Collie Basin

Geological setting

The Collie Basin in southwest Western Australia (Figure 10) is about 27 km long and 13 km wide. The northwest-southeast trending basin is divided into two asymmetrical lobes, the Cardiff and Premier Sub-basins, separated by the Stockton Ridge (Ashton *et al.*, 1995). The basin contains about 1000 m of Permian sedimentary rocks overlain by Cretaceous sediments. The Early Permian Stockton Formation is the lowermost unit in the basin, consisting of pebble conglomerate and sandstone at the base overlaid by poorly-bedded mudstone and granite, dolerite and metasediment clasts believed to be of glacial to fluvioglacial origin. The Collie Coal Measures overlying the Stockton Formation contains feldspathic sandstone, interbedded sandstone/shale units, minor siltstones, shales, mudstones and various coal seams. The Ewington Member of the Collie Coal Measures varies from 48 to 64 m and can be correlated across the entire basin. The Collieburn and Cardiff Members are the middle and upper coal-bearing members in the Cardiff Sub-basin, and have aggregate coal thicknesses of about 20 and 23 m, respectively (Ashton *et al.*, 1995). The southern region of the Premier Sub-basin hosts the middle Chicken Creek and upper Muja Members, whereas the central and northern regions of the Premier Sub-basin hosts the Premier Member. The coal measures are overlain by sandstone, claystone and conglomerate of the Nakina Formation (Ashton *et al.*, 1995).

Coal and Petroleum resources

There are up to 55 significant coal seams in the Collie Coal Measures, and the thickness of the worked seams varies between 1.5 and 5.0 m (DM, 1990). The Hebe seam has an average thickness of 12 m thick, making it the thickest in the coalfield. The coal is of sub-bituminous rank with low ash, medium volatile, and high moisture contents, and vitrinite reflectance values varying between 0.30 and 0.50%. It has been mined predominantly for power generation (Ashton *et al.*, 1995).

4.5.4 Perth Basin

Geological setting

The Perth Basin is a north-south trending elongate trough on the most western edge of Western Australia (Figure 10). The basin is approximately 173,000 km^2 in area located half onshore and half offshore (GA, 2011). The basin consists of deep north-south trending rift basins of which the Dandaragan Trough is the deepest and is the main depocentre of Permian sediments to the north (GA, 2011a). The basin varies stratigraphically from north to south with continental and marine assemblages to the north and continental to the south (Figures 12 and 13). To the north, in ascending

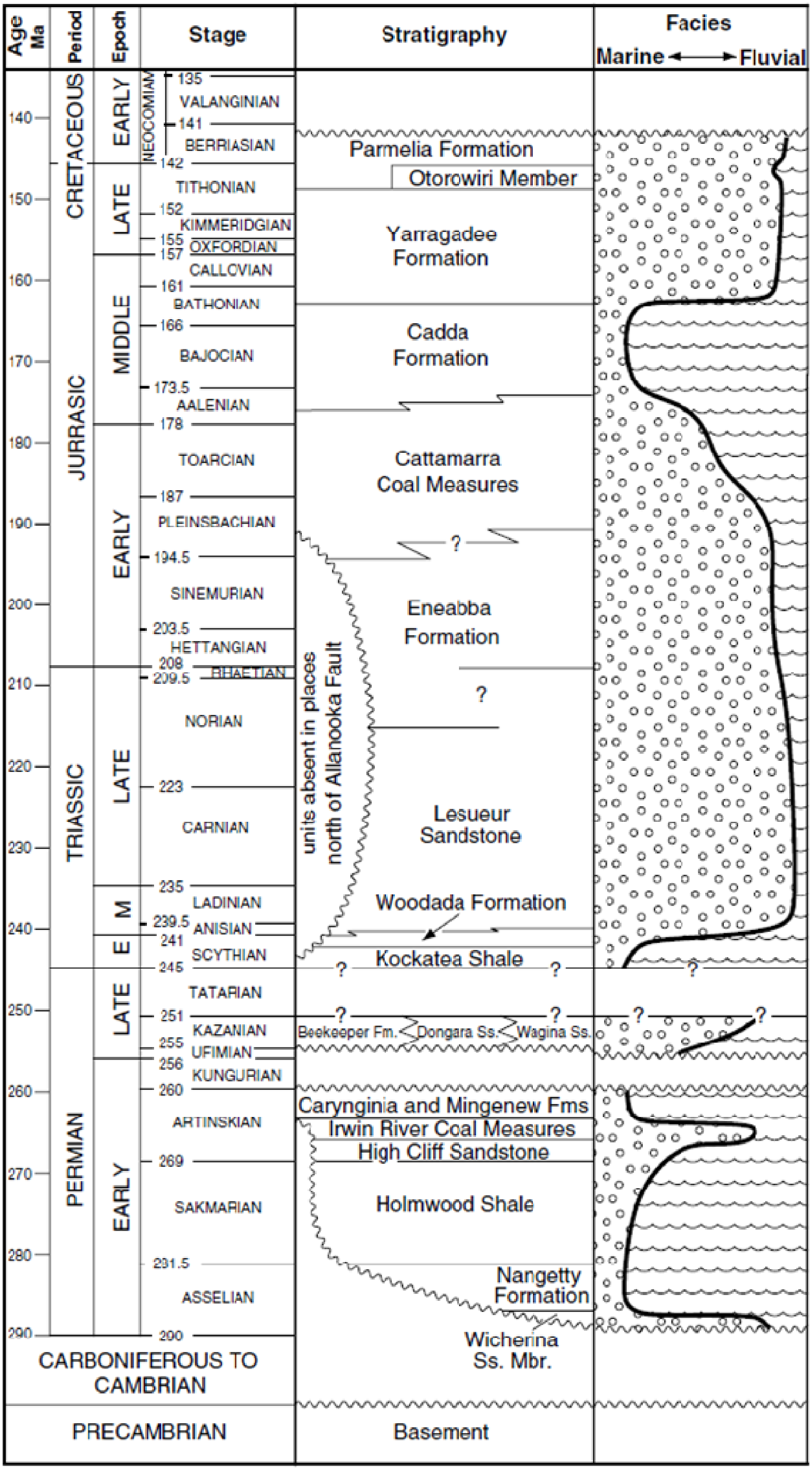


Figure 12: Stratigraphy of the northern Perth Basin (from Mory and Iasky, 1996).

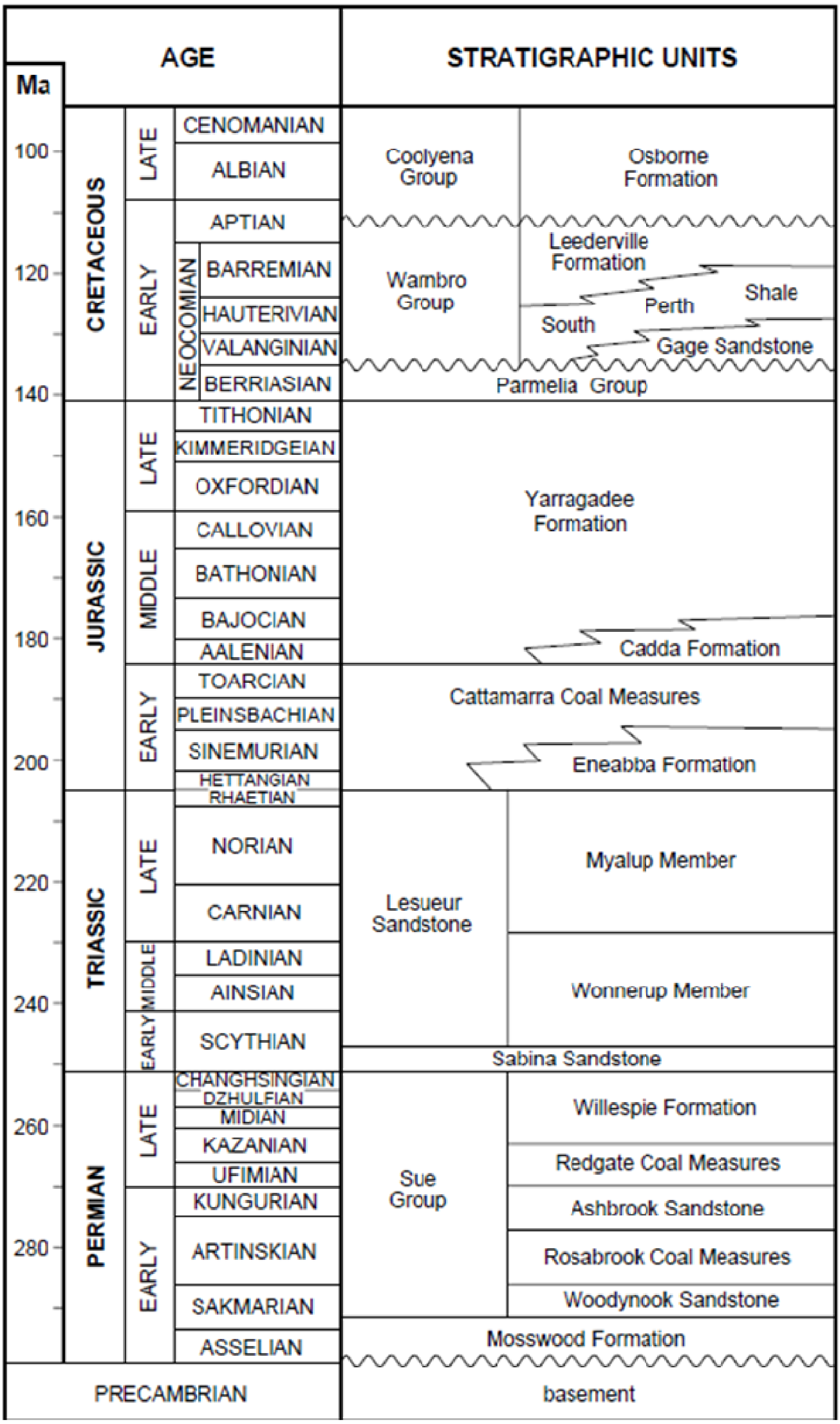


Figure 13: Stratigraphy of the central and southern Perth Basin (from Crostella and Backhouse, 2000).

stratigraphic order the Permian Nangetty Formation represents glacial sediments, underlying the Holmwood Shale, the High Cliff Sandstone, the Irwin River Coal Measures, and the Carynginia Formation, which, excluding the coal measures, are all marine deposits (Playford *et al.*, 1974). To the south the Permian sequence consists of a thick coal measure unit, the Sue Coal Measures, conformably overlain by the Upper Permian to Lower Triassic Sabina Sandstone. The total thickness of Permian rocks in the basin probably exceeds 2 600m (Playford *et al.*, 1974).

Coal and petroleum resources

The Perth Basin is prospective for both oil and gas and has several producing fields. The majority of these resources lie in the northern Perth Basin, of which the Dongara Field is the largest (DMP, 2011b). To the north the gas produced is mainly dry and the oil is paraffinic (DMP, 2011b). The main source of gas in the basin is the Permian Irwin River Coal Measures, an alternating sequence of fine grained sediments and coal measures (Playford *et al.*, 1974). The main source of oil is the Lower Triassic Kockatea Shale. In the southern Perth Basin the thin shale units required for a successful play are not present and hence commercial fields have not been discovered (DMP, 2008). The Irwin River Coal Measures to the north of the Perth Basin contain low grade sub-bituminous coals with high ash yields (Playford *et al.*, 1974). The seams vary in thickness from 0.3 m to up to 3.7 m (Playford *et al.*, 1974). Irwin River coals tend to have vitrinite contents varying between 45 and 55%, inertinite contents between 35 and 44%, and low amounts of liptinite (5 to 9%). Mineral matter content is also low (3 to 8%) and vitrinite reflectance ranges from 0.44 to 0.60% (Santoso, 1994). The Sue Coal Measures to the south also contain low grade sub-bituminous coals with high silt and clay contents. Individual coal seams are up to 5.5 m thick (Playford *et al.*, 1974). The coals have slightly higher liptinite contents (5 to 17%), with vitrinite contents ranging between 38 and 45%, and inertinite contents between 35 and 50%. Mineral matter content is less than 6% and vitrinite reflectances (0.55 to 0.65%) are slightly higher than the Irwin River Coal Measures (Santoso, 1994).

