

# National assessment of chemicals associated with coal seam gas extraction in Australia

*Technical report number 5*

## Literature review: Geogenic contaminants associated with coal seam gas operations

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## Citation

This report should be cited as:

Apte SC, Kookana RS, Batley GE and Williams M 2017, *Literature review: Geogenic contaminants associated with coal seam gas operations*, Project report prepared by the Land and Water Flagship, Commonwealth Scientific and Industrial Research Organisation (CSIRO) as part of the National Assessment of Chemicals Associated with Coal Seam Gas Extraction in Australia, Commonwealth of Australia, Canberra.

## Acknowledgements

This report is one in a series prepared under the National Assessment of Chemicals Associated with Coal Seam Gas Extraction in Australia. The project was commissioned by the Department of the Environment and Energy on advice from the Independent Expert Scientific Committee on Coal Seam Gas and Large Coal Mining Development (IESC). This report, entitled *Literature review: Geogenic contaminants associated with coal seam gas operations*, was prepared by Dr Simon Apte, Dr Rai Kookana, Dr Graeme Batley and Dr Mike Williams of the Commonwealth Scientific and Industrial Research Organisation (CSIRO). This literature review covers information available to the end of 2013. The review was completed in 2013, with minor updates between 2013 and 2016.

The report's authors gratefully acknowledge input from the Project Steering Committee, which comprised representatives from the National Industrial Chemicals Notification and Assessment Scheme (NICNAS), the Department of the Environment and Energy, the CSIRO, Geoscience Australia (GA), and an independent scientific member, Dr David Jones of DR Jones Environmental Excellence.

This report was subject to internal review processes during its development.

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2	Literature review: Human health implications	NICNAS
3	Literature review: Environmental risks posed by chemicals used coal seam gas operations	Department of the Environment and Energy
4	Literature review: Hydraulic fracture growth and well integrity	CSIRO
5	Literature review: Geogenic contaminants associated with coal seam gas operations	CSIRO
6	Literature review: Identification of potential pathways to shallow groundwater of fluids associated with hydraulic fracturing	CSIRO
<b><i>Identifying chemicals used in coal seam gas extraction</i></b>		
7	Identification of chemicals associated with coal seam gas extraction in Australia	NICNAS
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8	Human and environmental exposure conceptualisation: Soil to shallow groundwater pathways	CSIRO
9	Environmental exposure conceptualisation: Surface to surface water pathways	Department of the Environment and Energy
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11	Chemicals of low concern for human health based on an initial assessment of hazards	NICNAS
12	Human health hazards of chemicals associated with coal seam gas extraction in Australia	NICNAS
13	Human health risks associated with surface handling of chemicals used in coal seam gas extraction in Australia	NICNAS
<b><i>Assessing risks to the environment</i></b>		
14	Environmental risks associated with surface handling of chemicals used in coal seam gas extraction in Australia	Department of the Environment and Energy

# Foreword

## Purpose of the Assessment

This report is one in a series of technical reports that make up the *National Assessment of Chemicals Associated with Coal Seam Gas Extraction in Australia* (the Assessment).

Many chemicals used in the extraction of coal seam gas are also used in other industries. The Assessment was commissioned by the Australian Government in June 2012 in recognition of increased scientific and community interest in understanding the risks of chemical use in this industry. The Assessment aimed to develop an improved understanding of the occupational, public health and environmental risks associated with chemicals used in drilling and hydraulic fracturing for coal seam gas in an Australian context.

This research assessed and characterised the risks to human health and the environment from surface handling of chemicals used in coal seam gas extraction during the period 2010 to 2012. This included the transport, storage and mixing of chemicals, and the storage and handling of water pumped out of coal seam gas wells (flowback or produced water) that can contain chemicals. International evidence<sup>1</sup> showed the risks of chemical use were likely to be greatest during surface handling because the chemicals were undiluted and in the largest volumes. The Assessment did not consider the effects of chemical mixtures that are used in coal seam gas extraction, geogenic chemicals, or potential risks to deeper groundwater.

The Assessment findings significantly strengthen the evidence base and increase the level of knowledge about chemicals used in coal seam gas extraction in Australia. This information directly informs our understanding of which chemicals can continue to be used safely, and which chemicals are likely to require extra monitoring, industry management and regulatory consideration.

## Australia's regulatory framework

Australia has a strong framework of regulations and industrial practices which protects people and the environment from adverse effects of industrial chemical use. For coal seam gas extraction, there is existing legislation, regulations, standards and industry codes of practice that cover chemical use, including workplace and public health and safety, environmental protection, and the transport, handling, storage and disposal of chemicals. Coal seam gas projects must be assessed and approved under relevant Commonwealth, state and territory environmental laws, and are subject to conditions including how the companies manage chemical risk.

## Approach

Technical experts from the National Industrial Chemicals Notification and Assessment Scheme (NICNAS), the Commonwealth Scientific and Industrial Research Organisation (CSIRO), and the Department of the Environment and Energy conducted the Assessment. The Assessment drew on technical expertise in chemistry, hydrogeology, hydrology, geology, toxicology, ecotoxicology, natural resource management and risk assessment. The Independent Expert Scientific Committee on Coal Seam Gas and Large Coal Mining

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<sup>1</sup> See Mallants et al. 2017; Jeffrey et al. 2017; Adgate et al. 2014; Flewelling and Sharma 2014; DEHP 2014; Stringfellow et al. 2014; Groat and Grimshaw 2012; Vidic et al. 2013; Myers 2012; Rozell and Reaven 2012; The Royal Society and The Royal Academy of Engineering 2012; Rutovitz et al. 2011.

Development (IESC) provided advice on the Assessment. Experts from the United States Environmental Protection Authority, Health Canada and Australia reviewed the Assessment and found the Assessment and its methods to be robust and fit-for-purpose.

The Assessment was a very large and complex scientific undertaking. No comparable studies had been done in Australia or overseas and new models and methodologies were developed and tested in order to complete the Assessment. The Assessment was conducted in a number of iterative steps and inter-related processes, many of which needed to be done in sequence (Figure F.1). There were two separate streams of analysis – one for human health and one for the environment. The steps included for each were: literature reviews; identifying chemicals used in drilling and hydraulic fracturing for coal seam gas extraction; developing conceptual models of exposure pathways; models to predict soil, surface and shallow groundwater concentrations of identified chemicals; reviewing information on human health hazards; and identifying existing Australian work practices, to assess risks to human health and the environment.

The risk assessments did not take into account the full range of safety and handling precautions that are designed to protect people and the environment from the use of chemicals in coal seam gas extraction. This approach is standard practice for this type of assessment. In practice, safety and handling precautions are required, which means the likelihood of a risk occurring would actually be reduced for those chemicals that were identified as a potential risk to humans or the environment.

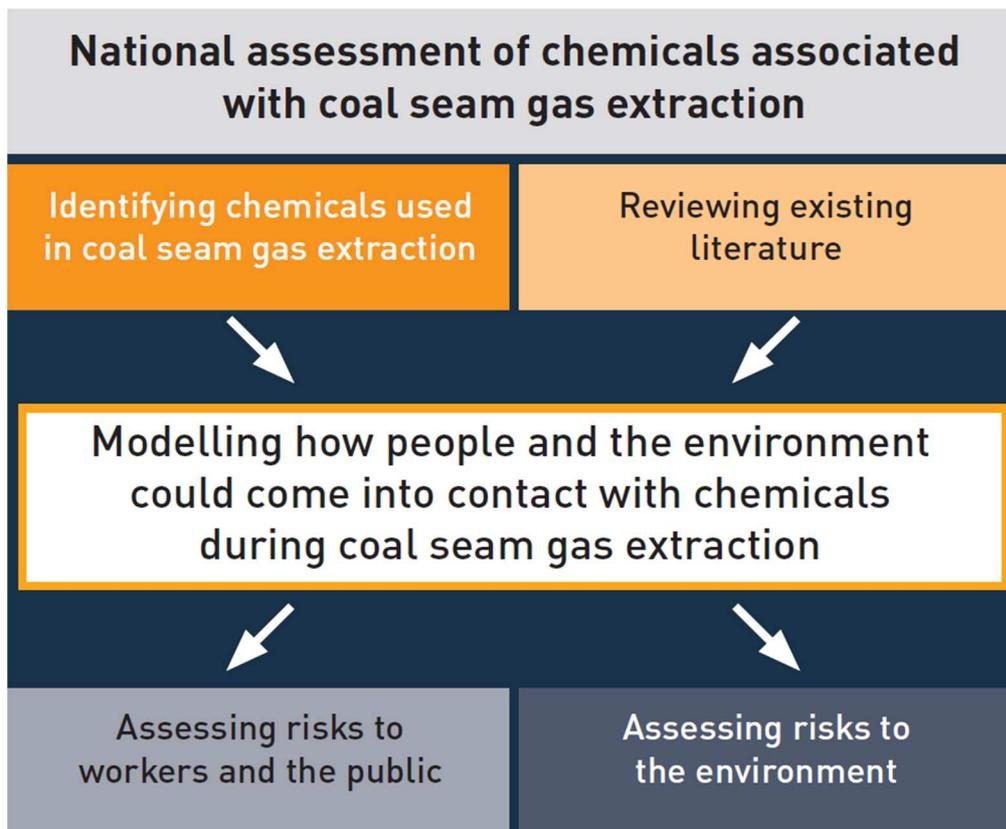


Figure F.1 Steps in the Assessment

## Collaborators

The Australian Government Department of the Environment and Energy designs and implements policies and programs, and administers national laws, to protect and conserve the environment and heritage, promote action on climate change, advance Australia's interests in the Antarctic, and improve our water use efficiency and the health of Australia's river systems.

Within the Department, the Office of Water Science is leading the Australian Government's efforts to improve understanding of the water-related impacts of coal seam gas and large coal mining. This includes managing the Australian Government's program of bioregional assessments and other priority research, and providing support to the Independent Expert Scientific Committee on Coal Seam Gas and Large Coal Mining Development (IESC). The IESC provides independent, expert scientific advice on coal seam gas and large coal mining proposals as requested by the Australian Government and state government regulators, and advice to the Australian Government on bioregional assessments and research priorities and projects.

The National Industrial Chemicals Notification and Assessment Scheme (NICNAS) is a statutory scheme administered by the Australian Government Department of Health. NICNAS aids in the protection of the Australian people and the environment by assessing the risks of industrial chemicals and providing information to promote their safe use.

CSIRO, the Commonwealth Scientific and Industrial Research Organisation, is Australia's national science agency and one of the largest and most diverse research agencies in the world. The agency's research is focused on building prosperity, growth, health and sustainability for Australia and the world. CSIRO delivers solutions for agribusiness, energy and transport, environment and natural resources, health, information technology, telecommunications, manufacturing and mineral resources.

## ***This report: Literature review: Geogenic contaminants associated with coal seam gas operations***

Concerns surrounding the use of hydraulic fracturing as part of the coal seam gas extraction process have mainly centered on the potential effects of a range of industrial chemicals that are the constituents of hydraulic fracturing fluids. However, as part of their natural geology, coal seams are known to contain a number of contaminants that have the potential to be mobilised by hydraulic fracturing activities. These so-called geogenic contaminants include trace elements (such as arsenic, manganese, barium, boron and zinc), radionuclides, organic contaminants (such as hydrocarbons and phenols) and other contaminants. Some chemicals used in hydraulic fracturing have the potential to release or mobilise geogenic contaminants in the coal seam (e.g. through the effects of chelating agents, acids, surfactants and solvents). Their release into waters introduced into or naturally present in the coal seams raises concerns for their potential impacts, both in natural groundwater and in produced waters being released to the surface sites.

