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

Technical report number 2 Literature review: Human health implications

This report was prepared by the National Industrial Chemicals Notification and Assessment Scheme (NICNAS)



Department of the Environment and Energy

Department of Health National Industrial Chemicals Notification and Assessment Scheme The national assessment of chemicals associated with coal seam gas extraction in Australia was commissioned by the Department of the Environment and Energy and prepared in collaboration with NICNAS and CSIRO

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Reports in this series

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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
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8	Human and environmental exposure conceptualisation: Soil to shallow groundwater pathways	CSIRO
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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
Assessing risks to the environment		
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 evidence¹ 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

¹ 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: Human health implications

This literature review covered potential human exposure pathways associated with handling drilling and hydraulic fracturing chemicals during coal seam gas operations (including surface handling incidents in Australia and overseas that led to chemical releases) and approaches to assessing human health risks from chemicals used in drilling and hydraulic fracturing.

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

Abbreviations

General abbreviations	Description	
ACGIH	American Conference of Governmental Industrial Hygienists	
API	American Petroleum Institute	
BTEX	Benzene, toluene, ethylbenzene and xylenes	
CAS	Chemical Abstract Services	
CEAA	Canadian Environmental Assessment Act 2012	
COPC	Chemicals of potential concern	
CSG	Coal seam gas	
CSIRO	Commonwealth Scientific and Industrial Research Organisation	
DAF	Dilution attenuation factor	
DECC	Department of Energy and Climate Change (UK)	
DERM	Department of Environment and Resource Management (now Environment and Heritage Protection - EHP) (Qld)	
DG	Directorate General (EU)	
DoE	Department of the Environment (Commonwealth) Formerly the Department of Sustainability, Environment, Water, Population and Communities (DSEWPaC)	
DSEWPaC	Department of Sustainability, Environment, Water, Population and Communities (now Department of the Environment)	
EPC	Exposure Point Concentration	
GIS	Geographic information system	
н	Hazard index	
HQ	Hazard quotient	
IEA	International Energy Agency	
IESC	Independent Expert Scientific Committee on Coal Seam Gas and Large Coal Mining Development	
IUR	Inhalation unit risk	
MCL	Maximum Contaminant Levels	
NICNAS	National Industrial Chemicals Notification and Assessment Scheme	
NORM	Naturally occurring radioactive material	
NSW	New South Wales	
OH&S	Occupational health and safety	
PBT	Persistence, bioaccumulation and aquatic, terrestrial and human health	

Literature review: Human health implications

General abbreviations	Description	
	toxicity	
PEL	Permissible Exposure Limit	
Qld	Queensland	
RBC	Risk-based concentration	
REL	Recommended Exposure Limit	
RfC	Reference concentration	
SA	South Australia	
US EPA	United States Environment Protection Agency	
VOC	Volatile organic compounds	
WA	Western Australia	

Units, chemicals and symbols	Description
m ³	Cubic metre
ML	Megalitre
psi	Pounds per square inch
hð	Micrograms

Glossary

Term	Description		
Aquifer	Rock or sediment in a formation, group of formations, or part of a formation, which is saturated and sufficiently permeable to transmit quantities of water to wells and springs		
Aquitard	A saturated geological unit that is less permeable than an aquifer and incapable of transmitting useful quantities of water. Aquitards often form a confining layer over an artesian aquifer		
Bounding estimate	A bounding estimate captures the highest possible exposure, or theoretical upper bound, for a given exposure pathway		
Casing	Steel or fibreglass pipe used to line a well and support the rock. Casing extends to the surface and is sealed by a cement sheath between the casing and the rock		
Coal seam gas	A form of natural gas (generally 95 to 97% pure methane, CH_4) typically extracted from permeable coal seams at depths of 300 to 1 000 m. Also called coal seam methane (CSM) or coalbed methane (CBM)		
Conventional gas (or oil)	Refers to gas or oil sourced from conventional underground porous sedimentary rock strata, The term 'conventional' in gas or oil production refers to gas or oil produced by wells in which the reservoir and fluid characteristics permit the gas or oil to flow readily to the wellbore. Conventional gas is colloquially termed 'natural gas'.		
Corrosion inhibitor	A chemical substance that minimises or prevents corrosion in metal equipment		
De-watering	The lowering of static groundwater levels through complete extraction of all readily available groundwater, usually by means of pumping from one or several groundwater bores		
Drill string	Drill infrastructure consisting of the drill bit, drill collars (to provide weight) and the drill pipe		
Drilling fluids	Fluids that are pumped down the wellbore to lubricate the drill bit, carry rock cuttings back up to the surface, control pressure and for other specific purposes. Also known as drilling muds		
Flowback water	The initial flow of water returned to a well after fracture stimulation and prior to production		
Formation (geological)	A geological formation is a body of earth material with distinctive and characteristic properties and a degree of homogeneity in its physical properties		
Formation water	Naturally occurring water that is within or surrounding the coal, rock or other formations underground		
Geogenic chemical	A naturally-occurring chemical originating, for example, from geological formations		
Groundwater	Water occurring naturally below ground level (whether in an aquifer or other low permeability material), or water occurring at a place below ground that has been pumped, diverted or released to that place for storage. This does not include water held in underground tanks, pipes or		

Term	Description		
	other works		
High-end estimate	Estimates at the high end of a normal distribution i.e. between 90 th and 99.9 th percentile		
Hydraulic fracturing	Also known as 'fracking', 'fraccing' or 'fracture stimulation', is one process by which hydrocarbon (oil and gas) bearing geological formations are 'stimulated' to enhance the flow of hydrocarbons and other fluids towards the well. In most cases is only undertaken where the permeability of the formation is initially insufficient to support sustained flow of gas. The hydraulic fracturing process involves the injection of fluids, gas, proppant and other additives under high pressure into a geological formation to create a conductive fracture. The fracture extends from the well into the coal reservoir, creating a large surface area through which gas and water are produced and then transported to the well via the conductive propped fracture channel		
Hydraulic fracturing fluidA fluid injected into a well under pressure to create or expand frac a target geological formation (to enhance production of natural ga or oil). It consists of a primary carrier fluid (usually water), a propp one or more additional chemicals to modify the fluid properties			
Intermediate casing	Casing set below the surface casing in deep holes where added support or control of the wellbore is needed. It goes between the surface casing and the conductor casing. In very deep wells, more than one string (connected pipes) of intermediate casing may be used		
Permeability	The measure of the ability of a rock, soil or sediment to yield or transmit a fluid. The magnitude of permeability depends largely on the porosity and the interconnectivity of pores/spaces in the ground		
рН	A measure of the acidity/alkalinity of a solution - a logarithmic scale from 1 (most acidic) to 14 (most alkaline); 7 is neutral		
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' (often salty water that is naturally present in the coal seam). This produced water moves through the coal formation to the well along with the gas, and is pumped out via the wellhead		
Proppant	A component of the hydraulic fracturing fluid system comprised of sand, ceramics or other granular material that 'prop' open fractures to prevent them from closing when the injection is stopped		
Surface water	Water that flows over land and in watercourses or artificial channels and can be captured, stored and supplemented from dams and reservoirs		
Surfactant	Used during the hydraulic fracturing process to decrease liquid surface tension and improve fluid movements		
Tight gas	Natural gas trapped in ultra-compact reservoirs characterised by very low porosity and permeability		
Turkey's nest	A plastic lined excavated pit used to store water		
Unconventional gas (or oil)	Refers to gas or oil sourced from unconventional reservoirs – i.e. where porosity, permeability or other characteristics differ from those of conventional sandstone reservoirs and that occasionally require stimulation or flow enhancement to facilitate productive flows of gas or oil.		

Term	Description	
Wellbore	The hole produced by drilling, with the final intended purpose being for production of oil, gas or water. The wellbore is the actual hole in the ear that is part of the completed well.	
Well integrity	A measure of the ability of the well and wellbore system to allow access to the reservoir while controlling fluid movement along the well or from the well into or out of the surrounding rock.	

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1 Overview of coal seam gas production

1.1 What is coal seam gas?

This literature review covers information available to the end of 2013. The review report was completed in 2013, with minor updates made between 2013 and 2017.

Coal seam gas is a hydrocarbon found naturally in the environment. It is essentially methane-rich gas held in underground coal seams. The gas is also referred to as coal seam methane or coal bed methane. Pressure from overlying rock and water in the coal seam holds the gas in place. Gas molecules are packed tightly as a monolayer on the large internal surface area of coal (US EPA 2009).

Coal seam gas is a form of 'unconventional' gas. Conventional gas, colloquially termed 'natural gas', refers to gas sourced from conventional underground porous sedimentary rock strata, usually associated with oil. The term 'conventional' in gas (and oil) production refers to gas and oil produced by wells in which the reservoir and fluid characteristics permit the gas and oil to flow readily to the wellbore (US EIA 2012).