4.5.5 Petrel Basin

Geological setting

The Petrel Sub-basin is a northwest-trending Palaeozoic rift situated in the eastern portion of the Bonaparte Basin (Figure 10). The faulted margins in the east and west converge onshore to form the southern termination (GA, 2011b). The sub-basin consists of a syncline that plunges to the northwest, with Lower Palaeozoic sediments exposed in the southern onshore area. Phanerozoic sediments are thin on the eastern, western and southern margins of the basin, but the thickness of the Upper Palaeozoic-Mesozoic section exceeds 15 km in the northern and central parts of the sub-basin (GA, 2011b). The Petrel Sub-basin was the principal depocentre within the Bonaparte Basin during the Late

Carboniferous to Permian (Pegum, 1997). Onshore deposits are mainly coarse clastic sediments overlain by lacustrine to estuarine sediments, whereas marine to deltaic siliciclastic sediments along with marginal marine sands, shales, limestones and coals were deposited offshore (Pegum, 1997). Permian-aged sediments of the sub-basin are contained within the Kulshill and Kinmore Groups, both of which are regarded as significant elements of the petroleum systems within the basin (GA, 2011b).

Coal and petroleum resources

The Lower Permian Keyling Formation of the Kulshill Group and the Upper Permian Hyland Bay Subgroup of the Kinmore Group are potential gas-prone source rocks (GA, 2011b). Potential source rocks in the Keyling Formation contain mainly terrestrial organic matter from delta-plain coals (mean TOC = 35% and mean HI = 230 mg S_2/g TOC) and marginal marine shales (mean TOC = 2.8% and mean HI = 95 mg S_2/g TOC) (Colwell and Kennard, 1996). The Late Permian pro-delta Hyland Bay Subgroup is also deltaic in origin but is more gas prone compared to the Keyling Formation. It has a mean TOC of 2% and a mean HI of 55 mg S_2/g TOC (Colwell and Kennard, 1996). The Torrens, Cape Hay and Tern Formations of the Hyland Bay Subgroup are considered to be good reservoirs within the Petrel and Tern gas fields. Regional seals are provided by the Permian Fossil Head Formation and the Triassic Mount Good Subgroup (GA, 2011b).

4.6 Basins (mainly) in TAS

4.6.1 Tasmania Basin

Geological setting

The Tasmania Basin is a shallow epicratonic basin covering most of central and eastern Tasmania (Figure 14). The basin contains Late Carboniferous to Early Triassic sediments of the Parmeener Supergroup with a maximum thickness of 1700 m (Bacon *et al.*, 2000). The sediments are typically flat lying (Bacon *et al.*, 2000). The Parmeener Supergroup can be divided into four sequences. The lower marine sequence is Late Carboniferous in age and consists of diamictites, sandstones, conglomerates and rare oil shales. The overlying lower freshwater sequence is Permian in age and contains quartzose sandstones and shales up to 60 m thick, with some coal and oil shales (O’Brien, 1989c). Within this sequence Tasmanite of up to 2 m in thickness is found (Bacon *et al.*, 2000). The Permian Upper Marine Sequence consists of calcareous siltstone, limestone, sandstone and mudstone units. The Upper Freshwater sequence is referenced to as the Cygnet Coal Measures. At Mount Cygnet, 50 km south of Hobart, two coal seams are present; the thickest being 90 cm (O’Brien, 1989c). These coal units represent intervals of fluvial and deltaic deposition in the largely marine sequence of the Parmeener Supergroup.

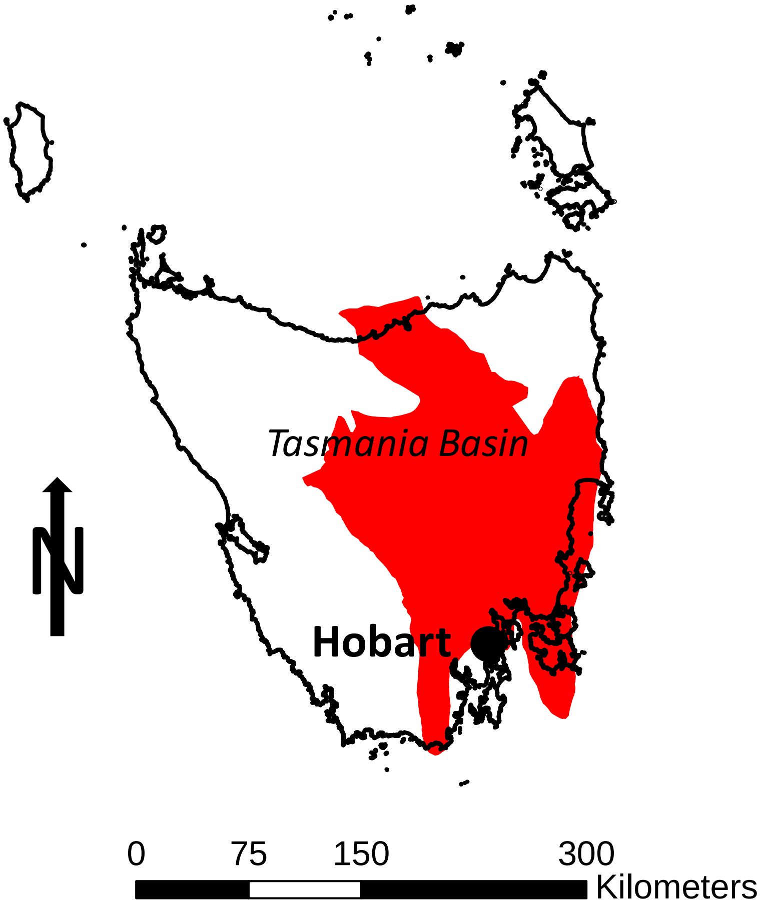


Figure 14: Location of Permian sedimentary basins in Tasmania.

Coal and petroleum resources

The Lower Permian dark mudstone of the Woody Island Formation and the Tasmanite Oil Shale of the Lower Freshwater Sequence have been identified for their hydrocarbon potential (Bacon *et al.*, 2000). The Woody Island Formation, consisting of dark grey, thick bedded mud and siltstones, has, according to collaborated data from Bacon *et al.* (2000), TOC values ranging from 1.1 – 2.4 %. However, Rock-Eval pyrolysis shows relatively poor quality type III to type II/III, with low hydrocarbon yields (Bacon *et al.*, 2000; Reid and Burrett, 2004). Based on Tmax, samples are immature to mature (Bacon *et al.*, 2000). In summary, the Woody Island Formation is deemed to be a lean potential source rock which is both oil and gas prone (Bacon *et al.*, 2000). The Tasmanite Oil Shale is a silty shale, rich in compacted green algal cysts with an aggregate thickness of up to 1.5 m (Bacon *et al.*, 2000). Rock-Eval pyrolysis shows a predominantly hydrogen rich, oil prone, type I kerogen with TOC in the range of 2.58 - 63.0% (Bacon *et al.*, 2000; Reid and Burrett, 2004). Other possible source rocks of the Parmeener Supergroup include the Macrae Mudstone and the coals of the lower Freshwater Sequence. However, this assumption is based on sparse data (Bacon *et al.* 2000). There is also source rock potential in the carbonaceous Liffey group. Coal horizons within the group have TOC levels of up to 65% (Reid and

Burrett, 2004). The rocks are both oil and gas prone and contain kerogen types I, II, III (Reid and Burrett, 2004). VR ranges from 0.57-1.74% but the higher values have been subjected to metamorphism (Cook, 2003).

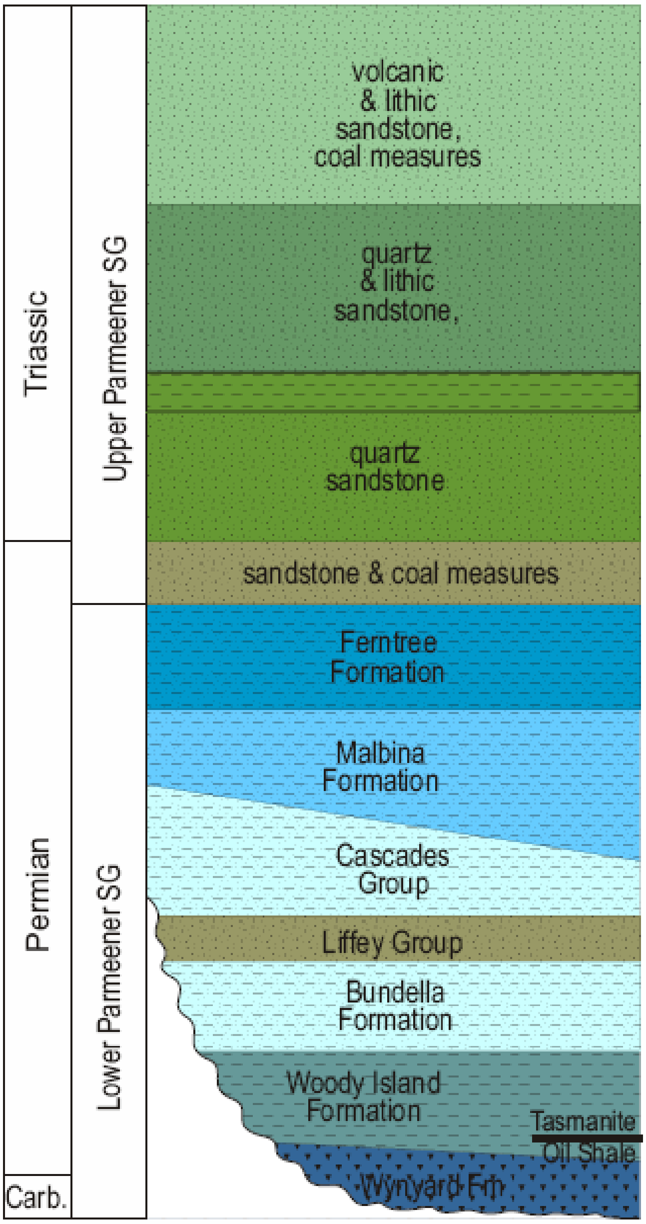


Figure 15: Stratigraphy of the Parmeener Supergroup of the Tasmania Basin (from Reid and Burrett, 2004).

5. ORGANIC CHEMISTRY OF PERMIAN COALS IN AUSTRALIA

5.1 Coal structure and ramifications for organic compounds found in coal-associated waters

In his comprehensive book about typology, physics, chemistry and constitution of coal van Krevelen (1993) states that "coal is a rock, a sediment, a conglomerate, a biological fossil, a complex colloidal system, an enigma in solid-state physics and an intriguing object for chemical and physical analyses". This sentence captures the multivariate and complex nature of coal, and it is important to recognise that the vast majority of organic material in all coals is tied up in macromolecules (Derbyshire *et al.*, 1989). This chapter summarises organic geochemical properties of Permian coals in Australia, with particular focus on aromatic hydrocarbons that encompass the more soluble alkylbenzene compounds benzene, toluene, ethylbenzene and xylenes (BTEX).

The majority of organic matter in coal is derived from lignin (Figure 16), but some originates from other material and is derived from; carbohydrates which have been highly modified; 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 much smaller volatile compounds which are the subject of this review is unlikely in any technique in which the macromolecular component is also observed. However, this is not to say they may not be present in significant quantities, much greater than would be expected given their volatility. This is since some may be entrapped as guests in host-guest complexes in the coal (Derbyshire *et al.*, 1989).

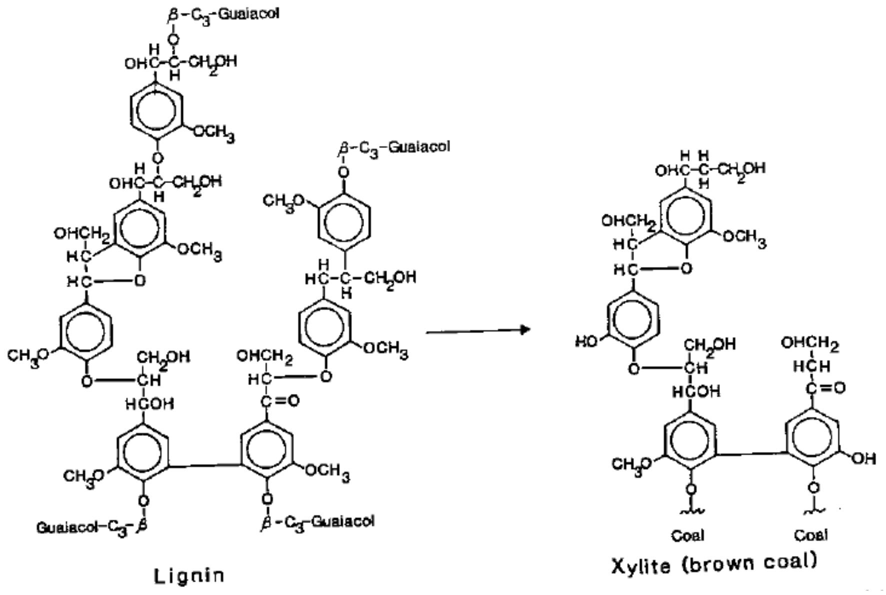


Figure 16: Proposed pathway for the transformation of lignin to xylite (brown coal), from van Krevelen (1993).