This review investigates geogenic contaminants of potential concern and the processes that may lead to their mobility during hydraulic fracturing and the production phase of coal seam gas operations. Since it is already established that produced waters from coal seam gas operations contain a range of dissolved salts comprised of major inorganic ions of geogenic origin (e.g. calcium, magnesium, potassium, silicate, sodium, bicarbonate, chloride and sulfate), this review is focused on synthesising the state of knowledge surrounding the mobilisation of trace geogenic contaminants, such as organic compounds, trace metals and radionuclides. A significant barrier encountered during the preparation of this review was the general lack of availability of data on trace contaminants concentrations in flowback and produced waters from coal seam gas operations. The broader literature on contaminant

concentrations in coals was therefore assessed as it gives valuable information on contaminants that may be of potential concern.

This literature review covers information available to the end of 2013. The review was completed in 2013, with minor updates between 2013 and 2016.

# Abbreviations

General abbreviations	Description
µg	Microgram
Bq	Becquerel
BTEX	Benzene, toluene, ethylbenzene, xylenes
C	Carbon
CMC	Critical micelle concentration (mmol/L)
CSG	Coal seam gas – naturally occurring gas in coal seams
CSIRO	Commonwealth Scientific and Industrial Research Organisation
DoE	Australian Government Department of the Environment
Gy	Gray
HCl	Hydrochloric acid
IESC	Independent Expert Scientific Committee on Coal Seam Gas and Large Coal Mining Development
kg	Kilogram
L	Litres
LOD	Limit of detection
m <sup>3</sup>	Cubic metre
mg	Milligram
mmol/L	millimole per litre
MPa	Megapascals
NAPL	Non-aqueous phase liquids
NICNAS	National Industrial Chemicals Notification and Assessment Scheme
NORM	Naturally occurring radioactive material
PAH	Polycyclic aromatic hydrocarbon
pK <sub>a</sub>	Acid dissociation constant
ppb	Parts per billion; equivalent to µg/L or µg/kg
ppm	Parts per million; equivalent to mg/L or mg/kg
Qld	Queensland
SI	International system of units (SI unit)
Sv	Sievert
TPH	Total petroleum hydrocarbon

<b>General abbreviations</b>	<b>Description</b>
UCG	Underground coal gasification
UK	United Kingdom
US	United States of America
US EPA	United States Environmental Protection Agency
UV	Ultraviolet
VOC	Volatile organic compounds
WHO	World Health Organisation

# Glossary

Term	Description
Alkane/Alkene/Alkyne	Hydrocarbons containing single/double/triple bonds between carbon atoms
Amine	Organic compounds with a sub-unit containing nitrogen
Aromatic	Hydrocarbons with carbon atoms arranged in a ring formation, with alternating single and double bonds; benzene is the basic aromatic sub-unit
Carcinogen	A substance directly involved in causing cancer
Chelating agent	A chelating agent is a chemical compound that can form several bonds to a single metal ion. Metal complexes formed with chelating agents are generally very strong and are called chelates
Coal measure	Geological strata of the carboniferous period usually containing coal deposits
Coal rank	The degree of alteration (or metamorphism) that occurs as a coal matures from peat to anthracite is referred to as the "rank" of the coal. Low-rank coals include lignite and sub-bituminous coals. These coals have a lower energy content because they have a low carbon content
Coal seam	Sedimentary layers consisting primarily of coal. Coal seams store both groundwater and gas, and generally contain poorer quality groundwater than aquifers that are used for drinking water or agriculture
Coal seam gas (CSG)	Naturally occurring gas in coal seams. It is generally 94 to 97% pure methane (CH <sub>4</sub> ) and is typically extracted from permeable coal seams at depths of 300 to 1000 m
Cosmogenic nuclides	Nuclides created by the interaction of atoms with cosmic radiation
Co-solvent	An additional solvent added to a solution to greatly enhance the ability to dissolve a solute
Critical micelle concentration (CMC)	The concentration of surfactants above which micelles form and all additional surfactants added to the system go to micelles
Flowback water	The fluid that returns to the surface following hydraulic fracturing but prior to gas production
Formation water	Naturally occurring groundwater that is within or surrounding the coal, rock, or other formations underground
Geogenic chemical	A naturally-occurring chemical originating from the Earth e.g. from geological formations
Heterocycle	An aromatic sub-unit where atoms other than carbon (such as oxygen or nitrogen) replace carbon atoms
Hydraulic fracturing	Also known as 'fracking', 'fraccing' or 'fracture stimulation'; the process by which hydrocarbon (oil and gas) bearing geological formations are 'stimulated' to enhance the flow of hydrocarbons and other fluids towards the well. The process involves the injection of fluids, gas, proppant and other additives under high pressure into a geological formation to create a network of small fractures radiating outwards from the well through which

Term	Description
	the gas, and any associated water, can flow
Hydraulic fracturing fluid	A fluid injected into a well under pressure to create or expand fractures in a target geological formation (to enhance production of natural gas and/or oil). It consists of a primary carrier fluid (usually water), a proppant and one or more additional chemicals to modify the fluid properties
Micelle	An aggregation of surfactant molecules resulting in the formation of colloidal-sized particle in a liquid. Micelles can be formed when a variety of molecules, including soaps and detergents, are added to water
Non-ionic hydrophobic organic compounds	Organic compounds (e.g. hydrocarbons) which are soluble in many organic solvents but only sparingly soluble in water
Organic compound	Any chemical compound that contains a significant amount of carbon
Primordial	Existing at, or from the beginning of time
Produced water	Water that is pumped out of the coal seams to release the natural gas during the production phase. Some of this water is returned fracturing fluid and some is natural 'formation water'. This produced water moves back through the wellhead with the gas
Proppant	A component of the hydraulic fracturing fluid comprised of sand, ceramics or other granular material that 'prop' open fractures to prevent them from closing when the injection pressure is stopped
Radionuclide	An unstable form of a chemical element that radioactively decays, resulting in the emission of nuclear radiation. Also called a radioisotope
Solvent	A liquid substance used to dissolve chemical compounds
Sorption	The process where one substance binds to another either through absorption (incorporation into a solid) or adsorption (binding to surface of a solid)
Surfactant	Used during the hydraulic fracturing process to decrease liquid surface tension and improve fluid movements
Trace element	An element present in a sample that has an average concentration of typically less than 100 parts per million (i.e. 100 mg/L or 100 mg/kg)

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# 1 Organic contaminants

Coal is primarily derived from decomposed plant material and is, therefore, a highly heterogeneous organic material, principally composed of carbon, oxygen, hydrogen and nitrogen (Orem and Finkelman 2003). The age, geological processes and plant material from which the coal is derived are all important in determining the rank of the coal, with high ranking coals having the greatest degree of alteration from the original plant material. Australian coal basins were generally derived from the Permian to Triassic period (250-300 million years ago) and are of a high ranking nature. For example, the Bowen Basin in Queensland contains coal formed in the Permian and Triassic period, with the coal ranking from high-volatile bituminous to anthracite (80% to >90% organic carbon content) (Orem and Finkelman 2003).

In general, as coal rank increases, its calorific value, extent of dehydration and organic carbon content also increases (Table 1.1). Lignite is the lowest ranking coal and, as it is formed from peat, it still contains identifiable traces of plant materials along with a diverse array of plant-based organic compounds, such as terpenoids and cellulose (Orem and Finkelman 2003). As ranking increases to sub-bituminous and bituminous, changes in the organic composition can occur, such as an increase in phenolic and aromatic (benzene-containing) compounds and, in particular, an increase in the amount of compounds containing multiple aromatic groups, such as polycyclic aromatic hydrocarbons (PAHs). Bituminous coal is usually sub-divided into groups ranging from the lower ranked, high-volatile bituminous up to the low-volatile bituminous. As is suggested by the nomenclature, high-volatile bituminous coal contains high concentrations of volatile organic compounds (VOCs) and concentrations of total extractable hydrocarbons are also found at high levels, relative to other coal ranks (Radke et al. 1980; Stout and Emsbo-Mattingly 2008).

As bituminous coal tends to anthracite, n-alkanes become more evenly distributed from C<sub>8</sub>-C<sub>44</sub>, biogenically derived compounds, such as terpenoids and heteroatoms (atoms other than C), reduce in concentration and aromatics become more condensed, with polyaromatic rings forming (Radke et al. 1980; Stout and Emsbo-Mattingly 2008). Anthracite coal is more geochemical in nature and contains a high proportion of condensed aromatic compounds and here graphitisation starts to occur (or organisation of carbon atoms into a semi-metallic structure with the exclusion of heteroatoms) (Orem and Finkelman 2003; Stout and Emsbo-Mattingly 2008).

The organic matter that forms the structural basis of coal is generally in the form of a macromolecular cross-linked polymeric material, within which lower molecular weight organic compounds are either weakly bonded to or trapped within this macromolecular matrix (Orem and Finkelman 2003). The nature of this macromolecular structure and of the organic components within is, therefore, highly dependent on the rank of coal. For example, the highest extractable yield of organic compounds in coal, using dichloromethane as a solvent, occurs in high-volatile bituminous coal, equivalent to around 20-30 g/kg (or 2-3%) (Schulz 1997).

The process of extracting coal seam gas, particularly due to the high pressure and warm temperature conditions prevailing within the coal measures, can also extract the geogenic, organic compounds present within the coal structure. These geogenic, organic compounds can include phenols, heterocyclic, aromatic and non-aromatic compounds and a myriad of hydrocarbons (Batley and Kookana 2012; Orem et al. 2007; Volk et al. 2011). The following sections of this review present an overview of a number of important classes of organic compounds and their reported concentrations in coal and water associated with coal seams (Table 1.1).

Table 1.1 Overview of coal rank and associated carbon content and likely organic constituents

Coal rank	% Organic carbon	Characteristics
Lignite	60-70	Identifiable plant fragments. Presence of cellulose, terpenoids, partially condensed aromatics
Sub-bituminous	70-80	No cellulose present. Terpenoids and high molecular weight (C <sub>25-36</sub> ) n-alkanes derived from plant waxes
Bituminous	80-90	Aromatic compounds condensing (polyaromatic formation), peak in aromatics and solvent extractable organic compounds at low-rank bituminous with rapid decline at high rank
Anthracite	>90	Further condensation of aromatics. Graphitisation (formation of carbon only lattice) with exclusion of O and H atoms

Table adapted from Orem and Finkelman (2003); Radke et al. (1980); Stout and Emsbo-Mattingly (2008)

## 1.1 BTEX

The class of compounds known as BTEX (benzene, toluene, ethylbenzene and xylenes), are VOCs commonly associated with refined petrochemicals but are also naturally present in crude oil, coal and gas deposits (ATSDR 2007; NHMRC 2011). All BTEX compounds are considered to be water soluble and it would be reasonable to expect their presence in water that has been in contact with coal. The volatile nature of BTEX compounds, however, suggests that they would most likely volatilise into the atmosphere especially under favourable conditions (Johnston et al. 1998). Benzene has been classified as a carcinogen following long-term exposure and, along with ethylbenzene, toluene and xylenes, can also have significant impacts on the central nervous system (ATSDR 2007; NHMRC 2011). Where benzene is detectable in drinking water, it is considered to have exceeded its Australian drinking water guideline concentration, which is 1 µg/L, or 1 part per billion (ppb) (NHMRC 2011). The drinking water guideline for benzene for the US and World Health Organisation (WHO) is higher than that of Australia, with concentrations of 5 and 10 µg/L, respectively (NHMRC 2011; US EPA 2012a; WHO 2011).