In contrast, unconventional gas and oil production refers to gas and oil sourced from unconventional reservoirs – that is, where porosity, permeability or other characteristics differ from those of conventional sandstone reservoirs and that occasionally require stimulation or flow enhancement to facilitate productive hydrocarbon flows (US EIA 2011; US EPA 2011).

In addition to coal seam gas, other types of unconventional gas are shale gas and tight gas. Shale gas is natural gas contained in shales or fine-grained carbonates. Tight gas is a more poorly defined category but is considered natural gas occurring in rock reservoirs of the lowest permeabilities (Geoscience Australia and ABARE 2010; Geoscience Australia 2010).

Coal seam gas is practically identical chemically to 'conventional' natural gas. In underground coal mining, methane released from coal during mining is a major safety hazard.

Within coal reservoirs, coal seam gas is found adsorbed onto the grain faces and micropores of coal by the geological maturation process of coalification. The gas is held in place by water pressure. Coal seams contain natural fractures (or cleats) that provide pathways through which gas contained in a large volume of coal seam - can flow. The gas can be extracted if the hydrostatic pressure is lowered within the coal seam by extracting water (i.e. de-watering).

Although coal seams contain natural fractures through which coal seam gas and water can be extracted, coal seam gas wells and wells for other forms of unconventional gas frequently require stimulation (or flow enhancement) via hydraulic fracturing to facilitate economically productive gas flows. Hydraulic fracturing, first developed in the United States (US) oil and gas industry in the late 1940s, is an established stimulation method. It is used to facilitate dewatering and elevate gas extraction from wells to economically productive levels (API 2010).

1.2 Coal seam gas production

1.2.1 Drilling and well construction

Following the exploration stages (undertaken to confirm the location and economic viability of a gas resource), coal seam gas extraction essentially involves well construction, a gas production phase and well decommissioning (when gas resources fall below economically viable levels).

Well construction involves stages of drilling and the installation of well infrastructure to prepare the well for long-term gas production. Final well completion may include hydraulic fracturing to ensure productive gas and water flows.

The American Petroleum Institute (API) has published best practice guidelines for planning and completing oil and gas wells in which hydraulic fracturing will be conducted (API 2009). The guidelines note that well integrity has two key aspects. The first is isolating the internal conduit of the well from surface and subsurface environments, which is important in protecting the environment. The second is isolating and containing the well's produced gas and fluid to a production conduit within the well to optimise production efficiency.

During well construction, groundwater is protected from the contents of the well by a combination of steel casings, cement sheaths and mechanical isolation devices. Proper well construction prevents fluid or gas leakage between the well conduit and surface and subsurface environments and, importantly, also provides subsurface zonal isolation (i.e. maintenance of barriers between formations through which the well penetrates).

Drilling and completing oil and gas wells consists of the following sequential activities (API 2009):

- Drilling the hole. Vertical wells are dug using a drill string consisting of the drill bit, drill collars (to put weight on the drill bit) and the drill pipe. While drilling, fluid is circulated down the drill string and up the space between the drill string and hole. The drilling fluid provides lubrication, removes cuttings and maintains pressure control of the well.
 Horizontal wells may be drilled following initial vertical drilling using a steerable down-hole motor to drive a drill bit powered by hydraulic pressure of the drilling fluid.
- Logging the hole. Sensing devices are run through the hole to record subsurface conditions. Logging determines the depths and thicknesses of subsurface formations to be targeted and also assists the positioning of steel casings to optimise zonal isolation.
- *Running the steel casing.* Casings are steel pipes threaded on each end, which are joined by couplings. After initial drilling, a conductor pipe is installed followed by sequentially deeper holes drilled to install surface casings, intermediate casings and production casings. Each installed casing is a sequentially smaller size to the previous installed casing such that shallow portions of the well feature multiple concentric casings.
- Cementing the casing in place. The purpose of cementing the casing is to provide zonal isolation between different subsurface formations and structural support for the well. The selection of materials for cementing (and casing) are important, but are secondary to the process of cement placement, which is essential for isolating the hydrocarbon bearing zones from groundwater zones. Complete displacement of drilling fluids by cement, with absence of voids, and tight bonding of the cement interfaces between the drilled hole and the casing immediately above the target formations, are key aims during cement placement.

- Logging through the casing to evaluate cement quality. Logging is the process of running measuring instruments down the well hole to map and record the structure of the well and geological formations. Logs are run during construction and also on a routine basis during the life of the well to determine the quality of joints between casings and the quality of the cement bond between the casings and formations. Positive pressure tests are also conducted to determine casing integrity.
- Perforating the casing at the hydrocarbon seam(s) to allow hydraulic fracturing. Perforations create communications for oil, water and gas between the inside of the production casing and the formation. The perforations are made by shaped charges which, when detonated, produce a stream of hot, high pressure gas that vaporises the steel casing, cement and the immediate target formation at precise locations.
- Hydraulic fracturing (see Section 1.2.2 below).
- *Monitoring well performance and integrity.* The API guidelines note that well conditions should be monitored throughout the life of a producing well to ensure well integrity.

In short, the API best practice guidelines emphasise that proper well design aims to contain hydrocarbons within the well, protect groundwater, isolate productive formations from other formations and facilitate proper execution of well stimulation techniques.

1.2.2 Hydraulic fracturing

Hydraulic fracturing is a well stimulation (flow enhancement) technique used in the oil and gas industry to increase the flow area for trapped hydrocarbons and water. The technique does this by creating or enhancing conductive pathways (i.e. fractures) extending outward from the wellbore into the hydrocarbon-bearing formation.

In coal seam gas production, hydraulic fracturing involves injecting a fluid or foam containing an inert, granular material called a proppant, commonly sand, under high pressure into the coal seam via the wellbore. The high pressure liquid is injected into the coal seam via perforations created in the production casing. The proppant carried in the water is deposited in the fractures and prevents them from closing when pumping pressure ceases. Since water is not the best carrier of large particulate proppants such as sand, additional chemicals are commonly added to make the fluid more viscous to effect a uniform suspension of proppant. Chemicals are also added in low concentrations for other specific purposes.

1.3 Chemicals associated with drilling and hydraulic fracturing

Besides regulatory, safety and economic considerations, the choice of chemicals used in drilling and hydraulic fracturing operations is determined in response to geological conditions to be encountered during operations. The following sections outline the types of chemicals used in drilling and hydraulic fracturing operations.

1.3.1 Chemicals in drilling fluids

Drilling fluids, often referred to as drilling muds, are a key requirement of the drilling process. While drilling, fluid is circulated down the drill string and up the space between the drill string and the hole (API 2009).

Drilling fluids and individual constituent chemicals perform a number of functions. These include clearing rock fragments from beneath the bit and carrying them to the surface, applying sufficient pressure against subsurface formations to prevent fluids and gases from

flowing into the well, keeping the newly drilled bore hole open until casing or lining has been cemented in place, cooling and lubricating the rotating drill string and bit and transmitting hydraulic power to the drill bit (for horizontal drilling) (OGP and IPIECA 2009).

Drilling fluids consist of a base liquid containing chemical additives, either liquid or solid, which are chosen based on specific drilling conditions, including changes in geology at various depths. In addition to liquids, pneumatic (or air-foam) fluid systems are reported to be used in sections of the petroleum industry (DEHP 2013a). Commonly, liquid drilling fluids are either water-based fluids or non-aqueous fluids. Non-aqueous fluids can be further grouped according to aromatic hydrocarbon content which, in recent years, has been influenced by both technical and environmental considerations (OGP and IPIECA 2009). Moreover, the general use of non-aqueous fluids has been the subject of conditions on recent coal seam gas drilling operations by environmental regulatory authorities in some jurisdictions in Australia (DEHP 2013a).

Table 1.1 provides a list of chemicals commonly used in water-based drilling fluids.

Types	Function	Additive
Clay stabiliser Prevents clay swelling and helps improve the cement/formation bond.		Calcium chloride, calcium chloride anhydrous, potassium chloride
Cement additive	Enhances strength of the bore.	Bentonite, calcium sulfate
pH control	Adjusts the pH of the fluid in order to maximise the effectiveness of other additives.	Sodium hydroxide, potassium hydroxide, calcium hydroxide, citric acid, sodium bicarbonate
Bactericides (or biocides)	Inhibits growth of bacteria in the wells that interfere with hydraulic fracturing and restrict gas flow.	Sodium hypochlorite, tetrakis(hydroxymethyl phosphonium sulfate, glutaraldehyde
Viscosity control	Adjusts viscosity of the fluid as per requirements.	Bentonite, polyanionic cellulose, carboxymethyl cellulose, synthetic polymers
Fluid loss	Fluid loss control.	Modified polyacrylates, lignosulfonates, resins, starch, synthetic polymers
Foaming agent	-	Anionic surfactants (similar to detergent)

Table 1.1 Chemicals in water based drilling fluids

Source: US EPA (2004)

Basic drilling fluid systems are often converted to more complex systems as the well deepens and the wellbore temperature and / or pressure increases. Several key factors affect the selection of additives to drilling fluid systems for a specific well. For example, organic polymers are added to the base fluid to raise the viscosity and aid in removal of drill cuttings (NSW Trade and Investment 2012).