The constituents of coal are essentially aromatic in structure and the water-soluble components of coal are also aromatic compounds. Van Krevelen (1993), p. 784, systematically lists the most important indications for the aromatic nature of coal, namely:

- Studies on the macerals – Vitrinite being derived from lignin in woody tissues, and 60% of the carbon in lignin being aromatic.
- Indications from ultimate analyses – Position of dominant macerals, vitrinite and inertinites on H/C-O/C diagrams.
- Indications from spectroscopic techniques – Adsorptions bands of Fourier Transform - Infrared (FTIR) and Nuclear Magnetic Resonance (NMR) providing the most direct proof of the aromatic character (see Figure 17).
- Identification from ultraviolet spectra – showing that coal extracts are typically aromatic.
- Identifications from the refractometric exaltation of coals and coal liquids – The specific refraction of coals and coal liquids shows a high incremental exaltation that can only be explained by the presence of aromatic ring clusters, since conjugated olefinic double bonds are absent in coals.
- Indications from electrical conductivity measurements – Higher rank coals are semiconductors. The energy barriers of semiconductivity show a good correlation with those of polycyclic aromatic model compounds.
- Indication from magnetic susceptibility measurements – The numerical values found for the dia- and paramagnetic susceptibilities of coals cannot be explained without the assumption of an appreciable aromaticity in coals.
- Indications from oxidation studies of coals – Wet oxidation of coals found mainly aromatic carboxylic acids as end products.
- Indications from pyrolytic studies – All organic chemical compounds which produce a considerable carbon residue on thermal decomposition are aromatic.

However, most of the aforementioned techniques reveal little about smaller-sized compounds in the coal structure, specifically monoaromatics. The exceptions are techniques which may drive these compounds directly from the matrix in an organised way, often thermally, e.g. by using pyrolysis or using thermovaporisation techniques. Flash pyrolysis coupled to gas chromatography - mass spectrometry (Py-GC-MS) may be useful since it allows small molecules to escape before they react as they may do in conventional, slow pyrolysis. An advantage of these techniques is that specific compound patterns which may be found in the pyrolysates could be used to type organic matter that may be encountered in waters that have been in contact with such coals.

Solvent extraction of coal will liberate a large quantity of organic matter, but the nature of the extract depends on extraction time and solvents used, and may be difficult to correlate with water-borne organic compounds. Extraction with organic solvents will predominantly extract untrapped organic compounds, although many may eventually escape due to a change in equilibrium concentration. To maximise insights into the coal structure extractions should be carried out over weeks, with removal of extractant at each extraction step in order to maximise the disequilibrium between the coal and the extractant.

An understanding of the macromolecular structure of coal is still important for predicting the behaviours of small molecules. As rank increases, small molecules, especially those attached through weak bonds evolve and can become internally trapped in the matrix as guests. Little work has been done to identify these *in situ*. It is probable that different macerals have different contents, since the macromolecular basis of these is different and they will mature with rank in different ways. In lignin derived macromolecules there will be large structures capable of holding these small molecules. This may also be possible in semi-intertinite because semi-inertinite consists of highly oxidised macromolecules possibly derived from lignin. In liptinites, the structures are more hydrophobic and more likely to retain non-polar rather than polar compounds (Gupta *et al.*, 2007). These interdependencies highlight the importance of organic petrology for studying the nature of coal.

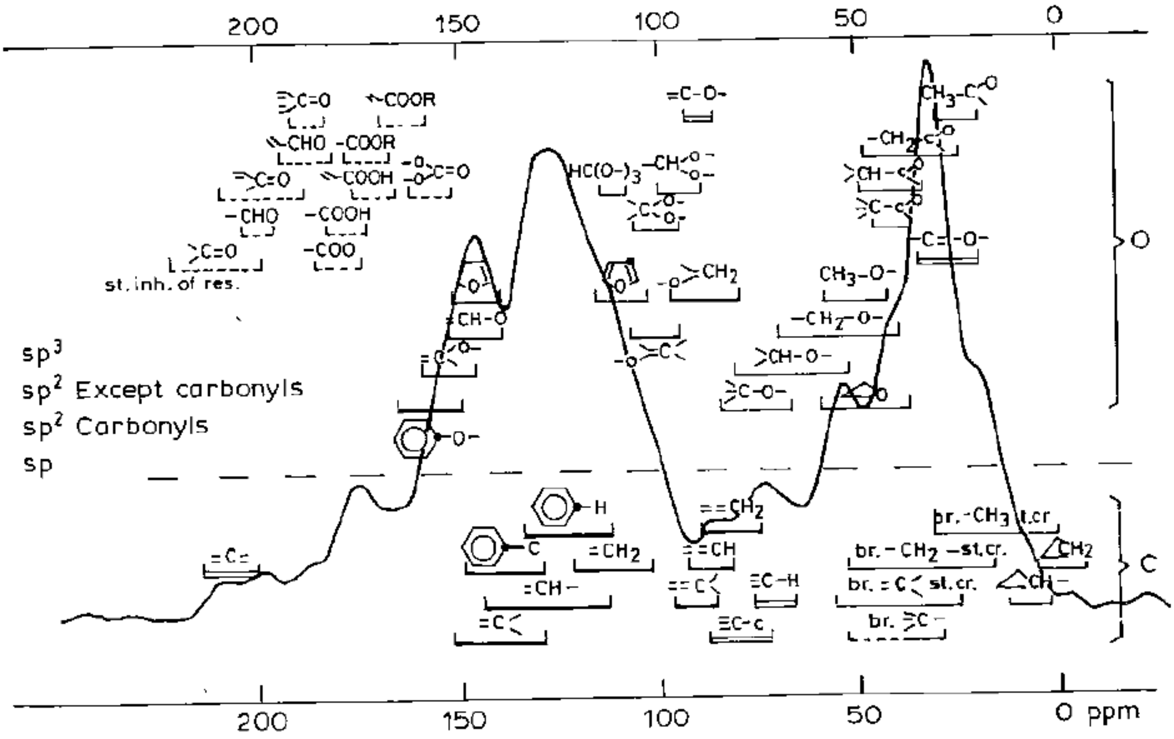


Figure 17: Carbon-13 NMR correlation chart, from van Krevelen (1993).

5.2 Organic chemistry of Australian Permian coals

5.2.1 Microscopic studies and elemental analyses

Organic petrology on Permian coals is routinely carried out on coal samples for quality control purposes and to estimate potential coal utilisation. Therefore, microscopic studies on Australian coals are many and too numerous to list exhaustively here. Good reviews of petrographic studies on Australian Permian coals are provided in Diessel (1992) Kershaw and Taylor (1992) and Taylor *et al.* (1998), amongst others. All Permian coals in Australia were deposited on the Gondwana supercontinent, which included all or parts of peninsular India, Australia, southern Africa, South America and Antarctica (e.g. Taylor *et al.*, 1998; Veevers, 2006). Gondwana coals tend to be less lustrous compared to Carboniferous coals, and on average contain, more mineral matter than most Carboniferous coals (Taylor *et al.*, 1998). Gondwana coals also tend to contain a higher proportion of inertinite. This association is believed to be a consequence of the environment of deposition and especially the climate, which is inferred to have been one of wet, cool summers and freezing winters (Taylor *et al.*, 1989). However, there are many exceptions to this rule. Studies using elemental analyses of coals are similarly numerous, and have often been combined with organic petrology (e.g. Gurba and Ward, 2000).

5.2.2 Fourier Transform Infrared Spectroscopy and NMR analysis

Fourier Transformed Infrared Spectroscopy (FTIR) and Nuclear Magnetic Resonance (NMR) are useful tools with which to gain insights into the structure of organic matter, and have been widely applied to coals (e.g. Guillen *et al.*, 1992; Ibarra *et al.*, 1996; Solomon and Carangelo, 1982; Supaluknari *et al.*, 1988a; 1988b). Excellent reviews on the use of NMR to identify coal structures have been conducted by Allen *et al.* (1984) and Genetti *et al.* (1999).

While many of the groundbreaking publications in this domain have been published in the 1970s-1990s, more recent studies still widely apply this technique to assess the distribution of different molecular moieties in the coal matrix. For example, one study (Wollenweber *et al.*, 2006) carried out a comprehensive organic-geochemical investigations of Permian, Carboniferous and Devonian coals with the aim to quantify differences in organic matter composition of the coals on a molecular level and to associate these differences with precursor plant matter, depositional environment and diagenesis. Li *et al.* (2010) investigated different macerals in bituminous coals of variable organic sulfur content using micro-Attenuated Total Reflectance – Fourier Transformed Infrared Spectroscopy (ATR–FTIR). ATR-FTIR spectra of vitrinite and inertinite macerals in low S and high S coals in their study showed some distinct differences in IR absorbance from various aliphatic and aromatic functional groups.

While it can be expected that the propensity of coals to dissociate water-soluble organic compounds into water will depend on the structure of the coal, no studies that specifically look at this interrelationship using FTIR and NRM spectroscopy were found in our literature review.

5.2.3 Pyrolysis and thermovaporisation

Rock Eval pyrolysis has been applied on Permian coals of Australia. However, conventional guidelines for interpreting Rock Eval data (e.g. Peters, 1986) have to be adjusted when assessing coal-bearing source rocks for their petroleum generation potential (Sykes and Snowdon, 2002). This review found many reports on Rock Eval data in databases maintained by the State Geological Surveys and in the open literature (e.g. Ahmed *et al.*, 2009). However, a systematic compilation of Rock Eval data was outside the scope of this present study. Thermovaporisation of coals and oil shows was also mentioned in a range of reports, but did not include any specific details on molecular distributions of products.

Pyrolysis - gas chromatography (Py-GC) coupled with mass spectrometry (MS) or other detectors (e.g. flame ionisation detector (FID) or thermal conductivity detector (TCD)) has been widely applied to gain insights into the structure of coal and kerogen (e.g. Solli and Leplat, 1986; Hartgers *et al.*, 1992; 1994b; Nip *et al.*, 1992, Figure 18) and to classify kerogen (Horsfield, 1989). This technique has also been applied to Australian coals. One study by Kralert *et al.* (1995) applied *in situ* methylation using aqueous tetramethylammonium hydroxide (TMAH) to study oxygen-containing organic constituents in a solvent-extracted Victorian brown coal. Pyrolysis has also been applied to reconstruct the kinetic behaviour of Australian coals during geological heating. Powell *et al.* (1991) investigated a series of Australian coals and terrestrial sediments ranging in age from Permian through to the Cainozoic using a combination of organic petrography, Rock-Eval pyrolysis, elemental analysis and quantitative Py-GC measurements. One of their findings was that the distribution and abundance of phenols in flash pyrolysates is related to depositional setting as well as degree of maturation. Boreham *et al.* (1998, 1999) conducted open system pyrolysis on a set of Bowen Basin coals and inferred two stages of thermogenic methane generation from these coals.

A multitude of studies investigated Australian torbanites of Permian age, since these sediments are of interest to characterise biopolymers derived from *Botryococcus* algae (e.g. Derenne *et al.*, 1994; Greenwood *et al.*, 1996; Han *et al.*, 1995; Hutton *et al.*, 1996; Largeau *et al.*, 1986). However, torbanites are not typical coals for CSG production, and no further detail on these studies is provided in this review. Ellis *et al.* identified a range of aromatic compounds which can be directly correlated to specific precursor organisms, e.g. phenylalkanes related to fossil algae (Ellis *et al.*, 1996a), dihydro-*ar*-curcumene derived from sesquiterpenoids of the bisabolane skeletal type, and hence from higher plants (Ellis *et al.*, 1995a), and isohexylalkylnaphthalenes associated with specific higher plant precursors as a result of rearrangement and A-ring opening of diterpenoid and triterpenoid natural products during aromatization (Ellis *et al.*, 1996b). A range of papers by the Curtin University group of organic geochemists also studied the formation of geosynthetic aromatic compounds in great detail (e.g. Alexander *et al.*, 1995; Bastow *et al.*, 1996; 2000; Ellis *et al.*, 1995b; Ioppolo-Armanios *et al.*, 1995). The majority of these papers also investigated Permian coals. Free hydrocarbons were also described in coals of the Late Permian Avon and Statford coal measures in the Gloucester Basin, however, no absolute concentrations are provided in this report, and the analytical detail of this report is sparse (Hunt et al., 1983).