Low µg/L concentrations of BTEX have been detected in wells associated with coal seam gas activity (Table 1.2). In Australia, very low but detectable concentrations of benzene (1-3 µg/L) were reported in wells in the northern Bowen Basin (Volk et al. 2011). This is comparable to concentrations from below its detection limit (<LOD) up to 7 µg/L detected in Canadian coal seam gas operations located in the province of Alberta (Lemay and Konhauser 2006). In this Canadian study, toluene and xylenes were also found to range from <LOD-5 µg/L and <LOD-7 µg/L respectively. These values for benzene are close to drinking water guidelines outlined above for Australia, the US and the WHO but substantially lower than guidelines recommended for toluene and xylenes.

## 1.2 Phenols

Phenols are a class of organic compound that are characterised by the adjoining of one or more hydroxyl (or an oxygen atom bonded with a hydrogen atom) groups to an aromatic ring. The simplest of the phenolic compounds, phenol, consists of a hydroxyl group bonded to a benzene ring. Phenolic compounds have been observed in both low-rank and bituminous coals (Siskin and Aczel 1983) and these are likely to be derived from cleavage of aromatic compounds as well as transformation of plant cell walls under high pressure and temperature during coal formation. As with many of the PAHs, the consequence of chronic, long-term

exposure to phenols has not been extensively investigated and no specific drinking water guidelines for phenols currently exist (Orem et al. 2007; NHMRC 2011; WHO 2011).

Certain phenols occur naturally within coal seams and are one of several examples of water-soluble components of the coal (Volk et al. 2011). The leaching of phenolic compounds from oil and coal reserves has also been highlighted as a source of geogenic contamination of natural waters (Phipps et al. 1981). Significant phenol concentrations have been reported in the waste produced from the processing of oil shale, with concentrations of phenolic compounds in the range of 24 to 195 mg/L reported in semi-coke dump leachates (Kahru et al. 2002). The US EPA has reported the contamination of groundwater, surface water and soil by a multitude of organic compounds, including phenols, in the area surrounding a disused coal strip mine containing a coal wash pond and coal stockpile (US EPA 2013). They also report that groundwater contamination is present at most sites where fossil fuel recovery was initiated in the 20 years prior to 1999 with water-soluble phenols migrating via fractures or other means into the groundwater at selected sites (US EPA 1999). Furthermore, phenols are also present in groundwater in the vicinity of low-rank coal deposits in the Balkan region (Orem et al. 2004).

Schulz (1997) showed that phenolic compounds could be leached from coal particles by both dichloromethane and simulated physiological fluids. The extraction of phenolic compounds was found to depend on coal rank, with lower concentrations recorded for higher rank coals. Furthermore, it was noted that phenolic compounds accounted for more than one third of the total organic components within water used in a UCG process (Schultz et al. 1978). Several phenolic compounds, including dimethylphenol and other alkylated (or containing groups of carbon atoms) phenols, have also been found in produced waters generated through coal seam gas exploration in the US in concentrations up to 5.89 mg/L (Orem et al. 2007).

### **1.3 Polycyclic aromatic hydrocarbons**

Polycyclic aromatic hydrocarbons (PAHs) are a class of organic compounds characterised by the presence of two or more fused aromatic rings. The properties of PAHs are influenced by the number of rings within the structure and the resultant interaction of the electron systems within these rings (Berko 1999). Frequently found in the environment, PAHs are also formed as a result of the incomplete combustion of organic material in both natural (forest fires) and anthropogenic (motor vehicle exhaust) processes (ATSDR 2009).

More than 100 PAHs have been identified in atmospheric testing (Lao et al. 1973; Lee et al. 1976), with a considerable amount either known or suspected to be carcinogenic. Of these, the US EPA has identified 16 priority pollutant PAHs (Achten and Hofmann 2009; Miles and Delfino 1999) (Table 1.2). Benzo[a]pyrene is used as the model compound for PAHs, since there is little human health data available for the other PAHs (NHMRC 2011; US EPA 2012a; WHO 2011). The carcinogenic potencies relative to benzo[a]pyrene of the other priority PAHs have been estimated with the drinking water guideline set by the WHO at 0.7 µg/L (NHMRC 2011; WHO 2011).

In coal, PAHs are present as a result of the normal coal formation processes resulting in condensation of lignin-rich materials, such as wood, as well as the gradual exclusion of non-carbon atoms (Achten and Hofmann 2009; Volk et al. 2011). Unprocessed coal obtained directly from the seam has been found to contain concentrations of up to thousands of mg/kg (parts per million) of PAHs, although lower mg/kg values were found to be more common and, of these concentrations, the priority PAHs made up only a fraction of the amount (Achten and Hofmann 2009). The highest concentration of the 16 priority PAHs was found in bituminous coals, with the coal rank shown to influence the nature of the PAH extracted (Achten and Hofmann 2009). This was confirmed in a study of 14 coals from China and the US, where Wang et al. (2010) noted that high molecular weight PAHs were more commonly

observed in low-rank coals, with smaller PAHs (2 and 3 aromatic rings) being more common in the high-rank coals. Both Laumann et al. (2011) and Stout and Emsbo-Mattingly (2008) found that particular reactions in the coal formation process will influence concentrations of extractable PAH.

Laumann et al. (2011), in their assessment of samples from 11 different coal regions, found that the concentration of extractable PAHs ranged from 14 to 2090 mg/kg. Highest concentrations were found in coals originating from Indonesia, the United Kingdom (UK), Germany and Australia. Laumann et al. (2011) extracted Australian coals from the Bowen and Sydney Basin regions. The Sydney Basin was found to have a maximum concentration of extractable PAHs (52 in total) of around 1 500 mg/kg, with the Bowen Basin maximum concentration being slightly lower at around 1 200 mg/kg. With regard to Australian coals, Kashimura et al. (2004) also identified several of the priority pollutant PAHs within a coal sampled from the LaTrobe Valley in Victoria.

The analysis of Eastern Nigerian coal and shale by Ogala and Iwegbue (2011) showed higher PAH concentrations in coal when compared to shale. The maximum PAH concentration in the Nigerian coal was found to be 4.1 mg/kg (parts per million), with the shale having a maximum concentration of 1.8 mg/kg.

The PAH contamination of water is generally considered to be of lesser concern due to the low water solubility of this class of compounds (de Maagd et al. 1998). Despite this, investigations by Orem et al. (2007) into production water generated from coal seam gas exploration in the Powder River region of Wyoming, showed that PAHs were the most commonly observed compounds in extracts of produced water. In this study, concentrations ranged from <LOD to 3.2 µg/L for individual PAHs and up to 23 µg/L for total PAHs. Despite the inherently low water solubility of PAHs and their tendency to attach to soils or sediments, PAHs can be still be found in water due to their association with particles dispersed or dissolved in the water column (Mackay and Gschwend 2001; Maxin and Kogel-Knabner 1995).

## **1.4 Total petroleum hydrocarbons**

Total petroleum hydrocarbons (TPHs) refer to the hydrocarbons, or organic compounds containing only carbon and hydrogen, naturally present in coal and oil deposits. The TPHs are denoted by the number of carbon atoms present in the hydrocarbon and are usually measured in groups containing from 6 (C<sub>6</sub>) to 36 carbon atoms (C<sub>36</sub>). Groups containing less than 6 carbon atoms (C<sub>6</sub>) are generally too volatile to reliably measure.

TPHs are usually split up into subsets, or fractions, which are associated with general physicochemical parameters and analytical convenience. For example, C<sub>6</sub>-C<sub>9</sub> are considered to represent the volatile fraction of TPHs, while the C<sub>10</sub>-C<sub>36</sub> fractions can also be sub-divided into further sub-fractions, representing the changing physicochemical properties (ATSDR 1999a; Sadler and Connell 2003). The TPHs contain several hundred different hydrocarbons, which represent a highly diverse range of compounds ranging from alkanes (carbon atoms are fully associated with single bonds between carbon and hydrogen atoms; also known as 'saturated'), alkenes and alkynes (hydrogen atoms are replaced by extra carbon interatomic bonding; also known as 'unsaturated'), cycloalkanes (carbon atoms are arranged in a circular structure) and aromatic (containing at least one benzene sub-unit). In general, the higher the number of carbon atoms that are present in a TPH, the lower its volatility and water solubility and the greater its affinity for solids.

The volatility of alkanes tends to be greater than that of aromatic TPHs, while the water solubility of alkanes is less than that of equivalent carbon-numbered aromatic TPHs (Sadler and Connell 2003). This demonstrates the inherent complexity of TPHs and the difficulty in

using their measured concentrations to undertake a risk assessment (ATSDR 1999a). Furthermore, the complexity of assessing individual compounds within the TPH class means that there are no drinking water guidelines covering their presence (NHMRC 2011; US EPA 2012a), although their presence in water is likely to affect taste and odour at concentrations far below levels which may lead to toxicity (WHO 2011).

Considering the inherently high loading of TPHs in coal, measured concentrations in waters associated with coal seams are relatively low. Maximum TPH concentrations in waters associated with the Australian coal seams in the Bowen Basin were up to 350 µg/L, while the C<sub>15</sub>-C<sub>28</sub> fraction in the Wittingham coal seams were up to 6.8 mg/L (Volk et al. 2011). Relative concentrations between TPH fractions in both of the Bowen Basin seams were similar, indicating that physicochemical properties such as water solubility are not the only factor that can predict concentrations of TPHs in waters associated with coal seams. As previously mentioned, inherently poorly water-soluble compounds, such as PAHs, can be still be found in water due to their association with particles dispersed in the water column.

## 1.5 Other organic compounds

Individual organic compounds that make up the TPH fraction, excluding PAHs, phenols and BTEX, number in the several hundreds and are represented by a diverse array of hydrocarbons. Hydrocarbons can be straight chains of carbon and hydrogen atoms (n-alkanes) or can be complex mixtures containing a mixture of straight chains and rings of carbon atoms, such as is found with terpenes and terpenoids, or terpenes containing oxygen atoms.

Terpenes (and terpenoids) are made up of isoprene subunits, which form the basis of biologically synthesised organic compounds, further highlighting the botanical origins of coal. Terpenes usually have carbon backbones containing C<sub>10</sub>, C<sub>15</sub>, C<sub>20</sub> and C<sub>30</sub> carbon atoms, indicating they range from semi-volatile compounds through to compounds with low volatility and water solubility. Organic compounds that contain atoms other than carbon and hydrogen, such as oxygen, sulfur and nitrogen, include terpenoids, the aromatic amines and heterocycles. Addition of atoms other than carbon can cause the compounds to become electrically charged, which can have important consequences on their fate. For example, a charged compound is likely to be considerably more water soluble than an analogous uncharged compound.