1.3.2 Chemicals in hydraulic fracturing fluids

Hydraulic fracturing fluids serve two main purposes - to transmit hydraulic pressure to propagate fractures within the coal seam and to carry proppant into the fractures. In coal seams, fluid pressure causes fractures to grow slowly, with an average velocity of less than

10 m per second initially, slowing to less than 1 m per second at the end of a fracture operation (CSIRO 2012).

Hydraulic fracturing fluids are engineered products containing chemical additives serving specific functions. Hydraulic fracturing fluid is typically made up of water, proppant and chemical additives to enhance the efficiency of the fracturing process. As the term implies, the 'proppant' functions to prop or hold fractures open. Sands are the most common proppants used. Resin-coated sand grains have been reported to improve the strength of the proppants (Economides and Nolte 2000) and ceramic particles are also used (Batley and Kookana 2012).

Although exact percentages vary, water and sand are reported to make up around 97 to 99 per cent and chemical additives make up about 1 to 3 per cent of the hydraulic fracturing fluid (CSIRO 2012). The composition of the chemical additives varies with the nature of the geological formation and the stage of hydraulic fracturing. Some fluids may also include nitrogen and carbon dioxide to help foaming (Gupta et al. 2005).

Each additive of the fracturing fluid serves a specific engineered purpose. The International Energy Agency (IEA) describes four primary roles for chemical additives in hydraulic fracturing fluids (IEA 2012):

- to keep the proppant suspended in the fluid while it is being pumped into the well and to ensure that the proppant ends up in the fractures being created
- to change the properties of the fluid over time. Characteristics that are needed to deliver proppant deep into subsurface fractures are not desirable at other stages in the process. Therefore, some additives such as encapsulated enzymes provide timedependent properties to the fluid (e.g. to make the fluid less viscous after fracturing so that the hydrocarbons flow more easily along the fractures to the well)
- to reduce friction and therefore the power required to inject the fluid into the well
- to reduce the risk that naturally occurring bacteria in source water may affect the performance of the fracturing fluid or proliferate in the reservoir, producing hydrogen sulfide.

Additional properties of chemical additives are to dissolve minerals and aid in fracture formation, restricting fluid loss and minimising corrosion of metal components (Batley and Kookana 2012).

1.3.3 Classes of additives

Table 1.2 lists the types, functions and examples of additives that have been proposed for use in hydraulic fracturing of gas wells. Chemicals used in the fracturing fluids can be classified into 14 classes based on their function in the fracturing process.

Types	Functions	Examples of chemical
Proppant	Keeps seam fractures open to allow gas/fluids to flow more freely to the wellbore.	Sand, sintered bauxite, ceramic beads
Acid	Dissolves minerals, removes cement and drilling mud from casing perforations prior to fracturing fluid injection, and initiates cracks in the formation.	Hydrochloric acid

Table 1.2 Types and functions of additives used in hydraulic fracturing (DEHP 2013b)

Types	Functions	Examples of chemical
Gelling agent	Thickens the fracturing fluid allowing the fluid to carry more proppant into the fractures. Adjusts viscosity of fracturing fluid.	Guar gum, hydroxyethyl cellulose
Breaker	Reduces the viscosity of the fluid by breaking the gel. Assists in releasing the proppants into the fractures.	Sodium persulfate
Antimicrobial agent	Inhibits growth of bacteria in the wells that interfere with fracturing and restrict gas flow.	2-methyl-2H-isothiazol-3- one, sodium hypochlorite
Crosslinker	Maintain fluid viscosity at higher temperatures.	Borate salts, potassium hydroxide
pH adjusting agent [buffer]	Adjusts and controls the pH of the fluid in order to maximise the effectiveness of other additives such as crosslinkers.	Sodium or potassium carbonate, acetic acid
Clay stabiliser	Prevents clay swelling and helps improve the cement/formation bond.	Potassium chloride, tetramethyl ammonium chloride
Corrosion inhibitor (including oxygen scavengers)	Reduces rust formation and pipe corrosion.	Methanol, ammonium bisulfate for oxygen scavengers
Scale inhibitor	Prevents scale deposits on pipes (precipitates of calcium carbonate, calcium sulfate, barium sulfate etc.)	Ammonium chloride, ethylene glycol
Friction reducer	Minimising friction between fluid and pipe. Allows fracture fluids to be injected at optimum rates and pressures.	Polyacrylamide, petroleum distillates
Surfactant	Reduces fracturing fluid surface tension and aid fluid recovery.	Methanol, ethanol, isopropanol, ethoxylated alcohol
Iron control	Prevents precipitation of metal oxides that plug the formation.	Citric acid

There are a number of different chemicals for each additive class. However, only one product of each class is typically utilised in any given hydraulic fracturing job. The selection may be driven by the formation and potential interactions between additives. In addition, not all additive classes are utilised in every fracturing job.

1.3.4 Chemicals in flowback and produced waters

An estimated 50 to 90 per cent of the fluid used for hydraulic fracturing is returned to the surface following fracturing (Ewing 2008). Yet in some circumstances, depending on the nature of the formation, none of the injected fluid may be recovered (US GAO 2012).

Water pumped out of coal seams in order to release coal seam gas after hydraulic fracturing is called produced water or formation water (GISERA 2014). The industry typically refers to flowback water as the water produced within a few days of the fracturing operation, and produced water after that, even though both types of water may have similar characteristics (Batley and Kookana 2012).

Both drilling and, to a greater extent, hydraulic fracturing cause mobilisation of chemicals that occur naturally in the subsurface, particularly in hydrocarbon-containing formations. Accordingly, the chemistry of injected water is altered as it interacts with the coal seam minerals and mixes with water associated with the coal deposits that become mobilised as part of the drilling operation. Complex biogeochemical reactions with chemical additives used in hydraulic fracturing fluid may occur (Batley and Kookana 2012).

Naturally occurring or geogenic chemicals found in flowback and produced waters include formation brines, trace elements, naturally occurring radioactive material (NORM) and various liquid hydrocarbons including heterocyclic compounds, aromatic amines, polycyclic aromatic hydrocarbons (PAHs), such as benzene, toluene, ethyl benzene and xylene (as a group, called BTEX) and other organic material (Orem et al. 2007).

Examples of some of the naturally occurring substances that may be mobilised particularly by hydraulic fracturing are shown in Table 1.3.

Naturally occurring substances	Examples		
Formation brines	Sodium chloride		
Gases	Natural gas (e.g. methane, ethane), carbon dioxide, hydrogen sulfide, nitrogen, helium		
Trace elements	Arsenic, boron, cadmium, copper, lead, mercury		
Naturally occurring radioactive material (NORM)	Radium, thorium, uranium		
Organic material	Organic acids, polycyclic aromatic hydrocarbons, volatile and semi-volatile organic compounds		

Table 1.3 Naturally occurring substances that may be mobilised during hydraulic fracturing

Contaminant concentrations in produced water are reported to generally decrease to background in as little as a week after fracturing (Batley and Kookana 2012). However, produced water quality is highly variable from site to site and is generally not fit for human consumption. Depending on its intended use and quality, produced water can be used directly, treated and then used, or directly reinjected.

Once produced water and gas (mostly methane) reach the surface, they are separated. Methane is collected and passed to a central compressor station and the produced water is piped to storage tanks for use or further treatment. The volume of water produced from the wells varies from a few thousand to hundreds of thousands of litres a day, depending on the groundwater pressures and geology, and this typically diminishes over the lifetime of a well (GISERA 2014).

1.3.5 Toxicity of chemicals associated with drilling and hydraulic fracturing

Chemicals used in drilling and hydraulic fracturing operations range from benign materials, such as guar gum and cellulose, to those that are classified as hazardous substances in Australia and other countries and must be labelled, packaged and handled accordingly (Colborn et al. 2012; Ewen et al. 2012). Some of these chemicals are also employed for many other purposes for industrial and domestic use (e.g. as components of home cleaning products).