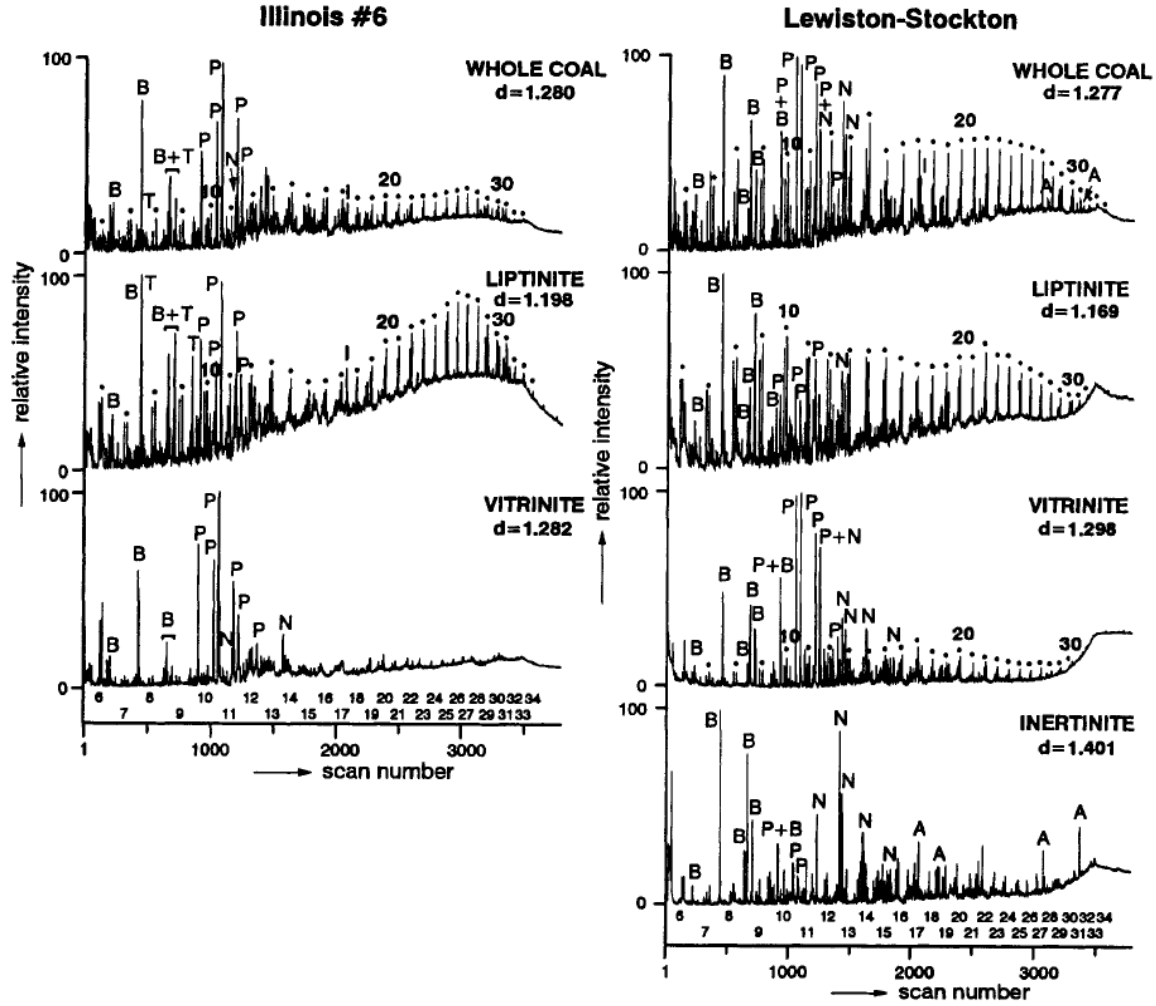


Figure 18: Example of Py-GC/MS traces, from Hartgers et al. (1994b) n-Alkanes are indicated by filled circles. Small numbers along the z-axis indicate total numbers of carbon atoms of n-alkaneln-alk-1-ene doublets. Key: B = (alky1)benzenes; T = (alky1)thiophenes; P = (alky1)phenols; N = (alkyl)-naphthalenes; A = polyaromatics; I = monounsaturated acyclic isoprenoids.

5.2.4 Solvent-extraction of organic matter followed by detailed geochemical analysis

Solvent extraction of coals is a technique with a long history, and was first applied systematically by de Marsilli around 1860, who obtained abundant extracts from coals with boiling benzene, alcohol, ether, chloroform and carbon disulphide. Soon after this, heterocyclic compounds with nitrogen such as pyridine and quinoline were used to obtain even higher yields of up to 50% of for some coals (van Krevelen, 1993). Depending on type and rank of coal, variable proportions 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 ground. Around 1930 more and more investigators came to support the theory that coal extracts are colloidal systems and therefore coal itself must be regarded as a solid colloid (van Krevelen, 1993). Products that can be extracted from coal are intimately bonded to the higher molecular weight proportion of the coal. Due to the importance of solvent extraction to gain insights into the nature and properties of coal, Van Krevelen (1993) dedicated an entire chapter of this monograph to the action of solvents on coal. Detailed analyses of solvent extracts, however, are usually confined to the maltene fraction of coal extracts, i.e. the fraction that is soluble in *n*-pentane, *n*-hexane or *n*-heptane.

High relative abundances of certain alkylbenzenes (i.e. 1,2,3-trimethylbenzene; 1,2,3,4-tetramethylbenzene and dihydro-ar-curcumene) in low maturity sediments and crude oils has led to the suggestion that they originate from natural products such as carotenoids, terpenoids and alkaloids (e.g. Erdman, 1961; Hartgers *et al.*, 1992; 1994a; 1994b). Other, more stable aromatic compounds with non-isoprenoidal carbon skeletons are thought to be the products of sedimentary reactions (Bastow *et al.*, 1999; van Aarssen *et al.*, 1999). The unique distribution or fingerprint of alkylbenzenes (including BTEX) present in individual coals (and associated water) resulting from natural products and sedimentary reactions could potentially be used to clarify whether or not the source of aromatic compounds in groundwater that may be encountered in coal basins is related to the coal.

Oil fields and oil shows are common in basins with Permian coals, most notably in the Cooper-Eromanga Basin, in the Bowen-Surat Basin, and in the Canning, Carnarvon, Petrel and Perth Basins. However, almost all of these basins also contain organic-rich sediments from stratigraphic intervals other than Permian coals that may have given rise to these oil shows. Molecular and isotope geochemistry has been applied to pinpoint the origin of these oils. Alexander *et al.* (1988) used the distribution of aromatic and saturated diterpane land plant markers to distinguish oils sourced from Permian versus younger source rocks. The advent of *Araucariaceae*, trees of the Kauri pine group that assumed prominence for the first time in the Early to Middle Jurassic resulted in a different distribution of these land plant markers for Permian and Jurassic oils that could be exploited for oil-source correlation. Using this approach Alexander *et al.* found evidence for both types of oils being present in the basin (Figure 19). Al-Arouri (1998) conducted a geochemical study of crude oils and samples of various Permian, Triassic and Jurassic organic-rich rock units from the southern Taroom Trough to test the prevailing Permian-source hypothesis for the petroleum reserves of the Bowen-Surat Basin. Based on molecular and isotopic evidence they defined two oil families, of which one was interpreted to be derived from Late Permian coal measures of the Blackwater Group along the south-eastern and south-western margins of the trough. Ahmed *et al.* (2009) presented a detailed study on molecular and isotopic characteristics of six oil shows and seeps from the Southern Coalfield, and suggested Permian coals to be the most likely source of these petroleum occurrences. Kinnon *et al.* (2010) aimed to determine whether water quality and stable isotope data can be correlated with gas and groundwater production and flow pathways, and identify zones of recharge and water mixing.

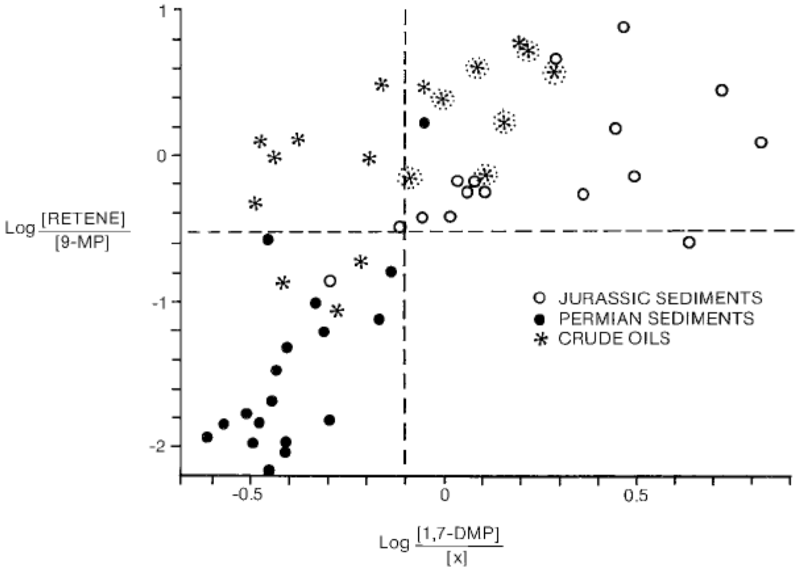


Figure 19: Log·log plot of source parameters based upon retene and dimethylphenanthrenes for Jurassic sediments, Permian sediments, and crude oils (from Alexander et al.*, 1988).*

5.3 Organic hydrochemistry of groundwaters associated with Permian coals in Australia

The organic hydrochemistry of groundwaters associated with coals can include a wide variety of oxygen-bearing aromatic compounds (e.g. phenols, aldehydes, ketones, and various carboxy-, hydroxyl- and methoxy-bearing compounds), nitrogen-bearing compounds (pyridines and amines), mono- and polycyclic aromatic hydrocarbons (PAHs) and aliphatic compounds (Santamaria and Fisher, 2003). These water-soluble organics are produced by the cleavage of the aromatic structures within the coal matrix either by thermal stress accompanied by burial, other forms of heating, chemical oxidation during burial, or as the consequence of the introduction of oxygenated water or air. Coals can also be solubilised to a limited extent by microorganisms (Klein *et al.*, 2001).

Lower rank coals contain a greater abundance of more easily cleaved bridge structures than higher ranked coals, and therefore solubilisation of lignite by microorganisms is more extensive than solubilisation of bituminous coal. The volatile matter and oxygen content of the coal are also principal factors influencing the extent of bioconversion (Reiss, 1992). For these reasons, groundwater associated with lower rank coals should have higher organic concentrations than those associated with higher ranked coals. Coals containing more volatiles and more oxygen should also yield more dissolved organics.

There is very limited published or publically available information available globally on the organic hydrochemistry of groundwater associated with coal seams, and even more limited data for the organic hydrochemistry of groundwater associated with Permian coal seams in Australia. A literature search of geo-databases, international journals, State groundwater databases, publicly available reports from mining and CSG companies and the Queensland Government CSG portal (http://www.derm.qld.gov.au/environmental_management/coal-seam-gas/groundwater.html) has yielded only limited organic geochemistry data for groundwater associated with Permian as well as non-Permian coal deposits in Australia.

5.3.1 BTEX

Benzene, toluene, ethylbenzene and xylene (BTEX) compounds are naturally found in crude oil, coal and gas deposits. Therefore they may naturally be present at low concentration in groundwater associated with these deposits (Leusch and Bartkow, 2011). While benzene is a known carcinogen, toluene, ethylbenzene and xylene are not recognised as carcinogenic (Leusch and Bartkow, 2011). Public health guidelines for BTEX are available for drinking water in the Australian Drinking Water Guidelines (ADWG; NHMRC 2004) and water quality criteria for ecosystem protection are available in the Australian and New Zealand Guidelines for Fresh and Marine Water Quality (ANZECC, 2000). A summary of these guidelines is shown in Table 1.

Table 1: Water quality guidelines for BTEX. Values are in ppb (µg/L).