Despite the large number of compounds represented by these classes of organic compounds and their potential to be present in coal formation waters, they are generally detected at low µg/L concentrations, close to their respective LODs (Lemay and Konhauser 2006; Orem and Finkelman 2003; Orem et al. 2007). This may be due to their low water solubility or their low levels in coals, relative to other classes of organic compounds. Since there were no quantitative analyses found for these compounds in solvent extracts of coals, it is difficult to determine whether their concentrations in coal contributed to this observation. In the case of the n-alkanes, the relatively high concentrations found in the produced water from Powder River Basin were unexpected due to their extremely low water solubility (Orem et al. 2007). Association of these compounds with colloids, or dissolved particulate matter, is one reason why the n-alkanes, along with other geogenic compounds with low water solubility, may also be observed in produced water, together with more water-soluble compounds.

Table 1.2 Measured concentrations of organic geogenic compounds in coal, associated water and coal seam gas operations

Compound class	Compound	Measured concentrations		References
		Coal (mg/kg)	Water (mg/L)	
BTEX	Benzene(s)	-	ND-0.007	Lemay and Konhauser (2006)
	Toluene	-	ND-0.005	Volk et al. (2011)
	Ethylbenzene	-	ND	Volk et al. (2011)
	Xylene(s)	-	ND-0.007	Volk et al. (2011)
Phenols	Phenol(s)	-	ND-0.00014	Lemay and Konhauser (2006)
	Alkylphenols	-	Up to 0.006	Orem et al. (2007)
PAHs	Acenaphthalene	ND-0.54	ND-0.00005	Achten and Hofmann (2009)
	Acenaphthylene	-	ND-0.00012	Laumann et al. (2011)
	Anthracene	0.07-2.48	ND-0.00002	Lemay and Konhauser (2006)
	Benz[a]anthracene	0.73	-	Izart et al. (2012)
	Benz[a]anthracene	-	0.000025	Mallants et al. (2017)
	Benzo[a]pyrene	ND-3.57	-	Kerst and Andersson (2001)
	Benzo[a]pyrene	-	0.000043	Mallants et al. (2017)
	Benzo[b]fluoranthene	ND-5.61	-	Stout and Emsbo-Mattingly (2008)
	Benzo[b]fluoranthene	-	0.000053	Mallants et al. (2017)
	Benzo[ghi]perylene	ND-2.23	-	Wang et al. (2010)
	Benzo[ghi]perylene	-	0.000043	Mallants et al. (2017)
	Benzo[k]fluoranthene	ND-2.7	-	Wang et al. (2010)
	Benzo[k]fluoranthene	-	0.000018	Mallants et al. (2017)
	Chrysene(s)	ND-6.41	-	Wang et al. (2010)
	Chrysene(s)	-	0.000036	Mallants et al. (2017)
	Dibenz[a,h]anthracene	ND-3.72	-	Wang et al. (2010)
	Dibenz[a,h]anthracene	-	0.000007	Mallants et al. (2017)
	Fluoranthene	ND-3.53	-	Wang et al. (2010)
	Fluoranthene	-	0.000032	Mallants et al. (2017)
	Fluorene(s)	0.03-3.4	ND-0.00045	Wang et al. (2010)
Indeno[1,2,3-cd]pyrene	ND-1.5	-	Wang et al. (2010)	

Compound class	Compound	Measured concentrations		References
		Coal (mg/kg)	Water (mg/L)	
	Indeno[1,2,3-cd]pyrene	-	0.000028	Mallants et al. (2017)
	Naphthalene(s)	0.11-4.04	ND-0.00178	Wang et al. (2010)
	Naphthalene	-	0.000028	Mallants et al. (2017)
	Phenanthrene(s)	0.07-11.4	ND-0.00016	Wang et al. (2010)
	Phenanthrene	-	0.000025	Mallants et al. (2017)
	Pyrene	ND-7.24	-	Wang et al. (2010)
	Pyrene	-	0.000036	Mallants et al. (2017)
	Total PAHs	ND-2429	-	Wang et al. (2010)
TPH	C6-C36	-	ND-0.35	Ahmed et al. (1999)
	C6-C9	-	ND-0.34	Lemay and Konhauser (2006)
	C6-C9	-	0.003	Mallants et al. (2017)
	C10-C14	-	ND-0.21	Volk et al. (2011)
	C10-C14	-	0.03-0.07	Mallants et al. (2017)
	C15-C28	-	ND-6.8	Volk et al. (2011)
	C15-C28	-	0.14-0.17	Mallants et al. (2017)
	C29-C36	-	ND-5.2	Volk et al. (2011)
	C29-C36	-	0.42	Mallants et al. (2017)
	C6-C10	-	ND-0.59	Volk et al. (2011)
	C11-C40+	-	ND-0.6	Volk et al. (2011)
	Total C6-C36	-	0.21	Mallants et al. (2017)
n-Alkanes	Docosane	-	0.002	Zong et al. (2009)
	Tricosane	-	0.0017	Zong et al. (2009)
	Tetracosane	-	0.0019	Zong et al. (2009)
	Pentacosane	-	0.0015	Zong et al. (2009)
	Hexacosane	-	0.0017	Zong et al. (2009)
Aromatic amine	Diphenylamine	-	0.00004-0.004	Orem et al. (2007)
	Diphenylamines	-	0.00003-0.0002	Orem et al. (2007)
	Methylphenylbenzeneamine	-	0.0004-0.004	Orem et al. (2007)
	Benzeneamines	-	0.00006-0.0003	Orem et al. (2007)

Compound class	Compound	Measured concentrations		References
		Coal (mg/kg)	Water (mg/L)	
Aromatic (other)	Benzaldehydes	-	0.0002-0.004	Schulz (1997)
Hetero-cycles	Benzothiazole	-	0.0005-0.014	Orem et al. (2007)
	Benzothiazoles	-	0.00005-0.0009	Piedad-Sanchez et al. (2004)
Terpenes	Diterpenes	-	0.00084-0.0013	Ahmed et al. (1999)
	Hopanes	-	0.00051	Izart et al. (2012)
	Steranes	-	0.0001-0.0004	Miranda et al. (1999)

ND: Not detected; Benzene(s): benzene and benzene with various substitutions (attached atoms)

## 1.6 Processes influencing the mobilisation of organic geogenic contaminants during hydraulic fracturing

Several physical and chemical factors and processes associated with the hydraulic fracturing process have the potential to influence the mobility of geogenic organic contaminants. To date, however, there have been few publications on this topic. On the basis of fundamental principles, it is expected that the mobility of organic compounds can be significantly influenced by the interactions between the physicochemical nature of the organic compound, the physical parameters of the hydraulic fracturing process and the presence of additives associated with the hydraulic fracturing fluid.

### 1.6.1 Physical factors and processes

Physical conditions of note relating to water in the coal seam, either naturally occurring or injected, include elevated temperature, pressures and acidity. Mobilisation processes that could be affected include the following:

- Organic compounds in the dissolved phase:** A wide range of organic compounds that may be present in formation water (e.g. Orem et al. 2007; US EPA 2011) could physically migrate during the hydraulic fracturing operation. The flowback water would therefore contain compounds introduced within the hydraulic fracturing fluid as well as mobilised water-soluble geogenic organic contaminants. Elevated temperatures associated with produced water are likely to enhance the solubility of organic compounds, including those that are usually highly insoluble in water. This effect can be quite substantial even over a relatively narrow temperature range, below the boiling point of water, for PAHs (Arias-Gonzalez et al. 2010; Reza and Trejo 2004). Elevating pressure can also affect the interaction of chemical bonding between organic compounds and water, which in turn influences the water solubility of the compounds (Sawamura 2007). This process is dependent on the nature of the organic compound, including the number of hydrophobic carbon groups present and whether the compound is aromatic or not. For example, the solubilities of benzene, toluene, ethylbenzene and xylenes (BTEX) increased up to maxima at around 100 MPa (Sawamura et al. 1989), which is within the bounds of pressures exerted under

hydraulic fracturing. However, a number of PAHs, including anthracene, phenanthrene and naphthalene, and biphenyl were found to have decreased in solubility as pressure increased (Sawamura 2007). The water solubility of these organic compounds needs to be assessed at elevated temperatures and pressures experienced in coal seams.

- **Organic contaminants associated with the solid phase:** Fine particles may be dispersed into solution under pressure from the coal seam and their transport to the surface with flowback and produced water could facilitate the transport of organic contaminants, such as those with low water solubility and a high affinity to solids. Some of these organic contaminants may remain attached to the particles and may eventually settle to the sediment phase of the water storage facility. On the other hand, some particles may be very fine and essentially remain suspended for a long time, slowly releasing (to both the liquid and the gaseous phases) some of the organic compounds through solubilisation or desorption processes.
- **Organic compounds in the vapour phase:** The extent of release of the VOCs to the environment is expected to depend on:
  - the actual leakage of the gaseous phase
  - the release of VOCs from the flowback and produced waters that are brought to the surface under high pressure but then are subjected to a relatively reduced atmospheric pressure during the storage and treatment of wastewater.

Emission of VOCs during the process of separating methane from other gases and from drilling mud has been raised as a potential issue during coal seam gas operations, including in Australia (Brown 2007; DfEA 2011). The fraction of gaseous phase in the flowback water may increase with time and this phase may contain volatile hydrocarbons (Meiners et al. 2012). According to a report by the Coal Seam Gas Well Head Safety Program of the Queensland Government (DEEDI 2011), while gas leakage from well heads have sometime been detected, the concentrations of toxic VOCs were either not detected or were considered insignificant.

- **Dilution effect of the hydraulic fracturing fluid:** The high volumes of water used in the hydraulic fracturing process may provide a very high level of dilution of the formation water that is mobilised by the operation. While the concentration of organic contaminants in formation water is obviously expected to decrease due to dilution, the change of concentration in solution could, however, facilitate further release of chemicals sorbed on coal leading to an overall greater total amount of compounds released from the formation. Whether the dilution is sufficient to bring the concentrations of the geogenic contaminants to below water quality guideline levels would depend on the concentration of the specific compound in the formation water. In an Australian study, Wood and Patterson (2011) reported an increase in the concentrations of TPHs, phenol and inorganic elements in the flowback water in comparison with formation water.

## 1.6.2 Chemical factors and processes

In addition to physical processes, there are a number of chemical interactions that may occur during the hydraulic fracturing operation that could potentially impact on the mobility of the resident organic geogenic contaminants. The hydraulic fracturing fluids contain a range of organic and inorganic additives, some of which have chemical properties that could directly interact with the geogenic compounds sorbed on the coal surfaces and enhance their release into either the flowback or produced water.

Some of the chemical processes that can potentially influence the mobility of geogenic contaminants are listed below.