2 Human exposure pathways to drilling and hydraulic fracturing chemicals

There are many pathways by which humans, both workers handling the chemicals at the fracturing sites as well as the general population, can be exposed to chemicals used in drilling and hydraulic fracturing activities. These exposures can occur at or near the site of fractured wells or at considerable distances from the wells depending on the movement of the injected fluids underground (Ewen et al. 2012).

The following scenarios and pathways – that can lead to human exposure to chemicals directly in occupational situations or indirectly through contamination of surface and groundwater – are reported in the literature.

2.1 Potential human exposures to chemicals associated with drilling

As discussed earlier, drilling a gas well comprises drilling deep into the ground, running steel pipes for well construction (casing) and cementing the casing in place to ensure isolation. The drilling operation uses fluids to reduce friction, prevent the bore hole from collapsing or caving in, and remove rock fragments or cuttings. The circulating system pumps the drilling fluids down the hole and out of the nozzles in the drilling bit, and returns them to the surface via the annulus where the debris is separated from the fluid. The additives (e.g. clays and polymers) increase drilling fluid viscosity and maintain the cuttings in suspension in the drilling fluid for a reasonable period of time, which enables them to be removed when the drilling fluid reaches the surface. The fluid is then recirculated through the hole. This process is repeated as drilling progresses.

After the hole is drilled to the required depth, the casing is run into the wellbore from the surface and cement is placed in the annular space between the casing and the borehole wall. The casing and cement provide structural integrity for the well and isolate formations in the earth from each other and from the surface.

No data on the typical volumes of drilling fluids used during drilling operations were available in the literature. Some reports indicated that during drilling, large volumes of drilling fluid are circulated in open or semi-enclosed systems (Broni-Bediako and Amorin 2010; OGP and IPIECA 2009).

Drilled solids brought to the surface along with the drilling fluids are separated with the help of a shaker, which is basically a wire-cloth that vibrates violently while the drilling fluid flows on top of it. The liquid phase of the mud and solids (those that are smaller than the wire mesh) pass through the screen, while larger solids are retained on the screen and are discarded.

Exposure to drilling fluids at the drilling site is mainly by skin contact and inhalation of aerosols and vapours (James et al. 2007; OSHA 2009) and can be repetitive due to the manual nature of the work involved. The potential for inhalation of dust is mainly in association with mixing operations.

Workers involved in gas extraction operations can be exposed to chemicals during various activities, such as the:

- transport of chemicals to and storage at coal seam gas extraction site
- handling of chemicals during drilling and hydraulic fracturing
- handling of flowback and produced water.

Transport of chemicals and equipment to the fracturing sites has been identified as a potential source of exposure to workers (SCER 2012; SCER 2013). Components of the drilling fluids are transported and stored on-site in tankers and in large, upright storage tanks in support trucks before use (US EPA 2004). Workers involved in the transport and storage of chemical products may be exposed to concentrated chemicals leaking from packages. Leaks and spills from surface storage vessels can range from less than a few litres during fluid line connection to the very rare leak of a truck load (over 5 000 L) (King 2012).

The preparation and use of drilling fluid systems may generate airborne contaminants, dust, mist and vapour in the workplace. Large volumes of drilling fluids are prepared on-site mechanically using rotor/stator mixers. The mixing hopper also provides an opportunity for exposure to chemicals and products. Powdered products or liquid additives are introduced to the mixing operation through the hopper. When preparing drilling fluids, the components are often circulated in an open system at elevated temperatures with agitation that can result in a combination of vapours, aerosol and / or dust above the mud pit. In the case of water-based fluids, the vapours comprise steam and dissolved additives (OGP and IPIECA 2009). Workers could be exposed to the vapours and any splash of liquid that occurs during the process.

During drilling, large volumes of fluids (i.e. drilling mud) are circulated through the wellbore with agitation at elevated temperatures to control pressure in the well and remove cuttings created by the drill bit from the well. There is significant potential for workers to be exposed to chemicals during this process (Broni-Bediako and Amorin 2010; HSE 2011).

Exposure could also occur when operating the shaker for mechanical agitation of the fluid (used to separate cuttings from the drilling fluids), washing the shakers and other equipment with high-pressure guns, which normally uses a hydrocarbon-based fluid, and during manual handling of unclean pipes (Broni-Bediako and Amorin 2010). Exposure is also possible through manual handling of soiled equipment, surfaces and spills, and from cleaning operations.

The drilling mud is monitored throughout the drilling process and a mud engineer periodically checks the mud by measuring its viscosity, density and other properties, and can be exposed to the chemicals during these tasks.

However, current descriptions of procedures for preparing drilling fluids in the oil and gas industry indicate that products and additives are handled in bulk form, from pre-loaded containers, and are added to the drilling fluid system from a remotely operated control zone, to minimise exposure at the rig site (OGP and IPIECA 2009). Overall, the extent of exposure to drilling chemicals at various work sites differs depending on the use of manual versus automated processes.

Public exposure to drilling fluid or its components is possible during transport if packaging is breached or in the event of a transport accident. Also, residents living closer to drilling sites could be exposed to vapours during fluid preparation and drilling operations, but no information about public exposure to drilling fluids is available in published literature.

2.2 Potential human exposures to chemicals associated with hydraulic fracturing

Hydraulic fracturing occurs after a well has been drilled and casings are installed in the wellbore. Perforations in well casings are created in the coal seam zone by localised blasts to enable fracturing fluid to flow through the perforations into the target zones. Hydraulic fracturing is then carried out by injecting fracturing fluid, comprising of water, chemical additives and sand (or other proppant) into the well at very high pressures. The pressure exceeds the rock strength and the fluid opens up or enlarges existing fractures in the rock. Once the formation is fractured, a propping agent is pumped into the fractures to keep them from closing as the pumping pressure is released. Natural gas begins to flow through the wellbore along with produced water. Workers continually monitor pressures and fluid properties during the process and adjust operations as necessary.

The hydraulic fracturing process starts with the preparation of fracturing fluids. Clean water from a turkey's nest (i.e. a plastic lined excavated pit used to store water) is pumped into the blender unit where it is mixed with guar gum and other additives to form a slurry. Components of the fracturing fluids are pumped directly from storage containers to mix tanks and mixed just prior to injection (US EPA 2004). The flow rate of each injected component is monitored carefully from an on-site control centre. The composition of the fracturing fluid varies with the coal formation characteristics. The high pressure pumps are attached to the blender unit and then draw the hydraulic fluid and pressurise it for injection into the well to fracture the seams. The fluid is injected into the coal seam at a rate of around 15 barrels per minute and at a pressure of 6 500 psi (Golder Associates 2011). For coal seam gas wells, typically 7 000 barrels (1.1 ML) of fluid are used per well (Golder Associates 2010). However, it is likely that overall fluid volumes will vary depending on the hydraulic fracturing fluid systems being used and the properties of the coal seams being fractured. After the coal seam has been fractured, sand is introduced into the fracturing fluid to prop open the fracture openings. Sand from the sand trailer unit is delivered to the blender unit at a measured rate.

At the end of the fracturing process, gel breakers are added to the fluid to break the gel complex and reduce viscosity of the fracturing fluid so that it can be extracted.

Workers could be exposed to fracturing chemicals during transportation and storage of chemicals and when preparing and injecting the fracturing fluid. Exposure is likely to be mainly dermal, although inhalation of vapours or dust could also occur.

Chemicals required for the fracturing process are delivered on-site and stored in blender units or in support trucks on-site. Although used in low concentrations, large amounts of chemicals are required for the process.

As described in the drilling process, workers involved in the transport and storage of chemicals could be exposed to the chemicals in instances where packaging is breached. Exposure during transport is likely to be minimal except in the case of an accident. Storage of chemicals in large containers or pits at the fracturing site has the potential to contaminate the area if a leak or spill occurs, due to a packaging breach or if the lining of the impoundments become permeable.

Chemical measuring and adding procedures are mostly automated; however, workers involved in these processes could be exposed to chemicals or their vapours during a malfunction of the system. Workers could also be exposed to fracturing chemicals if a splash or spill occurs during mixing/loading procedures, or when joining and cleaning valves or tubing (US EPA 2004).

Transporting huge quantities of sand (that contains silica) for use as a proppant could lead to worker exposure (OSHA 2012). Loading the sand onto and off trucks, onto and through sand movers, along transfer belts and into blenders generates considerable dust, including respirable crystalline silica. Inhalation exposure to silica dust is possible during these activities (Esswein et al. 2012).

Public exposure to chemicals during the transport of hydraulic fracturing fluids is unlikely, but may occur through contact with spilled fluid during a transport incident. Leaks from large storage tanks and mud pits can enter ponds and streams or migrate to groundwater, resulting in the contamination of water that is used for human consumption (UNEP 2012). There is thus a risk of indirect exposure of the public to chemicals through leaks and spills from stored chemicals. Potential off-site public exposure to sediments could occur if the mud pit is drained and sediment left to dry out and contribute to wind-borne dust (Golder Associates 2011).