Compound	**ADWG**[1]	**ANZECC (99% protection)**[2]
Benzene	1	600
Toluene	800 (25 for aesthetics)	180
Ethylbenzene	300 (3 for aesthetics)	50
Xylene	600 (20 for aesthetics)	200

[1] Australian Drinking Water Guidelines (NHMRC, 2004); [2] Australian and New Zealand Environment Conservation Council Environmental [2] Protection Guidelines (ANZECC, 2000);

There have been three recently reported instances in Queensland relating to BTEX compounds in groundwater sources associated with CSG and underground coal gasification (UCG). Two of these occurrences were in the Permian Bowen Basin, and the third was in the Surat Basin. Occurrences in the Surat Basin and Eromanga Basin are discussed in Section 5.4. It is important to note, however, that CSG extractions are very different to UCG extractions and therefore the occurrences of BTEX compounds in CSG and UCG sites are due to different processes and/or sources. Coal seam gas extraction methods always involve dewatering and fracture stimulation whereas UCG technology involves the combustion of coal seams in-situ by introducing air and an ignition source, and then drawing off the generated gases.

In November 2010 Arrow Energy announced that traces of benzene (1 to 3 ppb) were detected in three wells in its CSG permits in the northern Bowen Basin. Arrow Energy stated that chemicals containing benzene (or TEX compounds) were not used in hydraulic fracturing (Arrow Energy, 2010a http://www.arrowenergy.com.au/icms_docs/87336_Notification_of_Results_Media_Release.pdf, accessed 18 July 2011). Investigations are currently under way to determine if benzene is naturally occurring at this site or is elevated due to Arrow's activities (Arrow Energy, 2010b, http://www.arrowenergy.com.au/icms_docs/87070_Arrow_Secondary_Results_Notification.pdf, accessed 11 August 2011).

In May 2010, Cougar Energy found traces of toluene (up to 45 ppb) in a monitoring well at its pilot UCG plant near Kingaroy in Queensland. In June 2010, benzene was detected in a monitoring well at a level of 2 ppb. Cougar Energy received an Environmental Protection Order from the Queensland Government in July 2010 to cease operations of its pilot underground gasification plant (Sherrif *et al.*, 2010). In July 2011, the Queensland government banned any further trials at the site.

It is widely acknowledged that organic and inorganic contaminants can be released into the surrounding groundwater environment as a result of UCG (e.g. Humenick and Mattox, 1978; Stuermer *et al.*, 1982; Kapusta and Stanczyk, 2011; Liu *et al.*, 2007; Yang, 2009; Younger, 2011). Groundwater contamination is typically introduced either through the release of gas products produced by pyrolysis of the coal seam during the gasification phase or through aqueous leaching of the residual coal ash during the post-gasification phase (Liu *et al.*, 2007).

Organic contaminants are typically produced as volatiles during the gasification phase. During the gasification process, air is injected at a pressure equal to or greater than the surrounding hydrostatic pressure. Some of the volatile products in the gas phase can therefore be lost and dispersed to the surrounding strata. The connection between strata may be enhanced as a result of cracks created through the gasification process. However, where the integrity of aquitards between the coal seams and the surrounding aquifer units remains intact, contamination of these surrounding units is unlikely. Studies by Campbell *et al.* (1979) and Liu *et al.* (2007) identified that the major organic groundwater contaminants produced through the UCG process are phenolic compounds, PAHs, BTEX and TPH.

Apart from the three reported instances of BTEX occurrence in groundwater associated with CSG and UCG operations in QLD, there is very little readily or publicly available information. In March 2005, Sydney Gas reported that BTEX concentrations were below the limit of reporting (LOR) (<1 µg/L for benzene; <2 µg/L for toluene, ethylbenzene, meta & para-Xylene, and ortho-Xylene) in their gas exploration well, Jilliby 1 at Wyong, which penetrated the Great Northern Seam of the Permian Newcastle Coal Measures (Parsons Brinckerhoff, 2005).

AGL (Parsons Brinkerhoff, 2010) reported BTEX concentrations were below the limit of reporting (LOR) in gas exploration well HB02 at Broke in the Hunter Valley. The gas well penetrated the Blakefield Seam of the Permian Wittingham Coal Measures.

5.3.2 Phenols

Phenols naturally occur in coal seams and will partition into produced water depending on their molecular weight. Phenols with side chains greater than 5 carbon atoms are mainly associated with oil droplets (OGP, 2005).

Public health guidelines for some phenolic compounds are available for drinking water in the Australian Drinking Water Guidelines (ADWG; NHMRC 2004) and water quality criteria for ecosystem protection are available in the Australian and New Zealand Guidelines for Fresh and Marine Water Quality (ANZECC, 2000) (Table 2). However, halogenated phenols do not naturally

Table 2: Water quality guidelines for phenolic compounds. Values are in ppb (µg/L)

Compound	**ADWG[1]**	**ANZECC (99% protection)[2]**
Phenol		85
2,4-dimethylphenol		ID†
Nonylphenol		ID
2-chlorophenol*	0.3 (health), 0.0001 (aesthetic)	340
3-chlorophenol*		ID
4-chlorophenol*		160
2,3-dichlorophenol*		ID
2,4-dichlorophenol*	0.2 (health), 0.0003 (aesthetic)	120
2,5-dichlorophenol*		ID
2,6-dichlorophenol*		ID
3,5-dichlorophenol*		ID
2,3,4-trichloropheno*l		ID
2,3,5-trichlorophenol*		ID
2,3,6-trichlorophenol*		ID
2,4,5-trichlorophenol*		ID
2,4,6-trichlorophenol*	0.02 (health), 0.002 (aesthetic)	3
2,3,4,5-tetrachlorophenol*		ID
2,3,4,6-tetrachlorophenol*		10
2,3,5,6-tetrachlorophenol*		ID
2-nitrophenol		ID
3-nitrophenol		ID
4-nitro-phenol		13
2,4,6-trinitrophenol		ID

[1]Australian Drinking Water Guidelines (NHMRC, 2004); [2]Australian and New Zealand Environment Conservation Council Environmental Protection Guidelines (ANZECC, 2000); † ID insufficient data. * denotes anthropogenic, halogenated compounds.

occur in coals (they are man-made chemicals), and nitrophenols, although natural compounds in many plants, are not commonly occurring in hard coals.

There is very little readily or publicly available information on the presence of phenols in groundwaters associated with Australian Permian coals. Sydney Gas reported Total Phenol concentrations of 0.115 mg/L in groundwater (1 sample from 1 well) associated with the Permian Wittingham Coal Measures in the Hunter Valley (Parsons Brinckerhoff, 2006).

AGL (PB 2010) reported concentrations of phenolic compounds below the laboratory LOR in one of their gas exploration wells (6 samples from one well) in their Hunter Valley. The gas well penetrated the Blakefield Seam of the Permian Wittingham Coal Measures. The specific phenol compounds analysed are listed in Table 3 (note, not all of these phenols will naturally occur in coals).

Table 3: Concentrations of phenolic compounds in waters associated with the Permian Wittingham Coal Measures (PB, 2010).

Compound	Concentration
Phenol	<1.0
2-Chlorophenol*	<1.0
2-Methylphenol	<1.0
3-&4-Methylphenol	<2.0
2-Nitrophenol*	<1.0
2.4-Dimethylphenol	<1.0
2.4-Dichlorophenol*	<1.0
2.6-Dichlorophenol*	<1.0
4-Chloro-3-Methylphenol*	<1.0
2.4.6-Trichlorophenol	*<1.0
2.4.6-Trichlorophenol*	<1.0
Pentachlorophenol*	<2.0

* denotes phenols that are not, or unlikely to be derived from coals.

5.3.3 TPH

Total petroleum hydrocarbon is defined as the measurable amount of petroleum-based hydrocarbons in an environmental medium. There are over several hundred chemical compounds that are defined as petroleum-based. Because there are so many different chemicals in crude oil and in other petroleum products, 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) and which contain many individual chemicals.

Hydrocarbons associated with produced waters can be present as both dispersed droplets of non-aqueous phase liquid (i.e. oil), as colloidal and dispersed solids and in the dissolved phase. Due to their low solubility, some compounds such as the aliphatic hydrocarbons are found predominantly in the dispersed phase, while others such as aromatic compounds can be present in either phase depending on their molecular weight and structural complexity (OGP, 2005). It usually requires very careful and detailed analyses to determine the phase of the TPH in environmental samples. The phase also critically impinges on the interpretation of the results.

TPH data is available for Permian coal seams in the Bowen Basin at the Middlemount Mine (Middlemount Coal, 2011). TPH concentrations in the Middlemount Seam, Pisces Coal Seam and Fort Cooper Coal Measures were generally low, with maximum concentrations summarised in Table 4.

Table 4: Maximum TPH concentrations (µg/L), Middlemount Seam, Pisces Coal Seam and Fort Cooper Coal Measures (Middlemount Coal, 2011).

Total Petroleum Hydrocarbons	Middlemount Seam	Pisces Coal Seam	Fort Cooper Coal Measures
C_6-C_9 fraction	80	340	<20
C_{10}-C_{14} fraction	210	120	<50
C_{15}-C_{28} fraction	130	200	<100
C_{29}-C_{36} fraction	<50	90	<50
C_6-C_{36} (sum of total)	220	350	<50

TPH was also analysed in waters associated with the Permian Wittingham and Newcastle Coal Measures by ALS Environmental (Sydney) for Sydney Gas and AGL at their exploration sites in the Yarramalong and Hunter valleys (PB, 2005; 2006; 2010) using standard methods (USEPA SW 846 - 8015A and USEPA SW 846 – 8260B; USEPA 2008). Maximum measured values are reported in Table 5.

Table 5: TPH concentrations (µg/L), in the Newcastle and Wittingham Coal Measures.

Total Petroleum Hydrocarbons	Great Northern Seam	Blakefield Seam	Warkworth/Piercefield/Mt Arthur Seams	Blakefield Seam
Coal Measures	Newcastle	Wittingham	Wittingham	Wittingham
Reference	PB, 2005	PB, 2006	PB, 2006	PB, 2010
C_6-C_9 fraction	<20	<20	<20	<20
C_{10}-C_{14} fraction	<50	<50	<50	<50
C_{15}-C_{28} fraction	400	400	6,800	300
C_{29}-C_{36} fraction	660	500	5,190	240

5.3.4 Others (polycyclic aromatic hydrocarbons)

Polycyclic aromatic hydrocarbons (PAHs) are produced in coal as lignin-rich organic matter undergoes defunctionalisation and condensation during the normal coalification processes (Orem *et al.*, 1999). Their presence in groundwater is a result of leaching of coals (Orem *et al.*, 1999). Some PAHs are considered carcinogens. In Australia, drinking water guideline values have only been established for benzo-(a)-pyrene (0.01 µg/L) (NHMRC, 2004). A water quality criteria for naphthalene has been established for aquatic ecosystems in the ANZECC (2000) guidelines (16 µg/L; 99% trigger value) (ANZECC, 2000).

Sydney Gas reported PAH concentrations below laboratory LORs for their gas wells penetrating the Permian Wittingham Coal Measures (Parsons Brinkerhoff, 2006). The specific PAHs analysed are listed in Table 6.

Table 6: Concentrations (µg/L) of PAHs in waters associated with the Permian Wittingham Coal Measures (Parsons Brinkerhoff, 2006).

Compound	Blakefield Seam	Warkworth/Piercefield/Mt Arthur Seams
Napthalene	<1.0	<1.0
Acenaphthylene	<1.0	<1.0
Acenaphthene	<1.0	<1.0
Fluorene	<1.0	<1.0
Phenanthrene	<1.0	<1.0
Anthracene	<1.0	<1.0
Fluoranthene	<1.0	<1.0
Pyrene	<1.0	<1.0
Benz(a)anthracene	<1.0	<1.0
Chrysene	<1.0	<1.0
Benzo(b)fluoranthene	<1.0	<1.0
Benzo(k)fluoranthene	<1.0	<1.0
Benzo(a)pyrene	<0.5	<0.5
Indeno(1,2,3,cd)pyrene	<1.0	<1.0
Dibenz(a,h)anthracene	<1.0	<1.0
Benzo(g,h)perylene	<1.0	<1.0

5.4 Brief review of organic hydrochemistry of groundwaters associated with non-Permian coals in Australia

5.4.1 Surat Basin

Worley Parsons recently completed a literature review of the chemistry of coal seam waters in the Surat and Bowen Basins as part of the Commonwealth-funded Healthy Head Waters Project in the Queensland Murray-Darling Basin (Worley Parsons, 2010). The main objective of this study was to analyse the opportunities, risks and practicability of using groundwater produced during CSG development in addressing water sustainability and adjustment issues in the basin. The study found that extensive data was available for inorganic constituents and salinity, but no organic chemistry data was readily or publicly available.