- **Solubility enhancement by co-solvents:** It is well established that the solubility of non-ionic hydrophobic organic compounds increases disproportionately in a logarithmic-linear fashion, with an increase in the relative fraction of an organic co-solvent in water (e.g. Yalkowsky and Roseman 1981) – that is, even small concentrations of co-solvents, surfactants and other solubility-enhancing chemicals may increase the solubility of hydrophobic compounds significantly. Such increases have been demonstrated to be applicable to a range of contaminant source materials including soils and sediments; and liquids, such as oil and coal tar. Indeed, this is a very active area of research in the pharmaceutical industry and environmental engineering, as solubility is as much a major challenge to a formulation scientist as it is to environmental engineers involved in remediation of contaminated sites. In fact, co-solvency is the most commonly used technique to increase the aqueous solubility of drugs (Jouyban 2008; Yalkowsky and Roseman 1981). Similarly, the presence of co-solvents at waste disposal sites has been used to facilitate the transport of organic contaminants (Luthy et al. 1994); and other solubility enhancers such as surfactants and natural organic matter have been used to mobilise hydrophobic contaminants from non-aqueous phase liquids (NAPLs) in soils and groundwater aquifers to facilitate remediation (Luthy et al. 1994; Mulligan et al. 2001; Saichek and Reddy 2007).

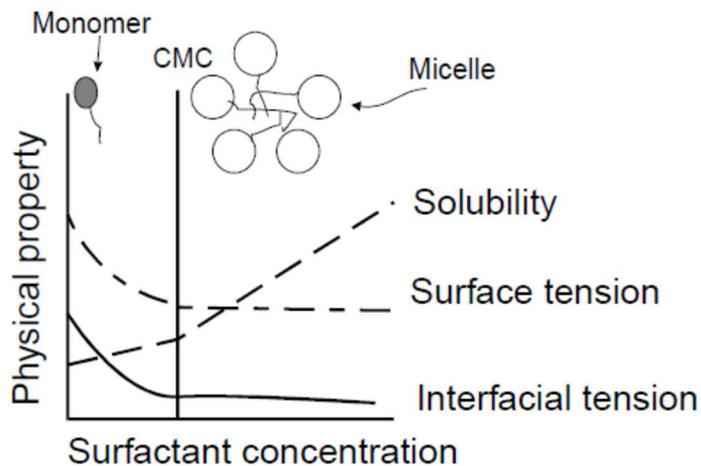
With hydraulic fracturing mixtures being a complex mixture of organic and inorganic additives, including co-solvents, surfactants and organic acids, the solubility of relatively water insoluble, or hydrophobic, geogenic contaminants could be enhanced. For example, Orem et al. (2007) were surprised at the presence of long chain n-alkanes (see Table 1.2) in produced water and surmised that this may have been due to their association with dissolved organic matter, without considering the influence of the diverse array of organic compounds in the produced water (Orem et al. 2007; US EPA 2011).

The extent of any enhancement of solubility and mobility of organic contaminant would depend not only on the chemistry of the organic contaminant in question but also on the nature and the fraction of organic co-solvent present in the hydraulic fracturing mixture. For hydrophobic and ionisable organic contaminants, such as substituted phenols, the effect of co-solvents is much more complex and is confounded by a number of indirect effects on both solution and solid phases (Lee et al. 1993). The co-solvents can also affect the dissociation of the organic compound in the aqueous phase, which is discussed later in this section. These complex interactions can sometimes result in decreased solubility of the contaminant in the presence of co-solvent too (Lee et al. 1990).

- **Solubility enhancement by surfactants:** Surfactants have a polar (hydrophilic) head and a non-polar (hydrophobic) tail of the molecule and thus have properties that can facilitate the solubility and mobility of otherwise sparingly soluble organic compounds. However, surfactants are most effective in enhancing solubility if their concentrations are above the critical micelle concentration (CMC) (Figure 1.1). Above CMCs, the hydrophobic interiors of the surfactant micelles act much like a drop of oil creating a favourable phase for organic contaminants to dissolve in. However, since CMCs are usually at reasonably high concentrations, ranging from 0.1 to 10 mmol/L (Connell et al. 1997) or 0.05 to 0.1% (Savjani et al. 2012), the CMC will not be reached in the hydraulic fracturing mixture. Also, the CMC has been found to increase to a maximum

in a range of surfactants at around 75 to 100 MPa (Sawamura et al. 2001; Tuddenham and Alexander 1962), which is likely to further reduce the possibility of CMC being reached under hydraulic fracturing conditions.

- **Changes in pH and the dissociation of contaminants:** The organic and inorganic constituents of the hydraulic fracturing fluids could change the ambient pH of the formation water and thus can potentially alter whether ionisable organic contaminants, such as phenols, are present as a charged (or ionised) species, an uncharged (or unionised or neutral) species or as mixture of both ionised and unionised. The changes in speciation, or the proportion of neutral and ionised species, can have a substantial effect on the solubility and consequent mobilisation of contaminants, depending on the pH value where ionisation for a specific compound occurs (defined by  $pK_a$ ). A change in pH of the formation or flowback water can also, therefore, elicit fairly complex interactions in terms of phase partitioning and equilibria, leading to either an enhanced or reduced potential for release of contaminants from coal seams. Such effects of pH change due to complex mixtures of solvents on ionisable compounds have been demonstrated by Fu and Luthy (1986) and Lee et al. (1990).



Source: Mulligan et al. (2001), with permission

Figure 1.1 Changes in contaminant solubility and surface tension with concentration of surfactant in solution

- **Reduction of free energy by salts:** Dissolved salts can have a major effect on the equilibria of compounds between solid and liquid phases. The salts present in the formation water or the hydraulic fracturing fluids could reduce the free energy of organic substances and consequently render them less soluble in saline water (the so-called drying or salting out effect). However, the opposite (salting in) has been also observed depending on the nature of the ions and organic compounds involved (e.g. Gorgenyi et al. 2006). A study involving four component mixtures of relevance to formation water, containing n-alkane, a cation and an anion, noted the salting out effect where the extent of this salting out was dependent on the nature of salts involved (Patel et al. 2003). An enhancement or a decline in the mobility of geogenic contaminants would depend on the relative changes in the salinity of formation water due to the introduction of hydraulic fracturing fluid. For example, if the hydraulic fracturing fluid is of a lower salinity than the formation water, leading to an overall

decrease in salinity, an increase in the solubility of the organic substances is expected and vice-versa. The formation waters sometimes can be supersaturated brines (AEA 2012).

- **Other chemical processes:** Given the complexity of the formation material, in terms of the number and the diversity of chemistry of contaminants potentially present in a coal measure, as well as the complex nature of hydraulic fracturing fluid mixtures interacting with it, a number of other interactions are possible. These include transformations that can occur due to the changes in the stability of organic compounds within the hydraulic fracturing fluid and within the coal formation. Transformation compounds may form either during the hydraulic fracturing process or during the subsequent treatment of produced water. Furthermore, depending on the conditions and the reactants present, the formation of new compounds cannot be ruled out due to the diverse array of organic compounds present under elevated temperature and pressure. For example, for every 10 °C increase in temperature, the speed of chemical reactions generally increase by a factor of between 2 and 6 (Schwarzenbach et al. 2003), increasing the likelihood of transformations occurring. Other factors that can enhance the rate of chemical reactions include the presence of metals and metal oxides, which can act as catalysts, and enhanced acidity, which can promote the degradation of some organic compounds (Schwarzenbach et al. 2003). Chemical transformations may therefore add to the already substantial diversity of organic compounds present through hydraulic fracturing fluid and geogenic inputs. The production of transformation products is also of relevance to the application of non-chemical disinfection technology, such as ultraviolet (UV) irradiation. Such technologies may be used instead of using biocides for disinfection of hydraulic fracturing fluids (Bloomberg 2013). It has been suggested that formation of some disinfection by-products may even increase when UV is used during drinking water treatment (Richardson et al. 2007).

## 2 Geogenic trace elements

### 2.1 Trace elements in coal

Trace elements present in coal and other mineral formations made accessible by the hydraulic fracturing of coal seams have the potential to be mobilised by the fluids introduced during the hydraulic fracturing process, and transported in the flowback and produced waters and, potentially, via natural groundwater flows.

The trace element composition of Australian coals has been well studied (Dale 2003; Swaine 1990) and a typical export coal composition is shown in Table 2.1.

Table 2.1 Trace element composition of Australian export coals

Element	Average (mg/kg)	Low (mg/kg)	High (mg/kg)	n
Antimony (Sb)	0.46	0.05	1.2	72
Arsenic (As)	0.93	0.1	2.7	89
Boron (B)	21	4	36	77
Cadmium (Cd)	0.09	0.01	0.28	89
Chlorine (Cl)	320	10	1500	57
Chromium (Cr)	9	3	24	77
Cobalt (Co)	3.7	1.2	12	44
Copper (Cu)	14	6.2	32	77
Fluorine (F)	98	35	340	57
Iodine (I)	6	2	14	28
Lead (Pb)	5.8	3.2	14	92
Manganese (Mn)	99	4	700	62
Mercury (Hg)	0.021	0.006	0.08	88
Molybdenum (Mo)	0.85	0.1	2.7	77
Nickel (Ni)	8.6	1.4	31	77
Selenium (Se)	0.47	0.12	1.1	90
Thorium (Th)	2.6	0.5	6.9	76
Uranium (U)	0.93	0.27	2.5	76
Vanadium (V)	23	7	62	77
Zinc (Zn)	14	4	51	77

Source: Dale (2006); n= number of samples

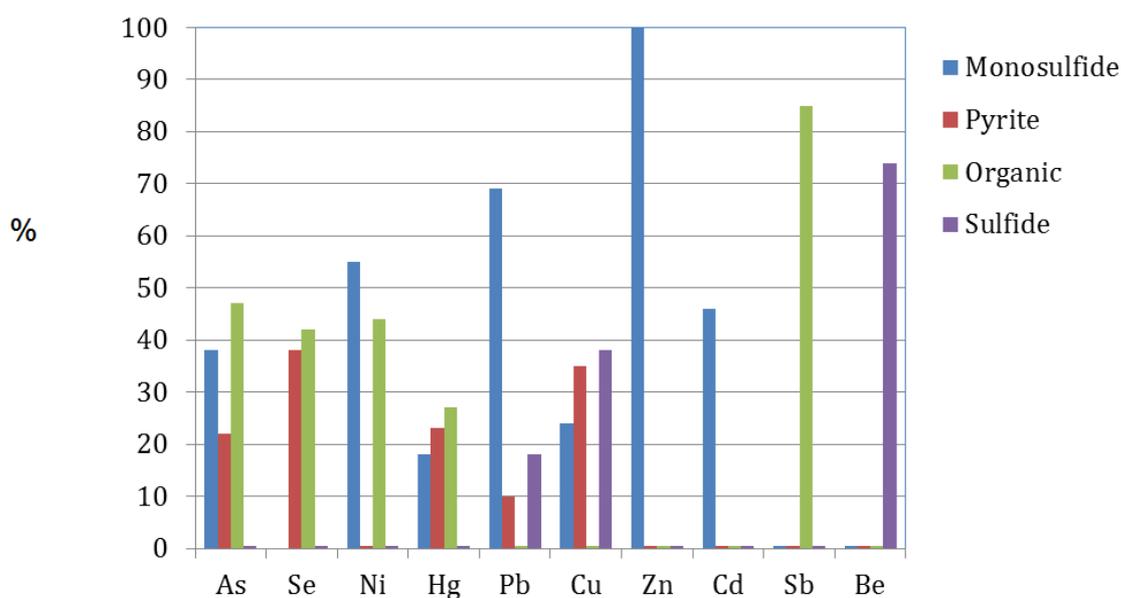
The elemental composition of coals can vary significantly depending on their origin. Coals with a marine origin typically contain much higher pyrite and organosulfur concentrations as

well as higher boron contents, by comparison with those deposited as freshwater peats. Coals of both types are a source of coal seam gas. Whilst none of the trace element concentrations (Table 2.1) are high by the standards used for environmental impacts screening of soils or sediments, it is their potential for mobilisation into the aqueous phase that is important.