Exposure of the public to fracturing chemicals is mainly by the oral route – through drinking contaminated water – although dermal exposure could also occur from handling contaminated water. Evaporation and transport of fracturing fluid components in the atmosphere could lead to public exposure to chemicals via the inhalation route (Witter et al. 2010).

A combination of steel casing and cement in the well forms barriers to leaks or flows during drilling, fracturing or production and ensures that high-pressure gas or liquid from drilling or hydraulic fracturing does not escape into shallower rock formations or water aquifers. Failure of these well casings / cement systems could provide migration routes for fracturing fluids into groundwater and aquifers (Manifold 2010), with a potential for public exposure to these chemicals.

Another potential source of public exposure is from the residual hydraulic fracturing fluids within the coal seams and leakage to water sources. Exposure may occur if any fracturing chemicals that remain within the fractured seam migrate to natural springs or water supply bores in close proximity to the coal seam (Golder Associates 2011).

2.3 Potential human exposures associated with handling of flowback and produced waters

Flowback or produced water brought to the surface could contain a number of chemicals, including those present in fracturing and drilling fluids and additional hydrocarbons, volatile organic compounds, metals and radioactive material from subsurface land formation (NYSDEC 2011). The first fluids to flow from the well are usually the last fluids injected (i.e. the water base of the fracturing fluid (Rozell and Reaven 2012).

Flowback and produced water are transported from the production site by tankers or pipelines to storage tanks where they are stored in lined open pits (ponds) or tanks and left to evaporate, stored in closed containment tanks for further treatment, re-injected into the ground or discharged as surface water (GISERA 2014; Clark and Veil 2009; US EPA 2011).

Workers could be exposed to flowback and produced water during loading, transporting or transferring to storage tanks. Containment tanks used for the storage of water can corrode over time, resulting in leaks, or may overflow if they exceed capacity and result in groundwater and surface water contamination. Spills from storage pits or transport pipes, due to broken valves, corroded pipes or cracks in lining have been reported earlier (Veil 2009). The sludge, if left to dry on the surface in waste pits, could potentially contaminate air, water and soil (McKenzie et al. 2012). Leachate from landfills is a frequent cause of groundwater contamination (Klinck and Stuart 1999).

The US Government Accountability Office (US GAO 2012) reported that the range of contaminants found in produced water can include:

- salts, which include chlorides, bromides and sulfides of calcium, magnesium and sodium
- metals, which include barium, manganese, iron and strontium, among others
- oil, grease and dissolved organics, which include benzene and toluene, among others
- NORM
- production chemicals, which may include friction reducers to help with water flow, biocides to prevent growth of microorganisms, and additives to prevent corrosion, among others.

Some chemicals in the fracturing fluid could interact with each other and with NORM under heat and pressure to form new unknown compounds, which are brought to the surface in flowback and produced waters (Allen and MacMillan 2012). Also, in areas with high natural radioactivity, these waters could also contain radioactive contaminants (Resnikoff et al. 2010).

The treatment and disposal of flowback and produced water are critical issues for unconventional gas production, especially in the case of the large amounts of water customarily used for hydraulic fracturing. Once separated out, there are different options available for dealing with this water. The optimal solution is to treat the water and bring it to a sufficient standard to enable it to be either discharged into local rivers or re-used (Clark and Veil 2009). Workers could be exposed to the contaminants present in the water during its treatment for re-use (McKenzie et al. 2012), with the extent of exposure depending on the method used for treatment.

Dermal exposure is also possible during the reinjection procedure. In particular, if the chemicals in the produced water being injected are not compatible with the chemicals already found in rock and the groundwater, precipitates may form and block pores. In this situation, additional injection pressure would be required (Veil 2009).

Public exposure to flowback and produced water could occur if the storage tanks leak or overflow, particularly during heavy rainfall. Exposure would mainly be dermal; however, oral exposure could occur if drinking water gets contaminated.

In conclusion, the main activities or tasks that pose risks to workers are associated with transporting large volumes of chemicals to each well site, mixing chemicals, drilling bores and pumping fluids at high pressure to fracture coal beds.

Transporting, storing and treating flowback and produced water containing chemicals that return to the surface during the fracturing process (including naturally occurring toxic chemicals in the formation that also surface during gas production) are other activities that pose risks to workers if not managed safely.

The general public could be exposed to drilling and fracturing chemicals during their transportation to the drilling and fracturing sites if packaging is breached or if any chemical spill occurs as a result of a vehicular accident. Inhalation and oral exposure to chemicals could occur from contamination of air and drinking water resulting from drilling and fracturing processes.

Following is a summary of the possible exposure pathways for the general public and workers involved in coal seam gas operations:

Public exposure

Oral exposure to chemicals may occur via:

- drinking water
- food (contaminated fruit, vegetables, meat, dairy)
- soil (toddlers putting contaminated soil in their mouths).

Dermal exposure to chemicals may occur via:

- swimming/bathing/washing in contaminated water
- dermal contact with contaminated soil
- dust / vapours, indoor air, soil particulate.

Inhalation exposure to chemicals may occur from:

• dust / vapours, indoor air, soil particulate.

Occupational exposure

Dermal and inhalation exposure to chemicals may occur during:

- transport of chemicals (leaks, splashes, accidents)
- storage of chemicals (packaging breaches)
- handling (formulation of drilling and fracturing fluids spills, splashes)
- incidents during drilling and hydraulic fracturing processes (valve failure, tube leakages etc.)
- storage, use and treatment of produced water
- laboratory analysis of fluids.

3 Human exposures and health impacts from chemicals as reported in literature

3.1 Impacts on workers

Given the types of operations reported, exposure of workers to drilling and hydraulic fracturing chemicals is most likely to occur via inhalation and dermal exposure routes.

Reports on adverse health effects in workers from chemicals used in drilling and hydraulic fracturing are limited. Witter et al. (2008) conducted a detailed review of the available medical literature on the health effects of hazardous substances associated with oil and gas extraction and production. They noted that although health effects from hazardous chemicals used in oil and gas production are well documented, the literature search did not find any studies specifically documenting the health effects of chemicals handled by workers during drilling and hydraulic fracturing for coal seam gas. The authors attributed this to large scale hydraulic fracturing for coal seam gas extraction being a recent phenomenon and that some chemicals used in coal seam gas operations are considered proprietary and their identity is not generally available (Witter et al. 2008). This literature search did not reveal any studies on worker exposure to coal seam gas chemicals.

3.1.1 Inhalation exposure

The main health effects that may arise, based on toxicity of drilling fluid components and possible exposures, include irritation of the respiratory system (Searl and Galea 2011). Water vapour from the use of water-based fluids is noted as a potential cause of respiratory irritation in individuals with irritable airways and of infections associated with water-borne pathogens (Searl and Galea 2011).

In the US, the National Institute of Occupational Safety and Health (NIOSH) has recently conducted air monitoring studies in Pennsylvania and five other states (11 shale gas sites) to evaluate worker exposure to crystalline silica during hydraulic fracturing (Esswein et al. 2012). The transportation and loading of sand into blender hoppers generates considerable respirable dust with resultant exposure of workers. Inhalation of fine dusts of respirable crystalline silica is associated with silicosis, an incurable but preventable lung disease (Davis 1996).

The NIOSH results revealed that worker exposure to respirable crystalline silica consistently exceeded relevant occupational health limits [the Occupational Safety and Health Administration Permissible Exposure Limit (PEL), NIOSH Recommended Exposure Limit (REL), and the American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Value] (Esswein et al. 2012).

Based on workplace observations, NIOSH researchers identified at least seven primary points of dust release or generation from hydraulic fracturing equipment or operations; they were:

• dust ejected from thief hatches (access ports) on top of the sand movers during refilling operations while the machines are running (hot loading)

- dust ejected and pulsed through open side fill ports on the sand movers during refilling operations
- dust generated by on-site vehicle traffic
- dust released from the transfer belt under the sand movers
- dust created as sand drops into, or is agitated within, the blender hopper and on transfer belts
- dust released from operations of transfer belts between the sand mover and the blender
- dust released from the top of the end of the sand transfer belt (dragon's tail) on sand movers.

The study also found that sand mover and blender operators, and workers downwind of these operations, had the highest silica exposures, especially during hot loading. Workers upwind and not in the immediate area of sand movers (e.g. sand delivery truck spotters) also had exposures above the NIOSH REL, possibly from the dust created by traffic at the well site. Worker and area samples collected in enclosed but non-filtered cab vehicles (e.g. chemical and blender trucks) were above the REL, even when spending most of the day in the cab. Worker and area samples collected in enclosed vehicles with air conditioning and filtration (e.g. data vans) had silica exposures below the NIOSH REL.