Australian Pacific LNG (APLNG) provided a summary of water chemistry from 47 wells within the Talinga gas field in south central QLD (Surat Basin) as part of their Condabri CSG Water Management Plan to DERM (APLNG, 2010). Average concentrations of BTEX compounds, phenolic compounds and PAHs were below detection limits, while ranges of detected levels were not reported. Low concentrations of TPH were detected. The specific organic analytes analysed are listed in Table 7. APLNG announced in October 2010 the discovery of BTEX traces in fluid samples in eight CSG exploration gas wells in the Surat Basin, but no specific information is publicly available. The samples were collected from wells that had been stimulated by hydraulic fracturing; however APLNG stated that BTEX had not been used in fracture fluids and this was confirmed by APLNG's supplier

Table 7: Average concentrations of organic compounds in forty seven wells in the Talinga gas field (APLNG, 2010).

Compound	**Average value (µg/L)**
2,4,5-Trichlorophenol*	<0.3
2,4,6-Trichlorophenol*	<0.3
2-Chlorohphenol*	<0.3
4-Methyphenol	<0.3
4-Nitrophenol*	<0.26
Acenapthene	<0.01
Acenaphthylene	<0.01
Anthracene	<0.01
Benzene	<1
Benzo(a)pyrene	<0.01
Ethylbenzene	<2
Phenanthrene	<0.01
Phenol	<0.3
Pyrene	<0.01
Toluene	<2
TPH (C_6-C_9)	<25
TPH (C_{10}-C_{14})	83.5
TPH (C_{15}-C_{28})	74.7
TPH (C_{28}-C_{36})	94.4
Xylene (Meta, Para, Ortho)	<6

* denotes compounds that are not, or unlikely to be derived from coals.

(Sherrif *et al.*, 2010). An investigation identified possible sources of BTEX contaminants, including small amounts of lubricants and diesel which may have been introduced inadvertently during operations. TEX chemicals were identified as being present in trace amounts in mineral oil which was used as in additive in hydraulic fracture stimulation (APLNG, 2010; http://origintogether.com/wp-content/factsheets/press/APLNG%20BTEX%20 Investigation%20Results.pdf accessed 18 July, 2011). The investigation also indicated that trace levels of BTEX may naturally occur under certain conditions (APLNG, 2010; http://origintogether.com/wp-content/factsheets/press/APLNG%20BTEX%20Investigation%20Results.pdf accessed 18 July, 2011).

5.4.2 Eromanga Basin

In 1995 the NSW Department of Mineral Resources began a project to sample water and/or gas from artesian water bores in the Great Australian (Artesian) Basin (GAB) for analysis of the quantity and composition of dissolved gas. Samples were collected from a large number of bores in the Eromanga and Surat Basin. Water samples were collected directly from the flumes of flowing bores, from pressure plugs in the head works of bores, or from pumped sub-artesian bores. CSIRO analysed groundwater samples using gas chromatography to analyse quantity and composition of dissolved hydrocarbons and incorporated mass spectrometry to measure C^{13} isotope composition of methane and carbon dioxide. Gas concentrations were expressed as mol ppm by volume of a given gas in the sampling bottle headspace above the water. More detail on analytical methods in addition to data tables and interpretations can be found in Pallasser et al. (1995) and Pallasser (1996, 1997, 1998, 2000).

The results of this study are distributed in a data package issued by Industry & Investment NSW Government (2010) and in the report and data package Packham and Jovevski (2001). Packham and Jovevski (2001) state that Department of Mineral Resources has sampled the dissolved gas content of 215 water bores within the Great Artesian Basin from bores that mostly reached Namurian Sandstone aquifers. They note significant gas anomalies of methane, ethane, propane and occasionally higher alkanes, in particular in the Brewarrina and Milparinka areas. Methane concentrations ranging from 0 to 226,200 ppm are provided in the report, while ethane concentrations of 0 ppm to l,748 ppm are stated. The regional distribution of these values is provided in Figure 39 of Packham and Jovevski (2001).

Tables of water bore chemistries in the data package Industry & Investment NSW Government (2010) quote a wide range of methane concentrations of 186,000 - 5 ppm waters for the Murray and Darling basins, and are supplemented by two interpretative reports (Moffit and Weatherall, 2003, 2004). While methane values are presented graphically in Figure 11 in Moffit and Weatherall (2004), the report concludes that head-space gas analyses showed no anomalous methane values.

5.5 Brief review of organic hydrochemistry of groundwater associated with non-Australian coals

5.5.1 Europe

The extensive literature search did not yield information relating to the occurrence of TPH/BTEX Carboniferous or Permian coals in Europe, or any coals/peat deposits older than Pliocene.

5.5.2 USA

Hydrochemical studies of waters associated with the coal bed methane industry in the United States have focused on the inorganic chemistry. The Produced Waters database (http://energy.cr.usgs.gov/prov/prodwat/index.htm) provides tens of thousands of analyses of inorganic constituents from produced waters from the various coal bed methane (CBM) producing states within the United States. Although it is recognised that dissolved organic substances may also be present in some CBM produced waters, these substances in CBM produced waters are neither well documented nor researched (Committee on Management and Effects of Coalbed Methane Development and Produced Water in the Western United States, 2010).

There is little information on Carboniferous coals. However, more chemical studies are available on shallower Cainozoic coals. The major studies looking at organic chemistry of waters associated with coal seams have been undertaken in the Powder River Basin, Wyoming (Orem *et al*., 2007) and in Louisiana (Bunnell *et al*., 2003; 2006). The coals in the Powder River Basin are Cainozoic age lignite and subbituminous coals, and Palaeogene low-rank (lignite) in Louisiana. These coals are much younger than the Carboniferous-Permian coals that are the subject of this literature review and they have substantially different geological and hydrogeological attributes. The water chemistry data is presented here as general information, and is not presented as being representative or typical of older consolidated Permian coals.

Orem *et al.* (2007) analysed organic compounds in produced water samples from CBM wells in the Powder River Basin, Wyoming, as part of a larger study of the potential health and environmental effects of organic compounds derived from coals. Samples were analysed using gas chromatography – mass spectrometry (GC-MS) analysis and individual organic compounds in the sample chromatograms were identified by comparison of mass spectral features to libraries of mass spectral data (NIST98 and Wiley 7). Only a small fraction of the total peaks in each chromatogram were identified. The identified organic compounds (sorted by compound class), the wells they were identified in and their concentrations are presented in Table 8. The compounds identified in the GC-MS total ion current (TIC) chromatographs included: PAHs and functional derivatives of PAHs (Figure 20), benzene derivatives, biphenyls, aromatic amines, heterocyclic aromatic NSO compounds, and various polar non-aromatic compounds (*n*-alkanes, fatty acids, ethers, cyclic aliphatic compounds and others).

PAHs and their functional derivatives were found to be the most frequently occurring compounds. The major groups of PAHs identified included: naphthalene and derivatives, fluorene and derivatives, indene and derivatives, anthracene and derivatives, phenanthrene and derivatives, and pyrene and derivatives. The probable source of PAHs in produced waters from CBM wells was concluded to be leaching from sub-bituminous coal, based on similarities between the spectrum of PAHs present in the produced water and those typically present in coal (Orem *et al*., 2007). Concentrations of total PAHs ranged up to 23 µg/L, with concentrations of individual compounds ranging from about <0.01 to 18 µg/L. As expected, the lower molecular weight PAHs were highest in both number of compounds and concentrations due to greater solubility in the aqueous phase.

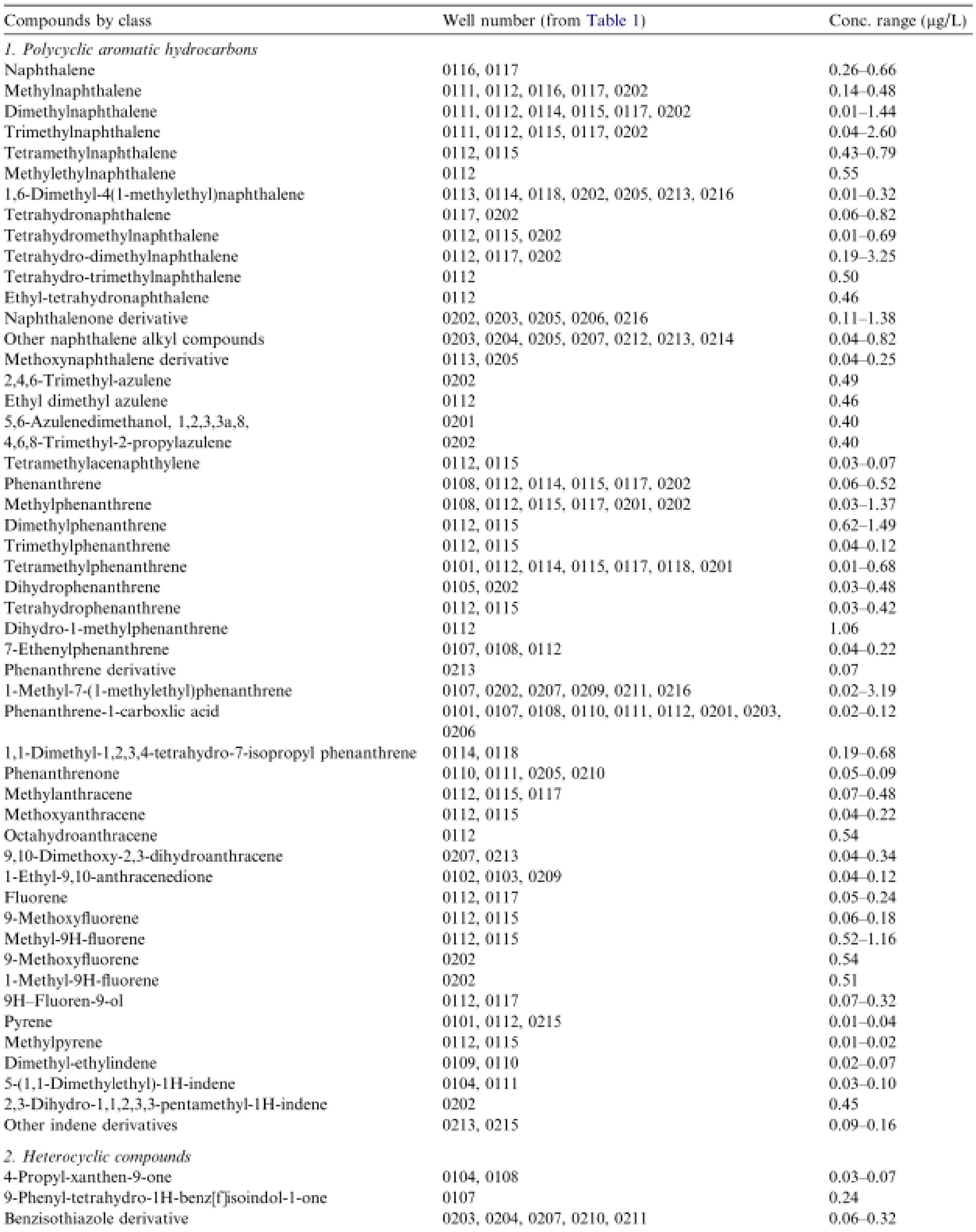
Derivatives of phenols and biphenyls were also found in the Powder River samples (up to concentrations of 16.17 µg/L. These compound classes are widely recognised in coal and Orem *et al.* (2007) attribute their presence most likely due to alteration of lignin biopolymer during coalification.

Orem *et al*., 2007 found a large number of aromatic NSOs in the Powder River samples, including derivatives of quinolone, pyranine, pyridine, benzothiozole, dibenzothiophene. Concentrations >14 µg/L were detected. These compounds were previously identified in groundwater associated with low-rank coals (Orem *et al.*, 1999) and were therefore concluded to be the result of leaching of coal.

Numerous phthalates were also detected in the Powder River samples, however, phthalates do not occur in nature, and their presence is most likely attributed to PVC in well adhesives, valves or fittings (Orem *et al*., 2007). Concentrations ranged up to 18-19 µg/L. Volatile organic compounds have also been analysed in produced water from the Powder River Basin (Jackson and Reddy 2007; 2010).

The presence of long-chain saturated hydrocarbons (e.g. docosane, cyclodocosane, hexacosane, heptacosane) at concentrations >1 µg/L was unexpected by the authors due to the low solubility of these compounds in aqueous solution. However, enhanced solubility may have occurred through binding to colloidal matter (Orem *et al*., 2007).