Most trace elements will be associated with mineral matter, although many have an organic association with the plant material that was the precursor to coal formation. The extent to which trace elements can be mobilised from the coal seam matrix by water or other solutions that it contacts will be determined by their chemical form and associations within the coal mineral matrix. Typical minerals in coal formations include (Swaine 1990):

- sulfur minerals: pyrite ( $\text{FeS}_2$ ), and other pyritic minerals such as arsenopyrite ( $\text{FeAsS}$ ) and chalcopyrite; monosulfides ( $\text{FeS}$ ,  $\text{ZnS}$ )
- iron minerals: haematite ( $\text{Fe}_2\text{O}_3$ ), siderite ( $\text{FeCO}_3$ )
- silicates: kaolinite, illite, smectite.

Figure 2.1 shows the average percentages of trace elements associated with different mineral groups in Australian coals. Immediately obvious is the strong dominance of the monosulfides as the host phases for many of the elements (Ni, Pb, Zn and Cd).



Source: Dale et al. (2003)

Figure 2.1 Average association of trace elements with mineral groups in selected Australian thermal coals

## 2.2 Mobilisation of trace elements from coal

A number of studies have examined the leachability of coals (Riley et al. 2012; Dale et al. 1999; Finkelman 1994, 1995; Conway 2001). Mild leaching with distilled water or simulated acid rain (Riley 2003) gave an indication of the potential for release of trace elements into groundwater or injected surface waters. The pH of distilled water leachates in this study were around 9 and no trace elements exceeded water quality guideline values for ecosystem

protection (ANZECC/ARMCANZ 2000). The simulated acid rain leach showed only zinc and manganese as metals of potential concern.

Leaching with a salt solution (such as ammonium acetate) measures what has been termed an 'exchangeable' fraction that would be expected to be released by higher ionic strength waters, such as might be found in coal seams (Riley et al. 2012). Table 2.2 shows that only boron and manganese were elevated in distilled water leachates of six selected Australian coals (Riley et al. 2012). Their concentrations increased further with a sequential leach (with ammonium acetate solution) when cobalt, copper, vanadium and zinc concentrations were additionally elevated above Australian and New Zealand guidelines.

The leachable concentrations will also depend on the surface area and particle size of the coal minerals, so a finely crushed sample would release more trace elements than a coarse sample. The tabulated leachate concentrations therefore represent a worst case. Moreover, the extent to which these concentrations would be attenuated in the field is unknown. These data provide a guide, only, to those elements that may be present in produced waters as geogenic contaminants.

Table 2.2 Trace elements from the sequential leaching of Australian coal samples

	Distilled water leach (µg/L)							1 M Ammonium acetate leach <sup>a</sup> (µg/L)						
	coal A	coal B	coal C	coal D	coal E	coal F	mean	coal A	coal B	coal C	coal D	coal E	coal F	mean
<b>As</b>	0.5	0.1	0.1	0.1	0.1	5.5	1	0.3	0.3	0.3	0.3	0.3	0.3	0.3
<b>B</b>	115	30	265	10	140	50	102	30	2.5	90	2.5	30	2.5	26
<b>Co</b>	5	0.3	3	0.5	0.3	7	3	1	3	3.5	3.5	4.5	28	7
<b>Cu</b>	8	0.3	3	0.5	0.3	2	2	1	5	36	34	1	1	13
<b>Mn</b>	103	16	1450	30	45	12.5	283	45	64	1600	1200	1450	75	740
<b>V</b>	0.3	0.3	0.5	0.3	0.3	17	3	0.3	0.3	1	2.5	1	15	3
<b>Zn</b>	133	0.3	0.3	0.3	1.5	39	29	8	100	0.3	9	11	255	64

<sup>a</sup> Calculated from data in Riley et al. (2012)

The use of dilute hydrochloric acid, citric acid and other potentially metal-binding additives in hydraulic fracturing fluids has the potential to release additional trace elements (Batley and Kookana 2012). Leachable concentrations can be estimated from some of the published data for selective extractions (Riley et al. 2012), but they are crude estimates and serve only to indicate those elements that might pose a concern.

Table 2.3 presents data for concentrations of trace metals in 6M hydrochloric acid leachates of six Australian coals. As expected, iron is readily solubilised with concentrations near 0.5 g/L. This acid extraction specifically dissolves carbonate and oxyhydroxide forms of iron, and would also be expected to dissolve monosulfides, but not pyrites (which require dilute nitric acid) or silicates (which require hydrofluoric acid). The released iron might pose operational problems in the hydraulic fracturing process if the acid was later neutralised and solutions became oxidised, when iron oxyhydroxides would precipitate and cause fouling. For this reason, citrate is typically added to complex iron. However, citric acid will also complex other metals. Based on the leachate concentrations in Table 2.3, arsenic, boron, cobalt, copper, manganese, lead, vanadium, thorium and zinc are also elements that should be considered further, noting again that the measured concentrations are likely to be overestimates of what might be released in a field situation.

Table 2.3 Concentrations of trace elements in 6 M HCl leachates of Australian coals

Element	Coal A (µg/L)	Coal B (µg/L)	Coal C (µg/L)	Coal D (µg/L)	Coal E (µg/L)	Coal F (µg/L)	Mean (µg/L)
As	61	8.5	71	29	9.5	31	35
B	175	125	1250	0.25	175	130	310
Cd	1	1.5	2.5	1	3	4.5	2
Co	35	36	25	115	90	135	73
Cr	42	43.5	105	150	38	28	68
Cu	38	85	280	50	500	550	251
Fe	67 300	115 000	256 000	760 000	975 000	10 700	364 000
Mn	346	1040	4130	6550	18 600	135	5130
Ni	25	28	71	130	85	160	83
Pb	228	243	243	135	310	345	251
Th	41	79	20	36	110	95	63
U	7.5	12.5	2.5	8	16.5	10	10
V	124	120	115	550	650	445	334
Zn	737	655	430	550	1200	2550	1020

Calculated from data in Riley et al. (2012)

## 3 Geogenic radionuclides

### 3.1 Introduction

A radionuclide is an atom with an unstable nucleus that is able to undergo radioactive decay, resulting in the emission of gamma ray(s) and/or subatomic particles, such as alpha or beta particles. Radionuclides are naturally present in the environment and the term naturally occurring radioactive material (NORM) is used to separate naturally occurring radioactivity from that which is created anthropogenically (e.g. production of radionuclides in fission reactors). Terrestrial NORM consists of radioactive materials that come out of the Earth's crust and mantle. In some cases, human activities may result in increased radiological exposure to NORM.

The most common radioactive decay products are summarised in Table 3.1. The established SI unit of radioactive decay since 1975 is the Becquerel (Bq). One Becquerel is equivalent to one disintegration per second for any radionuclide. However, the Curie is also used as an alternative unit (particularly in North America). One Curie is equivalent to 37 Giga Becquerels ( $3.7 \times 10^{10}$ ) and is roughly the activity of 1 gram of the radium isotope radium-226. The Sievert (Sv) is also used to describe units of ionising radiation. The Sievert is a measure of the health effects of low levels of ionising radiation on the human body. One Sievert carries with it a 5.5% chance of eventually developing cancer. In contrast, the physical quantity of an absorbed ionising radiation dose<sup>2</sup> is measured by units referred to as Gray (Gy) (ICRP 2007).

Naturally occurring radionuclides have three main sources:

1. primordial – present since the Earth was formed. They originate mainly from the interior of stars. Examples include: uranium-235, uranium-238, thorium-232 and potassium-40
2. the progeny of three primordial radionuclides: uranium-235, uranium-238 and thorium-232
3. cosmogenic – formed by the interaction of cosmic radiation with components of the Earth's atmosphere. For example, carbon-14 and tritium (hydrogen-3).

In the context of geogenic contaminants associated with coal seam gas operations, cosmogenic radionuclides which are a relatively small component of NORM, will not be discussed further.

The decay series of uranium-238, the major isotope of uranium, is shown in **Error! Reference source not found.** Note that the series ends at lead-206, which is a stable non-radioactive nuclide. Another major source of terrestrial NORM is potassium-40. It decays by release of a beta particle to calcium-40, and comprises 0.012% of natural potassium which is otherwise made up of stable potassium-39 and potassium-41. The human body contains about 3700 Bq of natural potassium-40 (or 53 Bq/kg for 70 kg person).

NORM occurring geologically (including in coal) arises mainly from the elements potassium, uranium and thorium and from their daughters (Salmon et al. 1984). A number of other radionuclides (e.g. isotopes of rubidium and lanthanum) also exist but the isotopes concerned are either so scarce or have such low activities that they make a negligible contribution to the natural radioactivity inventory. Typical NORM concentrations in major rock

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<sup>2</sup> [http://en.wikipedia.org/wiki/Absorbed\\_dose](http://en.wikipedia.org/wiki/Absorbed_dose)

types and soils are given in Table 3.2. As can be seen, the most abundant form of natural radioactivity in rocks is potassium-40. In freshwaters, most radioactivity is due to radium-226 (1599 year half-life) and its daughters.

Table 3.1 Radioactive decay products

Particle symbol and name	Chemical symbol	Comment	Effect of particle emission on nucleus
Alpha ( $\alpha$ )	${}^4_2\text{He}$	Helium nucleus	Atomic number reduced by 2, mass number reduced by 4
Beta ( $\beta$ )	-e	Neutron decays to form a fast moving electron and a proton	Atomic number increased by 1
Gamma ( $\gamma$ )	none	High energy photon	None

Table 3.2 Summary of the concentrations of major radionuclides in common rock types and soil

Rock type	Potassium-40		Thorium-232		Uranium-238	
	Total K (%)	Bq/kg	mg/kg	Bq/kg	mg/kg	Bq/kg
Basalt (crustal average)	0.8	300	3-4	10-15	0.5-1	7-10
Granite	>4	>1000	17	70	3	40
Sandstones	2.7	800	12	50	3.7	40
Carbonate rocks	0.3	70	2	8	2	25
Continental upper crust (average)	2.8	850	10.7	44	2.8	36
Soils	1.5	400	9	37	1-8	66

Source: adapted from Table 1 in IAEA (2003)

Table 3.3 Radioactive decay series for Uranium-238

Type of Radiation	Nuclide	Half Life
	Uranium-238	$4.5 \times 10^9$ years
$\alpha$	↓	
	Thorium-234	24.5 days
$\beta$	↓	
	Protactinium-234	1.14 minutes
$\beta$	↓	
	Uranium-234	$2.33 \times 10^5$ years

Type of Radiation	Nuclide	Half Life
$\alpha$	↓	
	Thorium-230	8.3x10 <sup>4</sup> years
$\alpha$	↓	
	Radium-226	1590 years
$\alpha$	↓	
	Radon-222	3.83 days
$\alpha$	↓	
	Polonium-218	3.05 minutes
$\alpha$	↓	
	Lead-214	26.8 minutes
$\beta$	↓	
	Bismuth-214	19.7 minutes
$\beta$	↓	
	Polonium-214	1.5 x10 <sup>-4</sup> seconds
$\alpha$	↓	
	Lead-210	22 years
$\beta$	↓	
	Bismuth-210	5 days
$\beta$	↓	
	Polonium-210	140 days
$\alpha$	↓	
	Lead-206	Stable

Source: adapted from Griffin (2011)

### 3.2 Impacts of radiation on living organisms and guidelines for exposure

At very high doses, ionising radiation destroys body tissues and death occurs immediately or soon after exposure (ATSDR 1999b). Low doses of ionising radiation have numerous physiological effects, such as slowing the process of cell division, abnormal growths of cells, cell death and radiation-induced mutations of small pieces of chromosomes during the process of chromosome breakage and repair (ATSDR 1999b; Manahan 2010). If such changes occur in egg- or sperm-producing cells, the subsequent defects may be inherited by the offspring (ATSDR 1999b). The effects of low doses of radiation may not show up for years after exposure (ATSDR 1999b; US EPA 2012b).