In an air sampling study conducted in Colorado from 2005 to 2007, researchers found air concentrations of volatile organic chemicals around oil and gas development areas approached or exceeded health-based standards (GCPHD 2010). The extent to which these levels correlated with drilling and hydraulic fracturing activities for unconventional gas activities is not known.

Workers can also be exposed to vapours from drilling fluids by inhalation as well as skin contact, although with the use of water-based drilling fluids, inhalation exposure is expected to be minimal.

In Australia, the CSIRO and the former Australian Government Department of Climate Change and Energy Efficiency investigated fugitive emissions of methane from coal seam gas. The project aimed to make close-in measurements at selected coal seam gas operations to quantify fugitive emission fluxes from various parts of the production process (e.g. wells, surface infrastructure) (Day et al. 2014).

The National Chemicals Assessment project is not examining air emissions of chemicals used in drilling or hydraulic fracturing operations.

3.1.2 Dermal exposure

Published reports examining dermal exposure of workers to chemicals in hydraulic fracturing fluids or produced water were not identified.

In addition to respiratory impacts, a toxicological review of the possible effects associated with exposure to drilling fluid concluded that the main health effects that may arise from exposure to drilling fluids of any composition are irritation of the skin, eyes and respiratory system (Searl and Galea 2011). The exact nature of effects is determined by the chemical composition of the fluid. Physicochemical effects such as defatting of the skin may occur, resulting in drying and cracking of the skin. Defatting of the skin allows compounds to permeate through the skin more readily (McDougal et al. 2000). Based on reports from other occupational settings, repeated dermal exposure to water-based drilling fluids could result in contact dermatitis from repeated wetting of the skin (Searl and Galea 2011).

Most chemicals are absorbed through the skin and can cause other health effects or contribute to the dose absorbed by inhaling the chemical from the air (Broni-Bediako and Amorin 2010). The potential dermal exposure is not limited to the hands and forearms, but could extend to other parts of the body. Actual exposure depends on the drilling fluid system and the use of personal protection equipment (Broni-Bediako and Amorin 2010).

Potential chemical changes in drilling fluids during use and recycling could result in more toxic substances being released (Gardner 2003). Due to elevated temperatures and increased pressures, organic components might break down, or chemical reactions might occur, to form more toxic substances (OGP and IPIECA 2009).

Of particular concern is that the base oil in the drilling fluids, being high in aromatics, might contain, or form, polycyclic aromatic hydrocarbons (PAHs), while muds (drilling fluids) based on alkyl benzenes might break down to yield free benzene (Broni-Bediako and Amorin 2010). However, oil-based drilling fluids are not permitted to be used in coal seam gas operations in some jurisdictions in Australia (NSW Trade and Investment 2012; DEHP 2013a).

No health effects have been reported in literature of workers exposed to drilling or hydraulic fracturing chemicals through contact with flowback or produced water.

3.2 Impacts on the public

A literature review of published health effects from oil and gas developments described earlier (Witter et al. 2008) also examined impacts on public health. No studies were found describing direct impacts of chemicals used during drilling or hydraulic fracturing on the public.

Despite this, significant concern has been reported in literature about the potential for contamination of water supplies and ambient air as a result of unconventional gas production. Concerns have also been raised that drilling and hydraulic fracturing for natural gas, particularly in urban areas, have not been accompanied by studies that demonstrate its safety (Finkel and Law 2011).

Schwartz and Parker (2011) speculate that individuals and communities near shale gas drilling operations may be at risk of exposure not only to air, soil, surface water and groundwater contaminated with multiple chemicals used in hydraulic fracturing, but also to particles of dust and soot and to ionising radiation from flowback and produced waters. According to these authors, many of these exposures will be at low concentrations and may not carry significant risk at any one point in time, but the combined and cumulative effects over the years need to be considered.

On the other hand, the unconventional gas industry has expressed concerns that, due to lack of knowledge, all environmental contaminations are attributed to hydraulic fracturing, although they could result from processes during oil and gas exploration that are distinct from hydraulic fracturing, such as naturally over-pressurised wells and natural gas migration (ALL Consulting 2012).

There are many studies that have assessed the toxicity of chemicals used in drilling and hydraulic fracturing from the viewpoint of public health. These studies compiled lists of products and chemicals used in coal seam gas operations, searched available information on their toxicity and created profiles of possible health effects on the general population arising from exposure to these chemicals (Colborn et al. 2011; Lloyd-Smith and Senjen 2011; McKenzie et al. 2012).

Other studies have measured water and ambient air contaminants around hydraulic fracturing sites and attempted to link exposure to the ill-health experienced by people and

animals living in those areas (CDPHE and DCEED 2010; Gullion et al. 2011; Bamberger and Oswald 2012; McKenzie et al. 2012; Steinzor et al. 2012). The qualitative nature of some of the studies and lack of suitable controls make it difficult to generalise the effects and arrive at robust conclusions.

No long-term population studies comparing public health pre- and post-hydraulic fracturing are currently available (Ehrenberg 2012). The US EPA is currently conducting a detailed study of the environmental and human health impacts of hydraulic fracturing (US EPA 2011). The study aims to examine the full lifecycle of water in hydraulic fracturing, from water acquisition through to the mixing of chemicals and the fracturing process to the post-fracturing stage, including the management of returned and produced water and its ultimate treatment and / or disposal. The study also plans to identify all chemicals used in or released during hydraulic fracturing and summarise available data on the toxicity of chemicals.

The following paragraphs summarise reports and studies on public exposure to chemicals associated with hydraulic fracturing available in the literature. Most of these reports relate to exposure during hydraulic fracturing for shale gas prevalently carried out in the USA as compared to the fracturing of coal seams in Australia.

3.2.1 Inhalation exposure

In the US, ambient air monitoring studies have been carried out in many areas where hydraulic fracturing was conducted. Results indicated emissions of complex mixtures of pollutants from the natural gas resource, tanks containing drilling muds, fracturing fluids and produced water (Walther 2011; Zielinska et al. 2011). Most of these studies were, however, conducted in areas where gas is extracted from shale formations. In Australia, gas is extracted mainly from coal seams and therefore the number, types and concentrations of air contaminants may be different from those observed in the US studies.

In one study, in Sublette County in Wyoming (Walther 2011), ambient concentrations of 51 toxic air contaminants (TACs) were monitored in air samples collected over a 24-hour period, with the aim to describe the exposure of the general population of the county to toxic air contaminants. Screening analysis of the data indicated that there was no potential for significant acute health impacts from the TACs measured in the study.

In another air sampling study carried out in Garfield County in Colorado in 2012, McKenzie et al. (2012) collected and analysed 24-hour ambient air samples for chemical contaminants. Based on the exposure assessments and health indices calculated for residents living less than half a mile from a gas well and those living more than half a mile from a gas well, the authors demonstrated that residents living closer to the fracturing sites had a greater risk of health-related impacts than those living further away.

A recent US report surveyed residents living in 'gas patches' across 14 Pennsylvania counties for health effects. Air and water tests were also conducted at more than half of the 55 households surveyed (Steinzor et al. 2012). After gas drilling began, residents in these communities developed new health problems, thought to be related to exposure to these chemicals. More than 25 different disease symptoms were recorded among the residents, most prevalent being increased fatigue, nasal and throat irritation, shortness of breath and joint pain.

In this study 19 volatile organic compounds (VOCs) including benzene, toluene, ethylbenzene, and xylenes, were detected in air samples. However, because of the shortterm nature of the air canister testing (24 hours) and the single water tests conducted at households, the results were considered to reflect conditions at particular 'moments in time'. Factors that could impact on the testing results, such as the stage of drilling, weather conditions, wind speeds, topography and geology were not taken into account. Colborn et al. (2012) sampled air quality before, during and after drilling and hydraulic fracturing of a new natural gas well pad close to residential areas in the US. Weekly air sampling for one year revealed that the number of non-methane hydrocarbons (NMHCs) and their concentrations were highest during the initial drilling phase and did not increase during hydraulic fracturing. Methylene chloride, a toxic solvent not reported in products used in drilling or hydraulic fracturing, was detected 73 per cent of the time, several times in high concentrations. Methylene chloride and some other NMHCs were not components of drilling or fracturing fluids and the authors suggest that their source and potential exposure scenarios need to be explored with respect to exposure of individuals working on the pads and living nearby.

In Australia, incidents of gas leaks and water contamination due to spills and overflows related to coal seam gas have been reported in Queensland and NSW, although no studies have been carried out examining health effects on workers or people living near coal seam gas sites.