Table 8: Selected compounds identified in produced water samples from 2001 and 2002 samples collected from CBM wells in the Powder River Basin, Wyoming, and their estimated concentration in µg/L (Orem et al.*, 2007).*



Compounds by class	Well number (from Table 1)	Conc. range (µg/L)
1. Polycyclic aromatic hydrocarbons		
Naphthalene	0116, 0117	0.26–0.66
Methylnaphthalene	0111, 0112, 0116, 0117, 0202	0.14–0.48
Dimethylnaphthalene	0111, 0112, 0114, 0115, 0117, 0202	0.01–1.44
Trimethylnaphthalene	0111, 0112, 0115, 0117, 0202	0.04–2.60
Tetramethylnaphthalene	0112, 0115	0.43–0.79
Methylethylnaphthalene	0112	0.55
1,6-Dimethyl-4(1-methylethyl)naphthalene	0113, 0114, 0118, 0202, 0205, 0213, 0216	0.01–0.32
Tetrahydronaphthalene	0117, 0202	0.06–0.82
Tetrahydromethylnaphthalene	0112, 0115, 0202	0.01–0.69
Tetrahydro-dimethylnaphthalene	0112, 0117, 0202	0.19–3.25
Tetrahydro-trimethylnaphthalene	0112	0.50
Ethyl-tetrahydronaphthalene	0112	0.46
Naphthalenone derivative	0202, 0203, 0205, 0206, 0216	0.11–1.38
Other naphthalene alkyl compounds	0203, 0204, 0205, 0207, 0212, 0213, 0214	0.04–0.82
Methoxynaphthalene derivative	0113, 0205	0.04–0.25
2,4,6-Trimethyl-azulene	0202	0.49
Ethyl dimethyl azulene	0112	0.46
5,6-Azulenedimethanol, 1,2,3,3a,8,	0201	0.40
4,6,8-Trimethyl-2-propylazulene	0202	0.40
Tetramethylacenaphthylene	0112, 0115	0.03–0.07
Phenanthrene	0108, 0112, 0114, 0115, 0117, 0202	0.06–0.52
Methylphenanthrene	0108, 0112, 0115, 0117, 0201, 0202	0.03–1.37
Dimethylphenanthrene	0112, 0115	0.62–1.49
Trimethylphenanthrene	0112, 0115	0.04–0.12
Tetramethylphenanthrene	0101, 0112, 0114, 0115, 0117, 0118, 0201	0.01–0.68
Dihydrophenanthrene	0105, 0202	0.03–0.48
Tetrahydrophenanthrene	0112, 0115	0.03–0.42
Dihydro-1-methylphenanthrene	0112	1.06
7-Ethenylphenanthrene	0107, 0108, 0112	0.04–0.22
Phenanthrene derivative	0213	0.07
1-Methyl-7-(1-methylethyl)phenanthrene	0107, 0202, 0207, 0209, 0211, 0216	0.02–3.19
Phenanthrene-1-carboxlic acid	0101, 0107, 0108, 0110, 0111, 0112, 0201, 0203, 0206	0.02–0.12
1,1-Dimethyl-1,2,3,4-tetrahydro-7-isopropyl phenanthrene	0114, 0118	0.19–0.68
Phenanthrenone	0110, 0111, 0205, 0210	0.05–0.09
Methylanthracene	0112, 0115, 0117	0.07–0.48
Methoxyanthracene	0112, 0115	0.04–0.22
Octahydroanthracene	0112	0.54
9,10-Dimethoxy-2,3-dihydroanthracene	0207, 0213	0.04–0.34
1-Ethyl-9,10-anthracenedione	0102, 0103, 0209	0.04–0.12
Fluorene	0112, 0117	0.05–0.24
9-Methoxyfluorene	0112, 0115	0.06–0.18
Methyl-9H-fluorene	0112, 0115	0.52–1.16
9-Methoxyfluorene	0202	0.54
1-Methyl-9H-fluorene	0202	0.51
9H–Fluoren-9-ol	0112, 0117	0.07–0.32
Pyrene	0101, 0112, 0215	0.01–0.04
Methylpyrene	0112, 0115	0.01–0.02
Dimethyl-ethylindene	0109, 0110	0.02–0.07
5-(1,1-Dimethylethyl)-1H-indene	0104, 0111	0.03–0.10
2,3-Dihydro-1,1,2,3,3-pentamethyl-1H-indene	0202	0.45
Other indene derivatives	0213, 0215	0.09–0.16
2. Heterocyclic compounds		
4-Propyl-xanthen-9-one	0104, 0108	0.03–0.07
9-Phenyl-tetrahydro-1H-benz[f]isoindol-1-one	0107	0.24
Benzisothiazole derivative	0203, 0204, 0207, 0210, 0211	0.06–0.32

Compounds by class	Well number (from Table 1)	Conc. range (µg/L)
Benzothiazole	0116, 0117	0.51–14.27
2-(Methylthio)-benzothiazole	0111, 0116, 0117	0.05–0.54
2-Mercaptobenzothiazole	0116	0.89
2(3H)-Benzothiazolone	0116, 0209	0.04–3.90
Quinolo-furazan derivative	0116	0.82
Pyreno[4,5-c]furan	0202	1.83
Methyl-2-quinolinecarboxylic acid	0117	6.65
Drometrizole	0117	0.91
3,4-Dihydro-1,9(2H,10H)acridinedione	0118, 0210, 0216, 0218	0.02–1.35
Caffeine	0201, 0208, 0211, 0212	0.09–0.50
1-Allyl-3-methylindole-2-carbaldehyde	0202	0.49
3-(Hexahydro-1H-azepin-1-yl)-1,1-dioxide-1,2-benzisothiazole	0202	0.66
1-Allyl-3-methylindole-2-carbaldehyde	0202	1.49
2-Ethylhexyl diphenyl phosphate (Octicizer)	0211, 0212, 0214, 0215, 0216, 0218	0.10–0.75
Other heterocyclics	Most wells	Up to 17.87
3. Aromatic amines		
Dioctyldiphenylamine	0101, 0103, 0107, 0108, 0110, 0111	0.03–0.18
Bis-(octylphenyl)-amine	0112, 0117	0.05–0.19
Diphenylamine	0116, 0211	0.04–3.73
2-Methyl-*N*-phenyl-benzenamine	0116, 0117	0.41–3.53
Other benzenamines	0206, 0209, 0201,0212	0.06–0.25
1,4-[13C]-1,2,3,4-Tetrahydro-5-naphthaleneamine	0201	0.33
4. Phenols		
Nonyl-phenol	0203, 0210, 0212, 0217, 0218	0.09–7.91
Dimethylphenol	0116	1.38
4-(1-Methyl-phenylethyl)-phenol	0116	1.18
2,6-Bis(dimethylethyl)-phenol	0116	0.31
4,4′-(1-Methylethylidene)bis-phenol	Most wells	Up to 16.17
p-Tert-butylphenol	0203, 0213	0.07–0.19
Other alkyl phenols	Most wells	Up to 5.89
5. Other aromatics		
Benzenemethanol	0117	0.33
Other benzene alkyl compounds	0203, 0205, 0206, 0207, 0209, 0211, 0216, 0218	0.02–0.62
Ethyl phenylmethyl benzene	0111	0.10
Dimethyl phthalate	0203, 0213, 0216,	0.11–0.28
Dibutyl phthalate	Most wells	Up to 1.27
Di-*n*-octyl phthalate	0209, 0215, 0216	0.58–4.63
Benzyl butyl phthalate	0204, 0209, 0212, 0214, 0216, 0.218	0.04–0.33
Diethyl phthalate	Most wells	Up to 14.90
Didecyl phthalate	Most wells	Up to 7.23
Other phthalates	Most wells	Up to 18.68
Triphenyl phosphate	0206, 0207, 0212	0.07–0.21
Di-tetra-butyl-4-hydroxbenzaldehyde	0108, 0206	0.16–0.53
Biphenyl	0112, 0117	0.16–0.30
Methyl-biphenyl	0112, 0117	0.15–1.00
Dimethyl-biphenyl	0112, 0115	0.07–2.01
Propane-diphenyl	0109, 0111, 0114	0.03–0.22
1-(2-Hydroxy-5-methylphenyl)-2-hexen-1-one	0111	0.29
Diphenylmethane	0112, 0115	0.01–0.43
2,3′,5-Trimethyldiphenylmethane	0209, 0215	0.04–0.05
4,4-Diacetyldiphenylmethane	0117	0.37
1-1Methylenebis(4-methyl)-benzene	0112, 0201	0.09–0.11

Compounds by class	Well number (from Table 1)	Conc. range (μg/L)
9-Phenyl-tetrahydro-1H-benz[f]isoindol-1-one	0107	0.24
Trimethoxy-benzaldehyde	0112	0.39
Methyl-(2,5-dimethoxyphenol)-methanoate	0112	0.31
4-Hydroxy-3-methoxy-benzaldehyde	0217	4.31
3,5-Di-tetra-butyl-4-hydroxybenzaldehyde	0116	0.42
Methyl(Z)-3,3-diphenyl-4-hexenoate	0202	2.00
3-(4-Methoxyphenyl)-2-ethylhexylester-2-propenoic acid	0112, 0202	0.01–2.78
3-(4-Methoxyphenyl)-2-propenoic acid	Most wells	0.06–0.16
Other aromatic compounds	Most wells	0.01–0.42
6. Non-aromatic compounds		
2,6-Bis(dimethylethyl)-2,5-cyclohexadiene-1,4-dione	0109, 0111, 0112, 0114, 0202	0.04–0.28
2,5-Cyclohexadiene-1,4-dione	0104, 0105, 0110, 0113, 0203	0.01–0.08
8-Isopropyl-2,5-dimethyl-terralin	0112	0.36
n-Hexadecanoic acid	0201, 0202	0.63–2.56
Phosphoric acid, tributyl ester	0201, 0203, 0210, 0217	0.10–18.96
2a,7a-(Epoxymethano)-2H-cyclobutyl	0201	0.33
Dodecanoic acid	Most 2001 wells, 0201, 0202, 0208	1.33–1.70
Tetradecanoic acid	0201, 0208	0.15–0.54
Bis(2-ethylhexyl)-hexanedioic acid	0201, 0208	0.13–0.70
1,2-Di-but-2-enyl-cyclohexanone	0201	0.09
2-[2-[4-(1,1,3,3-Tetramethylbutyl)phenoxy]ethoxy]-ethanol	Most 2001 wells, 0201, 0204, 0206, 0207, 0211, 0212	0.08–1.34
2-(2-Butoxyethoxy)-ethanol	0202	0.45
Butanoic acid, butyl ester	0202	0.44
Tricyclo[4.4.0.0(3,9)]decane	0202	0.26
Dimethyl-tetracyclo[5.2.1.0(2,6)-0(3,5)]decane	0202	0.27
7-Tetradecyne	0202	0.38
Tetradecane	0202	0.54
8-Hexadecyne	0202	0.28
Pentadecanoic acid	0202	0.84
2,6,10-Trimethyl-dodecane	0202	0.96
2-Methyl-8-propyl-dodecane	0202	0.52
1,2-Di-but-2-enyl-cyclohexane	0202	0.77
4-(4-Ethylcyclohexyl)-cyclohexene	0202	1.66
1-Butyl-2-ethyloctahydro-4,7-epoxy	0202	0.90
2-Methyl-nonadecane	0202	2.58
2-Dodecen-1-yl(−)succinic anhydride	0202	1.16
1-Nonadecene	0202	2.15
1,7,11-Trimethylcyclotetradecane	0202	1.06
Ethyl-cyclodocosane	0202	1.54
1-Docosene	0202	2.33
Tetracosane	0202	1.86
1-Hexacosene	0202	2.04
Docosane	0202	1.94
7-Bromomethyl-pentadec-7-ene	0202	2.77
Hexacosane	0202	1.73
2,6,10,14-Tetramethyl-hexadecane	0202	1.65
1-Chloro-octadecane	0202	2.12
Heptacosane	0202	0.95
(Z)-9-Tricosene	0202	0.98
Sterane	0202	0.51
Cholesterol	0208	0.26
Squalene	Most wells	Up to 0.24
Pentacosane	0202	1.54
Cyclotriacontane	0202	1.08
28-Nor-17.α.(H)-hopane	0202	1.26
Ethyl-cyclodocosane	0202	0.65
28-Nor-17.α.(H)-hopane	0202	0.84
1,7,11-Trimethyl-cyclotetradecane	0202	0.47