The Australian and New Zealand water quality guideline trigger values (ANZECC and ARMCANZ 2000) for the radiological quality of irrigation water and livestock drinking waters are given in Table 3.4. The main risks to human health due to radioactivity in irrigation water arise from the transfer of radionuclides to crop and animal products for human consumption.

For livestock, the main water-related risks arise from the transfer of radionuclides from irrigation or stock drinking water to animals and animal products intended for human consumption. The setting of guidelines in terms of radionuclide activity is somewhat questionable as it is not indicative of overall radioactive dose. By contrast, for the protection of Australian drinking waters intended for human consumption, a dose-based approach is employed. The recommended guideline is 1 mSievert/year (NHMRC 2004). The annual dose is calculated using measurements of specific radionuclide activities in water samples.

Table 3.4 Australian Water Quality Guidelines: trigger values for radioactive contaminants for irrigation water and livestock drinking water

Radionuclide	Trigger concentration (Bq/L)
Radium-226	5
Radium-228	2
Uranium-238	0.2
Gross alpha	0.5
Gross beta (excluding potassium-40)	0.5

Source: ANZECC and ARMCANZ (2000)

### 3.3 Radionuclides in coal

While coal does contain traces of naturally occurring radionuclides such as uranium and thorium, their decay series products, and potassium-40, the radioactivity of coal in seams is generally not enhanced compared to the average values for Earth crust (IAEA 2003). For instance, comparisons with average crustal abundance data (uranium: 2.7 mg/kg and thorium: 9.6 mg/kg) (Taylor 1964) reveal that coals are depleted in uranium and thorium. The average uranium (U) and thorium (Th) contents of Australian bituminous coals are 1.3 and 3.5 mg/kg, respectively (Dale 2003). These values are quite close to the global averages for coal of 1.5 mg U/kg and 4.6 mg Th/kg.

The radioactivity of coal depends on the type of coal and its location but generally is below the average radioactivity levels in soils. Australian export thermal coal has a typical radioactivity of 432 to 1025 Bq/kg compared to the average radioactivity of the Earth's crust of 1434 Bq/kg and Australian garden soil of 1480 Bq/kg (Dale 2003). The typical activities of the key radionuclides present in Australian coals are summarised in Table 3.5. Note the contributions from potassium-40 and the two radium radionuclides. By comparison, a survey of radioactivity in British coals (Salmon et al. 1984) found mean values for both uranium and radium activity of 14.5 Bq/kg, for thorium 12.5 Bq/kg and for potassium 150 Bq/kg.

Differences in radionuclide concentrations between different coal types may be associated with variations in sulfur content and the concentrations of various mineral components (e.g. carbonates). Most thorium in coal is contained in common phosphate minerals such as monazite or apatite. In contrast, uranium is found in both the mineral and organic fractions of coal (IAEA 2010).

Table 3.5 Typical radionuclide activity in Australian coal

Radionuclide	Activity (Bq/kg)
Total activity	432-1025
Uranium-238	8.5-47
Lead-210	20-33
Polonium-210	16-28
Thorium-232	11-69
Radium-226	19-24
Radium-226	11-64
Potassium-40	23-140

Source: IAEA (2003)

### 3.4 Radionuclides in coal seam gas produced waters

Produced waters resulting from coal seam gas operations may contain some NORM as they have been in contact with natural rock formations, which naturally contain radionuclides. In addition, hydraulic fracturing agents may interact with mineral phases and result in the release of radionuclides. In the conventional gas industry, formation waters (which are often brines with low sulfate concentrations) preferentially dissolve radium relative to the parents' uranium and thorium. Thus, radium and its progeny are present in larger concentrations than uranium and thorium in the water (IAEA 2003).

In general, radium concentrations are correlated with water salinity. For example, in mine waters from the Upper Silesian Coal Basin in Poland, the total salinity (total dissolved solids) may be sometimes higher than 200 g/L. The radium concentration in these waters can reach 390 Bq/L of radium-226 and 120 Bq/L of radium-228. The radium in such brines can co-precipitate with barium and sulfate, provided that sufficient sulfate and barium are available. The radioactivity of these deposits can be thousands of times higher than that in waste rocks (IAEA 2003).

There is little available information in the literature on radionuclide concentrations in coal seam gas produced waters or other environmental media. Available data relating to two Australian coal seam gas operations are summarised in Table 3.6. The APLNG (2011) report describes radon activities of 0.3 Bq/L in untreated coal seam gas-derived (i.e. produced) waters held in a feed pond prior to treatment at their Spring Gully (Qld) operation. This compared to a water quality limit of 0.5 Bq/L (set by the Queensland Government).

An additional issue is the fate of radionuclides in holding or storage ponds. Because many radionuclides have a high affinity for sediment phases, it is possible these will pre-concentrate in sludges and/or sediments present in such ponds. This is known to be an issue in the oil and conventional gas industries (IAEA 2003); however, no data are currently publically available relating to coal seam gas operations.

Table 3.6 Radionuclide concentrations in untreated and treated produced waters from Australian coal seam gas operations

Radionuclides/ Radiological products	Activity (mBq/L)	Location	Reference
Radium-226	19	Surat Basin, aggregation pond that feeds Daandine RO facility	Arrow Energy (2011)
Radium-228	87	Surat Basin, aggregation pond that feeds Daandine RO facility	Arrow Energy (2011)
Alpha emitters	200	Spring Gully, Qld, untreated CSG water	APLNG (2011)
Beta emitters	140	Spring Gully, Qld, treated CSG water prior to discharge	APLNG (2011)
Radon	300	Spring Gully, Qld, untreated CSG water	APLNG (2011)
Radon	100	Spring Gully, Qld, treated CSG water prior to discharge	APLNG (2011)

### 3.5 Mobility of radionuclides during hydraulic fracturing

As noted in previous sections of this review, hydraulic fracturing agents used in coal seam gas operations may possess chemical and physical properties that enable the mobilisation of geogenic contaminants from coal seams. Along with trace organics and trace elements, radionuclides also fall into the category of contaminants that may be mobilised during hydraulic fracturing. Radioactivity detected in produced waters is of geogenic origin as it is not present in the fluids injected into the wells. In particular, the pH (acidity) and concentration of complexing agents present in hydraulic fracturing fluids are likely to be important factors influencing radionuclide mobility. These possibilities are best assessed experimentally as important variables can be controlled. We are currently unaware of any studies that have specifically looked into these interactions.

### 3.6 Radioactive residues

In the oil and conventional gas industry, it is well known that extraction process plant equipment may be contaminated internally with films, coatings or plating of concentrated NORM (IAEA 2003). The scales and sludges containing NORM are formed primarily during the extraction and production stages. Hard scales precipitate from the formation water onto the down-hole tubing in response to changes in temperature, pressure and salinity as the water is brought to the surface. The scale is typically a mixture of carbonate and sulfate minerals. One of these sulfate minerals is baryte ( $\text{BaSO}_4$ ), which is known to readily incorporate radium in its structure (IAEA 2003). The concentrations of radium-226 are the largest in these scales and are enhanced substantially from concentrations found in the natural environment. Likewise, radon and its progeny can be found in the gas and in films on the inside of the gas handling equipment. Lead-210 and polonium-210 that accumulate in films can be especially problematic (IAEA 2003). For instance, the activity of lead-210 in sludges and films in natural gas supply equipment can reach 40 000 Bq/kg (IAEA 2003).

When the plant is decommissioned, there are potential waste management concerns. NORM scale and sludges in production equipment from the oil and gas industry have been shown to have radionuclide activity concentrations as high as several million Bq/kg (IAEA 2003), which would place them at the upper end of the concentrations suitable for near surface disposal (these are extreme cases and not indicative of typical values). Average radionuclide

concentrations of 1000 to 100 000 Bq/kg are more common (IAEA 2003). The scales tend to be relatively insoluble, thus the radionuclides would be released slowly into the environment (IAEA 2003). Concentrations in films in natural gas equipment can range from background to 40 000 Bq/kg (IAEA 2003). We are unaware of any information on this topic that originates from coal seam gas operations.

## 4 Key findings and knowledge gaps

### 4.1 Summary

This literature review summarises knowledge on the occurrence of contaminants that may be mobilised from coal seams either during the process of hydraulic fracturing or as a component of produced waters.

Geogenic contaminants are naturally present in coal and coal seam water and may be brought to the surface during coal seam gas (CSG) extraction operations. This is supported by the observation that produced water from coal seam gas operations is reported to contain a range of inorganic salts of geogenic origin, and other geogenic organic chemical compounds, trace elements, and radioactive elements (radionuclides).

The use of hydraulic fracturing could potentially enhance the release of geogenic contaminants from the coal seams. This possibility is explored in detail in this review. It is well established that produced waters from coal seam gas operations contain a range of inorganic salts of geogenic origin (e.g. calcium, magnesium, potassium, silicate, sodium, bicarbonate, chloride and sulfate) therefore this review focused on synthesising the state of knowledge surrounding the mobilisation of trace geogenic contaminants such as organic compounds, trace metals and radioactive elements (radionuclides).

#### 4.1.1 Organic contaminants

Coal is principally composed of organic compounds due to its plant-based origins. The organic compounds present in the macromolecular coal matrix range from loosely associated compounds (e.g. methane) through to tightly bound compounds. These naturally present compounds are known as geogenic compounds and can include BTEX (benzene, toluene, ethylbenzene and xylenes), polycyclic aromatic hydrocarbons (PAHs), phenols and petroleum hydrocarbons (TPH). For example, PAHs are common constituents of coals; especially in higher ranking coals, with total PAH concentrations up to 2500 mg/kg or ~0.25% total weight. The PAHs of greatest concern, however, are generally found at concentrations in the low mg/kg concentrations in Australian east coast basins. PAHs, along with BTEX, phenols and TPHs, are of significance due to the known hazards they can present for human and environmental health.