In Tara, southwest Queensland, residents living near coal seam gas activities complained of severe headaches, nausea, vomiting, nose bleeds, rashes, and eye and throat irritation. According to local doctors, these symptoms were consistent with gas exposure (Berry 2012). A recent report also claimed that high levels of hippuric acid were detected in urine samples of a resident in Tara, indicating a possible exposure to toluene (McCarthy 2013).

Several doctors in the Tara area have also raised concerns that residents living near coal seam gas mining operations may be showing symptoms of gas exposure (Turnbull and Shoebridge 2012). However, a recent report by the Queensland Government Department of Health concluded that, based on the available clinical and environmental monitoring data, a clear link could not be drawn between the health complaints by some residents in the Tara region and impacts of the local coal seam gas industry on air, water or soil within the community (Queensland Health 2013).

3.2.2 Dermal exposure / water contamination

Dermal or oral exposure is mainly through contact with contaminated water. Rozell and Reaven (2012) identified five pathways of water contamination resulting from shale gas development activities that could affect the general population in the US: transportation spills, well casing leaks, leaks through fractured rock, drilling site surface discharge, and produced water. These pathways could also be applicable to coal seam gas extraction.

Investigating the impact of gas extraction on communities, Bamberger and Oswald (2012) documented 24 individual cases in the US in which humans (and animals) exposed to natural gas operations and related toxic substances suffered negative health impacts and even death. The study summarised the sources of exposure and health effects observed in farmers and farm animals where hydraulic fracturing had occurred. In the majority of cases, exposure was from contaminated well/spring water (17 incidents), followed by leakage of produced water from impoundments or dumping into creeks (11 incidents). Drilling and hydraulic fluids were accidently spilled in three cases.

In the majority of cases, owners of animals were exposed via well or spring water used for drinking, cooking, showering and bathing. Upper respiratory tract symptoms (including burning of the nose and throat) and burning of the eyes were most commonly reported. Headaches and symptoms associated with the gastrointestinal (vomiting, diarrhoea), dermatological (rashes), and vascular (nosebleeds) systems were also reported. The authors of this study cautioned that this was not a controlled experiment but may illustrate what could happen in areas experiencing extensive gas drilling.

Based on investigations following complaints of objectionable taste and odour in drinking water in Pavillion in Wyoming, the US EPA confirmed that drinking water wells were contaminated with fracturing fluids (DiGiulio et al. 2011). Hydraulic fracturing in that area had occurred at shallow depths. The Agency reported finding methane and dissolved hydrocarbons in several domestic wells. Further testing of water samples, from more domestic wells and soil samples near three surface pit sites, revealed elevated levels of methane and diesel range organics. Based on these results, the EPA determined that enhanced migration of gas had occurred within groundwater at depths used for domestic water supply and to domestic wells (DiGiulio et al. 2011).

According to the New York Department of Environmental Conservation's 2011 *Supplemental generic environmental impact statement* (NYSDEC 2011), spilled, leaked or released chemicals or wastes could flow to a surface water body or infiltrate the ground, reaching and contaminating subsurface soils and aquifers.

However, a recent study by the Energy Institute at the University of Texas at Austin analysed numerous reported contamination incidents associated with shale oil and gas development and concluded that there is at present little or no evidence of groundwater contamination from hydraulic fracturing of shales at normal depths. They did not find any evidence that chemicals from hydraulic fracturing fluid were found in aquifers as a result of fracturing operations (Groat and Grimshaw 2012).

A report prepared by ALL Consulting in the USA has listed some of the most prominently discussed incidents (ALL Consulting 2012). According to the authors of this report, none of the reported incidents were found to be caused by the process of hydraulic fracturing; rather they resulted from casing leaks (methane migration), accidental surface spills or leaks from production pits.

In Australia, a compilation by the Queensland Government of coal seam gas related incidents that occurred in Queensland in the first half of 2011 illustrates that surface contamination from coal seam gas operations was not uncommon. In this period, there were a total of 34 chemical-related incidents such as releases of coal seam gas water to the environment mainly during drilling activities or from faulty/opened valves, or by exceeding discharge limits to groundwater or surface water, set by the environmental authorities. Four instances were related to flooding of coal seam gas water storage dams and one to BTEX contamination. The source of this BTEX contamination was not reported (Rutovitz et al. 2011).

The following table lists some of the reported incidents of chemical releases resulting from gas extraction activities in Australia and overseas. It does not contain a full list of incidents but rather presents a 'sample' of events to illustrate the different incidents that could occur during coal seam gas operations resulting in worker or public exposure to coal seam gas chemicals. Information on coal seam gas incidents in the US was sourced from the ALL Consulting report (2012). Australian incidents are mainly sourced from media reports collated by a non-government organisation and have not been confirmed (Coal Seam Gas News 2012) (Table 3.1).

|--|

Type of release	Cause	Primary contaminant (reported as released)	Location and date of incident			
Incidents reported in Australia						
Uncontrolled release of foamy substance	Well blowout during maintenance	Not reported	Camden NSW, August 2011			
Release of 10 000 litres of saline to the environment	Pipe leakage at water treatment plant	Saline	Pilliga State Forest NSW, June 2011			
Release of untreated water	Overflowing pond due to heavy rain	Saline	Pilliga State Forest NSW, December 2010			
Release of 600 000 litres of water and gas in a farm	Pipeline rupture	Produced water and gas	Moranbah Qld, May 2011			
Release of drilling fluid into Condamine river	Pipeline leakage	Not reported	Western Darling Downs Qld, April 2012			
Release of gas and water from well head	Well blowout	Produced water and gas	Dalby Qld, May 2011			
Diesel spill	Not known	Diesel	Moranbah Qld, May 2011			
Traces of BTEX found in fluid samples from 8 exploration wells	Not known	BTEX chemicals	Surat Basin, West of Miles, October 2010			
Gas leakage	Crack in pipeline leading to well head	Not reported	Darling Downs Qld, September 2011			
Gas leakage	Damage during drilling	Not reported	Chinchilla Qld, May 2012			
Residents complain of odours and health problems	Suspected gas leaks	Not reported	Tara Qld, November 2012			
Overseas incidents						
Gas well blowout and possible groundwater contamination	Well blowout/ overpressure formation	Petroleum hydrocarbons	Wyoming US, August 2006			
Stored water discharge into Parachute Creek	Storage pit leak	Fracturing fluid	Colorado US, January 2008			
Contaminated drinking water supplies	Poorly constructed, sealed or cemented wells	Methane, iron and manganese above PADEP MCLs*	McKean, PA, US, April 2009			
Fluid and chemical release from vessels and piping connections	Equipment failure	Milky white substance	Louisiana US, April 2009			

Literature review: Human health implications

Type of release	Cause	Primary contaminant (reported as released)	Location and date of incident
Surface spill that caused a polluted wetland and a fish kill in Stevens Creek	Two liquid gel spills	Lubricant gel	Dimock, PA, US, September 2009
Release of wastewater	Overflow from a wastewater pit	Hydraulic fracturing fluids	Hopewell, PA, US, December 2009
Surface release	Discharged production fluids into a drainage ditch and through a vegetated area	Produced water	Troy, PA, US, February 2010
Fracturing fluid migration into drinking water well	Abandoned wells	Dark and light gelatinous materials and white fibres	Jackson, W Virginia, US. August 2011

* Pennsylvania Department of Environmental Protection. Maximum Contaminant Levels

4 Approaches to assessing human health risk from chemicals used in drilling and hydraulic fracturing

There are a number of reports in literature that have attempted to assess human health risks from chemicals used in gas extraction from shale or coal seams. The majority of these risk evaluations are of a qualitative nature, where the toxicity of chemicals in drilling and hydraulic fracturing fluid was assessed, but only the *potential* for harm to humans was estimated because of an absence of quantitative exposure data (Broomfield 2012; Bamberger and Oswald 2012; Colborn et al. 2012;). A few studies, however, attempted to quantify risk to workers and the general public by estimating potential exposure to chemicals during the actual hydraulic fracturing procedures or exposure arising from contamination of surface water by leakage of wells or accidental spillages.

The following section reviews different approaches reported in literature for assessing risks to human health from chemicals associated with coal seam gas extraction. The aim of the literature review was to describe and evaluate the strengths and weakness of the different approaches to assessing health risks so as to inform the most appropriate approach to assessing the potential risks associated with surface handling of chemicals in drilling and hydraulic fracturing for coal seam gas extraction.

Risk assessment is generally a four-step process consisting of hazard identification, exposure assessment, dose-response assessment and risk characterisation based on the outcomes of the exposure and dose response assessment.