Compounds by class	Well number (from Table 1)	Conc. range (μg/L)
1. Polycyclic aromatic hydrocarbons		
Naphthalene	0116, 0117	0.26–0.66
Methylnaphthalene	0111, 0112, 0116, 0117, 0202	0.14–0.48
Dimethylnaphthalene	0111, 0112, 0114, 0115, 0117, 0202	0.01–1.44
Trimethylnaphthalene	0111, 0112, 0115, 0117, 0202	0.04–2.60
Tetramethylnaphthalene	0112, 0115	0.43–0.79
Methylethylnaphthalene	0112	0.55
1,6-Dimethyl-4(1-methylethyl)naphthalene	0113, 0114, 0118, 0202, 0205, 0213, 0216	0.01–0.32
Tetrahydronaphthalene	0117, 0202	0.06–0.82
Tetrahydromethylnaphthalene	0112, 0115, 0202	0.01–0.69
Tetrahydro-dimethylnaphthalene	0112, 0117, 0202	0.19–3.25
Tetrahydro-trimethylnaphthalene	0112	0.50
Ethyl-tetrahydronaphthalene	0112	0.46
Naphthalenone derivative	0202, 0203, 0205, 0206, 0216	0.11–1.38
Other naphthalene alkyl compounds	0203, 0204, 0205, 0207, 0212, 0213, 0214	0.04–0.82
Methoxynaphthalene derivative	0113, 0205	0.04–0.25
2,4,6-Trimethyl-azulene	0202	0.49
Ethyl dimethyl azulene	0112	0.46
5,6-Azulenedimethanol, 1,2,3,3a,8,	0201	0.40
4,6,8-Trimethyl-2-propylazulene	0202	0.40
Tetramethylacenaphthylene	0112, 0115	0.03–0.07
Phenanthrene	0108, 0112, 0114, 0115, 0117, 0202	0.06–0.52
Methylphenanthrene	0108, 0112, 0115, 0117, 0201, 0202	0.03–1.37
Dimethylphenanthrene	0112, 0115	0.62–1.49
Trimethylphenanthrene	0112, 0115	0.04–0.12
Tetramethylphenanthrene	0101, 0112, 0114, 0115, 0117, 0118, 0201	0.01–0.68
Dihydrophenanthrene	0105, 0202	0.03–0.48
Tetrahydrophenanthrene	0112, 0115	0.03–0.42
Dihydro-1-methylphenanthrene	0112	1.06
7-Ethenylphenanthrene	0107, 0108, 0112	0.04–0.22
Phenanthrene derivative	0213	0.07
1-Methyl-7-(1-methylethyl)phenanthrene	0107, 0202, 0207, 0209, 0211, 0216	0.02–3.19
Phenanthrene-1-carboxlic acid	0101, 0107, 0108, 0110, 0111, 0112, 0201, 0203, 0206	0.02–0.12
1,1-Dimethyl-1,2,3,4-tetrahydro-7-isopropyl phenanthrene	0114, 0118	0.19–0.68
Phenanthrenone	0110, 0111, 0205, 0210	0.05–0.09
Methylanthracene	0112, 0115, 0117	0.07–0.48
Methoxyanthracene	0112, 0115	0.04–0.22
Octahydroanthracene	0112	0.54
9,10-Dimethoxy-2,3-dihydroanthracene	0207, 0213	0.04–0.34
1-Ethyl-9,10-anthracenedione	0102, 0103, 0209	0.04–0.12
Fluorene	0112, 0117	0.05–0.24
9-Methoxyfluorene	0112, 0115	0.06–0.18
Methyl-9H-fluorene	0112, 0115	0.52–1.16
9-Methoxyfluorene	0202	0.54
1-Methyl-9H-fluorene	0202	0.51
9H–Fluoren-9-ol	0112, 0117	0.07–0.32
Pyrene	0101, 0112, 0215	0.01–0.04
Methylpyrene	0112, 0115	0.01–0.02
Dimethyl-ethylindene	0109, 0110	0.02–0.07
5-(1,1-Dimethylethyl)-1H-indene	0104, 0111	0.03–0.10
2,3-Dihydro-1,1,2,3,3-pentamethyl-1H-indene	0202	0.45
Other indene derivatives	0213, 0215	0.09–0.16
2. Heterocyclic compounds		
4-Propyl-xanthen-9-one	0104, 0108	0.03–0.07
9-Phenyl-tetrahydro-1H-benz[f]isoindol-1-one	0107	0.24
Benzisothiazole derivative	0203, 0204, 0207, 0210, 0211	0.06–0.32

Compounds by class	Well number (from Table 1)	Conc. range (μg/L)
Methyl-2-octylcyclopropene-1-octane	0202	0.38
7-Bromomethyl-pentadec-7-ene	0202	0.92
22-Tricosenoic acid	0202	0.43
2-Octadecyl-propane-1,3-diol	0202	0.42
15-Isobutyl-(13.α.H)-isocopalane	0202	1.75
Tricosane	0202	1.70
17-Pentatriacontene	0202	1.00
Tridecanedial	0202	0.86
Isopropyl myristate	0202	1.79
Dihydro-(−)-neocloven-(II)	0202, 0216	0.10–1.04
Kaur-16-ene	0202, 0207, 0211, 0212. 0213	0.06–1.36
Other terpenoid compounds	Most wells	0.12–0.37

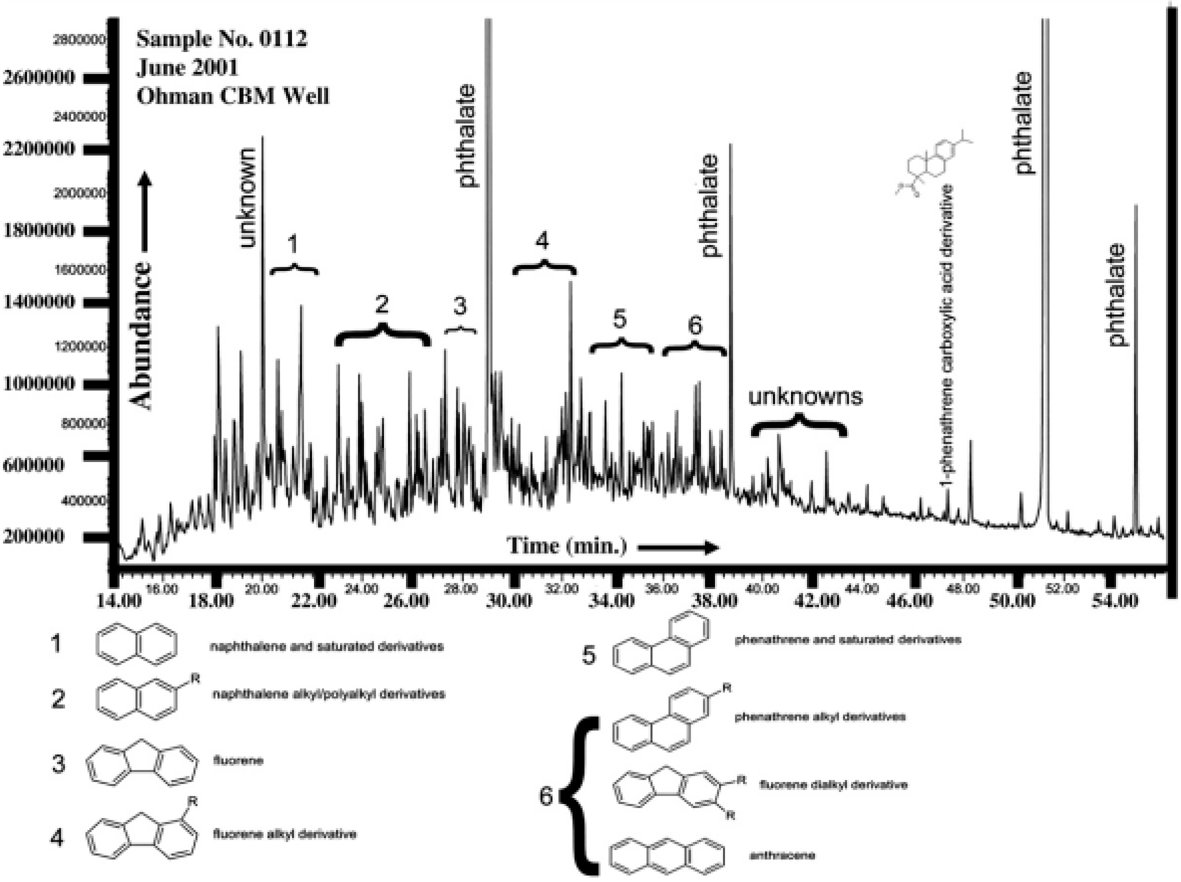


Figure 20: GC-MS TIC chromatogram of the pesticide grade dichloromethane (DCM) extract of produced water from well 0112, showing identified polycyclic aromatic hydrocarbons (Orem et al.*, 2007) .*

5.5.3 New Zealand coal provinces

A study of the chemical composition of groundwater from the Maramarua coalfield in the north island of New Zealand was undertaken by Taulis and Milke (2007). The Palaeogene coals in the area are sub-bituminous with low ash and sulphur contents. Although the study focused on mainly inorganic constituents, total petroleum hydrocarbons were also analysed. The reported TPH concentrations were as follows: C_7-C_9 (<0.03 mg/L), C_{10}-C_{14} (<0.05 mg/l), C_{15}-C_{36} (<0.1 mg/L), and total hydrocarbons (<0.2 mg/L).

5.5.4 Canadian coal provinces

A study of drinking water samples collected from water supply wells and lakes in the Sydney Basin, Nova Scotia, Canada was undertaken by Goodarzi and Mukhopadhyay (2000). Three water samples had elevated concentrations of various PAHs compared to detection limit. All samples were collected from the Upper Carboniferous Sydney Mines Formation and the South Bar Formation. There are 12 distinct coal seams within these formations, and all coals are of bituminous rank, with the majority of them being high to medium volatile bituminous. The authors attributed the presence of PAHs to the leaching of coal during the early depositional phase.

The Alberta Geological Survey, with support from the Alberta Energy Research Institute, has created a public domain database of high quality chemical analyses of groundwater from water supply wells known or strongly suspected to be completed in coal seams. The samples were collected in 2002 from three coal-bearing geological intervals in the Alberta Basin: the Cainozoic Paskapoo Formation, Cretaceous Scollard Formation, and the Late Cretaceous Horseshoe Canyon Formation. Inorganic and organic hydrochemistry, and isotope data for these formations is published in Lemay and Konhauser (2006). Organic chemistry results are summarised in Table 9.

Table 9: Organic chemistry results for Scollard and Paskapoo Formations (Lemay and Konhauser, 2006).

Compound	**Mean (mg/L)**	**Std. dev. (mg/L)**	**N**	**Max. (mg/L)**	**Min. (mg/L)**
Phenols	0.001	0.001	9	0.003	<0.001
Benzene			9		<0.001
Toluene			9	0.001	<0.001
Ethylbenzene			9		<0.001
Xylenes			9		<0.001
Purgeable hydrocarbons			9	0.59	<0.01
Extractable hydrocarbons			9		<0.1
PAHs					
Naphthalene			9		<0.0001
Acenaphthylene			9		<0.0001
Dimethyl phthalate			9		<0.0001
Acenapthene			9		<0.0001
Fluorene			9		<0.0001
Acridine			9		<0.0001
Chysene			9		<0.0001
Phenanthrene			9		<0.0001
Anthracene			9		<0.0001
Fluoranthene			9		<0.0001
Pyrene			9		<0.0002
Benzo(b)fluoranthene			9		<0.0001
Benzo(k)fluoranthene			9		<0.0001
Benzo(a)pyrene			9		<0.0001
Indeno(1,2,3-c,d)pyrene			9		<0.0001
Dibenzo(a,h)anthracene			9		<0.0001
Benzo(g,h,l)perylene			9		<0.0001
Benzo(a)anthracene			9		<0.0002

6. CONCLUSION

While many occurrences of oil shows are documented in Permian coal basins in Australia, there are only a few records on naturally elevated TPH in ground waters in these basins. Water soluble organic compounds such as phenols and BTEX have been encountered in Australian basins, but in many cases the origin of these organic components is unclear. Some of the detected compounds such as halogenated phenols clearly have no natural origin from coal. Others such as BTEX and PAH may to be derived from coal.

7. RECOMMENDATIONS

The establishment of natural background levels of organic compounds in water associated with Permian coals and a systematic study of the relationship of organics in water with coal type, rank and microbial processes seems desirable. Additional baseline data, together with periodic checks of organic compound concentrations throughout the production life of a gas well would assist in building a suitable database and understanding the occurrence and distribution of these compounds in deep groundwater systems. Fingerprinting of aromatic compounds in coals and how these translate into fingerprints leached into groundwater may offer a way to trace organics in future studies.

8. ACKNOWLEDGEMENT

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9. REFERENCES

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Contact Us

Phone: 1300 363 400
+61 3 9545 2176
Email: enquiries@csiro.au
Web: www.csiro.au

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