A limited number of assessments of produced water have demonstrated that a myriad of organic compounds are present, either due to extraction of geogenic compounds or through their introduction from hydraulic fracturing fluids. Organic compounds detected in produced water include the more prominent compounds of concern, including BTEX, PAHs and phenols, although they are usually detected at concentrations close to their limits of quantification (low µg/L or parts per billion). This is also the case for other classes of organic compounds, such as n-alkanes, aromatic amines, biphenyls and heterocyclic compounds, which are also detected at µg/L concentrations. The TPHs, which represent an integrated measurement of the large number of organic compounds in produced water, are often detected at considerably higher concentrations, up to low mg/L (parts per million). It is a considerable challenge, however, to define the compounds that contribute to these TPH concentrations.

The mobility of these organic compounds relates to their inherent solubility in water, although a number of processes relating to hydraulic fracturing can enhance the transfer of organic compounds from coal seams into produced water. The presence of solvents, surfactants and acid in hydraulic fracturing fluids and elevated temperatures and salinity in the coal seam

could have an important influence on the water solubility of geogenic organic compounds. Even organic compounds that are virtually insoluble in water can be transported on particulate matter dispersed in produced water due to the physical removal of particulate matter during hydraulic fracturing.

A diverse range of organic compounds are likely to be present in flowback and produced waters. Within this range of organic compounds, there are a number of well-known compounds with a previously defined risk profile relating to either human or environmental health. A substantial number of compounds, however, are either not identified within the produced water or, of those that are able to be identified, their risk profile is unknown. Furthermore, there is currently little peer-reviewed literature available identifying or quantifying the levels of organic compounds present in produced water and, of those available, they may not have relevance to conditions found in Australian hydraulic fracturing operations.

#### **4.1.2 Trace elements**

Trace elements present in coal and other mineral formations have the potential to be mobilised by hydraulic fracturing. This is a largely unexplored source of contaminants and will potentially supplement the existing background concentration of trace elements in both flowback and produced waters.

The trace element composition of Australian coals has been well characterised in a number of studies (Dale 2003; Swaine 1990). The elemental composition of coals can vary significantly depending on their origin. Coals with a marine origin typically contain high pyrite concentrations by comparison with those deposited as freshwater peats. Coals of both types are a source of coal seam gas. None of the trace element concentrations are high by the environmental standards for soils or sediments. Their potential for mobility is, however, important.

Most trace elements will be associated with mineral matter, although many have an organic association from the plant material that was the precursor to coal formation. The extent to which trace elements can be mobilised from the coal seam matrix by water or other solutions that it contacts will be determined by their chemical form and associations within the coal mineral matrix. Typical minerals in coal formations include:

- sulfur minerals: pyrite ( $\text{FeS}_2$ ), and other pyritic minerals such as arsenopyrite ( $\text{FeAsS}$ ) and chalcopyrite; monosulfides ( $\text{FeS}$ ,  $\text{ZnS}$ )
- iron minerals: haematite ( $\text{Fe}_2\text{O}_3$ ), siderite ( $\text{FeCO}_3$ )
- silicates: kaolinite, illite, smectite.

A number of studies have examined the leachability of coals. Mild leaching with distilled water or mildly acidic solutions may give an indication of the potential for release of trace elements into groundwater or injected surface waters. The use of dilute hydrochloric acid, citric acid and potentially metal-binding additives in hydraulic fracturing fluids has the potential to release additional trace elements. Leachable concentrations can be estimated from some of the published data for selective extractions but they are crude estimates and serve to indicate those elements that might pose a concern. Further experimentation would be required to obtain more definitive data.

#### **4.1.3 Radionuclides in coal**

Coal contains traces of naturally occurring radionuclides, such as uranium and thorium, their decay series products and potassium-40. The average uranium and thorium contents of Australian bituminous coals are 1.3 and 3.5 mg/kg respectively. These values are quite close

to the global averages for coal of 1.5 mg U/kg and 4.6 mg Th/kg. Comparisons with average crustal abundance data (2.7 mg U/kg and 9.6 mg Th/kg) reveal that coals are depleted in uranium and thorium.

Differences in radionuclide concentrations between different coal types may be associated with variations in sulfur content and the concentrations of various mineral components. Most thorium in coal is contained in common phosphate minerals such as monazite or apatite. In contrast, uranium is found in both the mineral and organic fractions of coal.

The radioactivity of coal depends on the type of coal and its location but generally is below the average radioactivity levels in soils. Australian export thermal coal has a typical radioactivity of 432 to 1025 Bq/kg compared to the average radioactivity of the Earth's crust of 1434 Bq/kg and Australian garden soil of 1480 Bq/kg.

Most interest has focused on the fate of radionuclides during coal combustion whereby radionuclides may be volatilised or concentrated in combustion residues. The leachability of soluble radionuclides from coal has received limited attention. As with trace elements, hydraulic fracturing chemicals (e.g. acids and complexing agents) may result in solubilisation of some radionuclides from coal. This possibility needs to be assessed experimentally.

Radon gas (half-life 3.8 days) is a radioactive decay product of radium and is the main source of exposure to radioactivity for terrestrial organisms including humans. Radium is a natural constituent of coal and radon fluxes to the surface may increase as a result of coal seam gas operations (e.g. radium will be present in produced waters). However, the risks posed are likely to be very low as the evolved gas is unlikely to accumulate in any confined spaces that are occupied by humans.

In the oil and conventional gas industry, it is well known that extraction process plant equipment may be contaminated internally with films, scales or sludges containing naturally occurring radionuclides. The scales and sludges are formed primarily during the extraction and production stages. The scale is typically a mixture of carbonate and sulfate minerals. One of these sulfate minerals is baryte ( $\text{BaSO}_4$ ), which is known to readily incorporate radium (radium-226) in its structure. We are unaware of any available information on this topic that originates from coal seam gas operations.

Overall, the review highlights the paucity of data on contaminant concentrations in produced waters and the associated need for mechanistic studies to better understand the interactions of hydraulic fracturing chemicals with coal seams and the consequent implications for contaminant mobilisation.

## **4.2 Key findings**

Flowback and produced waters from coal seam gas wells may contain not just the chemicals added from hydraulic fracturing, but also a range of naturally occurring (geogenic) chemicals released from coal seams as a result of well drilling and fracturing processes. The literature that was reviewed confirms that waters from coal seam gas operations contain a range of major ions of geogenic origin (e.g. calcium, magnesium, potassium, silicate, sodium, bicarbonate, chloride and sulfate), as well as naturally occurring geogenic organic chemical compounds, trace elements and radioactive elements (radionuclides).

This additional suite of chemicals present in coal seam formation water or within the coal matrix itself can be potentially brought to the surface in flowback and produced waters. Given the nature of chemicals present in hydraulic fracturing fluids and the elevated pressures used during hydraulic fracturing, there is a potential for naturally occurring chemicals to be mobilised from coal seams with or without the application of hydraulic fracturing.

### 4.2.1 Organic compounds

Coal is principally composed of organic compounds due to its plant-based origins. The organic compounds present in the macromolecular coal matrix range from loosely associated compounds (e.g. methane) through to tightly bound compounds. The compounds present can include BTEX, PAHs, phenols and TPHs.

A limited number of assessments of produced water have demonstrated the presence of BTEX, PAHs and phenols; although they are usually detected at concentrations close to the limits of quantification (low  $\mu\text{g/L}$  or parts per billion [ppb]). This is also the case for other classes of organic compounds, such as *n*-alkanes, aromatic amines, biphenyls and heterocyclic compounds, which are also detected at low ppb concentrations. The TPHs, which represent an integrated measurement of the array of organic compounds in produced water, are often detected at considerably higher concentrations, up to low  $\text{mg/L}$  (parts per million).

Potential mechanisms were identified from the literature by which hydraulic fracturing may enhance the passage of natural organic compounds from coal into produced water. Chemicals in hydraulic fracturing fluids such as salts, solvents and acids, as well as elevated ambient temperatures and pressures, can change the solubility of organic compounds so that they are more readily transported in produced waters. Also, compounds virtually insoluble in produced water can be transported on microscopically small coal particles produced from the well with the water.

This review highlighted a lack of knowledge about the potential for organic compounds present in Australian coal to be mobilised into flowback and produced waters.

### 4.2.2 Trace inorganic elements

Trace inorganic elements present in coal and other mineral formations and in groundwater have the potential to be brought to the surface in produced water. Hydraulic fracturing may, however, increase the mobilisation of trace elements into flowback waters. The trace element compositions of Australian coals have been well characterised by a number of studies. Elemental composition varies depending on the coal origin – for example, marine versus freshwater peat. Coals with a marine origin typically contain higher pyrite, organo-sulfur and boron concentrations in comparison to those deposited as freshwater peats.

The extent to which trace elements can be mobilised into groundwater or into flowback and produced waters following hydraulic fracturing depends on their chemical form and associations within the coal matrix. Available laboratory data on the leachability of Australian coals indicate that dilute acids and metal-binding additives used in hydraulic fracturing fluids have the potential to mobilise additional trace elements and increase their concentrations above those normally associated with coal seam groundwater. However, these data only serve to indicate those elements that might pose a concern and therefore should be monitored in produced water. This review suggests that more refined laboratory extraction studies of Australian coal may be warranted.

### 4.2.3 Radionuclides

Coal also contains traces of naturally occurring radioactive elements (radionuclides). Available data indicate that the average uranium and thorium contents of Australian bituminous coals are 1.3 and 3.5  $\text{mg/kg}$  (respectively) and that these values are quite close to the global averages for coal of 1.5  $\text{mg/kg}$  and 4.6  $\text{mg/kg}$  (respectively).

The radioactivity of coal depends on the type of coal and its location but is generally below average radioactivity levels of soil. Australian export thermal coal has a typical radioactivity of

432 to 1025 Bq/kg, compared to the average radioactivity of the Earth's crust of 1434 Bq/kg and Australian garden soil of 1480 Bq/kg.

The review showed that leaching of soluble radionuclides from coal has not been well studied. Similar to non-radioactive trace elements, hydraulic fracturing chemicals have the potential to mobilise radionuclides into produced water. Only limited information is available publicly in the literature on radionuclide concentrations in coal seam gas produced waters or other environmental media.

An additional identified issue with radionuclides is their fate in holding or storage ponds. Radionuclides may adsorb onto fine particles and concentrate with sludges and sediments present in storage ponds. Potential radioactive waste has been identified as an issue with the oil and conventional gas industries. However, no data are available relating to coal seam gas operations.

### **4.3 Knowledge gaps and limitations**

There is limited published information on the suite of chemicals used in hydraulic fracturing fluids in Australia. In the absence of published literature on coal seam gas, the sub-section of this review dealing with potential interactions of hydraulic fracturing fluids with geogenic organic contaminants is based on the engineering literature on contaminated sites and waste disposal sites involving complex mixtures of contaminants. Although partly relevant to the complex mixtures in hydraulic fracturing fluids, this component of the review is only indicative of likely processes that may occur to mobilise chemicals from coal seams.

The concentrations of organic contaminants in flowback or produced water are likely to be time dependent. Therefore, the limited overseas data on organic contaminants in produced water (e.g. Orem et al. 2007) reported here is only indicative of what might be present in Australian flowback or produced waters.

Overall, this review highlighted the paucity of data on contaminant concentrations in produced waters and also the need for mechanistic studies to better understand the interactions of hydraulic fracturing chemicals with coal seams and the consequent implications for contaminant mobilisation.

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