For unconventional gas operations, the risk characterisation is complex because a combination of different chemicals is used in the drilling and hydraulic fracturing process and chemicals occurring naturally in the coal seam formations are mobilised by these processes. A related issue is whether a mixture of chemicals, each present at less than guidance concentrations, may be hazardous due to additive effects, interactions, or both (ATSDR 2004). Additionally, in assessing the risk of toxic contaminants it is crucial to understand the sources of the contaminants and the pathways through which they move in the environment and factors that affect their concentration and structure along the many transport paths.

For unconventional gas operations, both short- and long-term exposures need to be considered for risk assessment. Individuals such as transport workers may have transient chemical exposures but communities in gas development areas may experience chronic exposures to environmental contaminants.

4.1 Qualitative risk assessments

4.1.1 Walther (2011)

Using the health risk screening methodology recommended by US EPA (2006), Walther (2011) evaluated the potential health impacts from air toxics near hydraulic fracturing sites (not just workplace exposure). The health risk assessment was conducted by comparing monitored concentrations of air toxics with their long-term and short-term screening concentrations (risk-based concentrations that were derived from standardised equations combining exposure information assumptions with toxicity data and were considered by the US EPA to be protective for humans, including sensitive groups, over a lifetime).

Ambient air concentrations of 51 chemicals were measured for a 14-month period at 12 different monitoring sites in the general vicinity of natural gas extraction fields in Sublette County in Wyoming, US. Air samples were collected over a 24-hour period on every sixth day at each of the 12 sites.

Screening concentrations for acute and chronic effects (cancer and non-cancer) for the 51 chemicals were obtained from a variety of sources, such as NIOSH values and US EPA Air Toxics Monitoring Data Sets.

A comparison of the monitored values to their screening concentrations indicated no potential for significant acute or long-term health effects from any of the air toxics measured in this study. The study concluded that the estimated health impacts of the 51 toxicants monitored were not high enough to suggest a need for a more refined health risk assessment of those chemicals in the ambient air in or near Sublette County.

4.1.2 Golder Associates (2011)

Golder Associates conducted a qualitative risk assessment for Santos for their coal seam gas extraction activities in the Roma, Fairview and Arcadia gasfields, located in the Surat and Bowen Basin of central and southeastern Queensland (Golder Associates 2011).

The risk assessment was undertaken in accordance with the national guidelines for risk assessment recommended by enHealth (enHealth 2004) and was conducted in two stages. Stage 1 involved a qualitative assessment of the environmental risks to the receiving environment associated with the injection of hydraulic fracturing fluids into the coal seams. Stage 2 of the assessment included a qualitative review of human health and terrestrial toxicity and assessment of surface and subsurface exposure pathways.

The toxicity of the chemicals used in the hydraulic fracturing process was assessed for persistence, bioaccumulation and aquatic, terrestrial and human health toxicity (PBT). Only chemicals classified as hazardous were selected for assessment. Toxicity information for the chemicals was collected from available international toxicity data. The review of toxicity was semi-quantitative and allowed the chemicals to be categorised as high, moderate or low hazard based on toxicity 'scores' for several parameters such as acute toxicity, carcinogenicity and neurotoxicity. The categories were numerically rated as high (3), moderate (2) and low (1). The overall toxicity of each chemical was generated by calculating the average of all parameters checked for each chemical. Chemicals identified as moderate or high in human toxicity ranking according to this process were considered chemicals of potential concern (COPC) for human health and were selected for further toxicity evaluation. While no 'high' hazard-ranked chemicals were identified as COPCs on the basis of a moderate human health hazard score.

The exposure assessment comprised an evaluation of surface and subsurface exposure pathways and mass balance calculations to identify the amount of each chemical additive of the hydraulic fracturing fluid at an exposure point. For the additives selected as COPCs, fate and transport modelling was used to identify the likely extent of movement from the coal seam gas well.

The results of fate and transport modelling performed for the organic COPCs indicated that the strong sorption capacity of the coal seam aquifers significantly limits the transport potential of the organic hydraulic fracturing fluid components in coal seams. Migration of

most of the organic COPCs was predicted to be less than 5 m beyond the hydraulic fracturing radius of influence over the 1 000 year simulation.

Evaluation of the subsurface fate and transport of the inorganic COPCs identified in this assessment was not considered to be warranted given that all of the inorganic COPCs would either rapidly dissociate into simple ions, would have limited mobility based on physical properties when hydrated (i.e. form a gel consistency), or have health risk characteristics that are not relevant to an aquifer environment (i.e. dust inhalation).

Potential exposure pathways were evaluated for on-site (i.e. within the drill pad; worker exposure), and those relevant for off-site (i.e. anything beyond the drill pad boundary; public exposure). For the off-site exposure assessment, several worst-case scenarios were assumed such as a homestead (adult and child residents) located down gradient of the drill pad with a water supply bore and a creek, and livestock and native flora and fauna present in the surrounding environment. An exposure pathway for a task was considered 'complete' if (a) source of contamination, (b) transport media, (c) exposure point and (d) exposure route could be identified. If any of these steps were not present, the exposure pathway was considered 'incomplete' and no further risk assessment was considered to be required for that scenario.

Exposure pathways for workers on-site were considered to be incomplete on the basis of adequate occupational health and safety (OH&S) procedures in place at work sites that prevented direct contact with chemicals during spills and when handling flowback water or sediments. Similarly, exposure was considered unlikely for all scenarios off-site with the implementation of operational controls including use of liners in storage pits, ensuring well integrity and capping or disposal of sludge.

Based on the hazard and exposure assessments and operational controls on-site and offsite, the overall risk to human health associated with chemicals involved in hydraulic fracturing was considered to be low.

4.1.3 Public health survey

Other risk assessment approaches include public health surveys in areas close to fracturing activities. One study conducted in Pennsylvania, US, by Earthworks, looked at links between health symptoms experienced by people living in the 'gas patches' and the proximity to gas extraction and production facilities (Steinzor et al. 2012). Health surveys were conducted of local residents in this region and the results analysed in relation to contaminants identified through water quality investigations and air quality monitoring.

The survey focused on a range of exposures, health symptoms and disease history. Responses were gathered to identify patterns that occur across locations and to improve understanding of the experiences of participants.

Environmental testing was conducted on the properties of a subset of survey participants (70 people in total) in order to identify the presence of pollutants that might be linked to both gas development and health symptoms. The samples were analysed using US EPA-approved TO-14 and TO-15 methods, which test for a wide range of volatile organic compounds (VOCs) such as BTEX chemicals. The water tests used samples drawn directly from household sinks or water wells and covered the standard Tier 1, Tier 2 and Tier 3 (including VOCs / BTEX) and in one case, Gross Alpha/Beta, Radon and Radium as well.

In total, 34 air tests and 9 water tests were conducted at 35 households in 9 counties. The air test detected a total of 19 VOCs in many of the samples with considerable consistency, although concentrations varied. The water samples revealed many chemicals that are

associated with oil and drilling operations. More than half of the water samples contained methane.

The survey asked questions designed to identify if there might be associations between symptoms and living near particular types of facilities (wells, waste impoundment pits and compressor stations). All the symptoms reported by respondents could potentially be caused by exposure to substances known to be associated with gas and oil facilities. The most prevalent symptoms among all participants were increased fatigue (62 per cent), nasal irritation (61 per cent), throat irritation (60 per cent), sinus problems (58 per cent), eyes burning (53 per cent), shortness of breath (52 per cent), joint pain (52 per cent), feeling weak and tired (52 per cent) and severe headaches (51 per cent).

It was noted that, in general, as the distance from facilities decreases, the percentage of respondents reporting the symptoms increased. For example, when facilities were 1 500 to 4 000 feet away, 27 per cent reported throat irritation; this increased to 63 per cent at 501 to 1 500 feet, and 74 per cent at less than 500 feet. For severe headaches, 30 per cent reported them at the longer distance, but about 60 per cent at the middle and short distances. In general, the closer to gas facilities respondents lived, the higher the rates of symptoms they reported. Many symptoms were commonly reported regardless of the distance from the facility (in particular sinus problems, nasal irritation, increased fatigue, feeling weak and tired, and shortness of breath).

The study concluded that:

- contaminants associated with oil and gas development are present in air and water in many communities where development is occurring
- many residents have developed health symptoms that they did not have before, indicating the strong possibility that they are occurring because of gas development.

The authors, however, contend that because of the short-term nature of the air canister testing (24 hours) and the single water tests conducted at households, the results reflect conditions at particular moments in time. Factors such as the stage of drilling, weather conditions, wind speeds, topography, geology, and whether facilities are in operation or shut may have had an impact on the testing results. In addition, some chemicals may have been present in water or air below detection limits or prior to when the tests were conducted, meaning that other exposures may have also occurred that caused the reported symptoms.

In addition, the project did not investigate additional factors that can influence health conditions or cause symptoms (e.g. through structured control groups in non-affected areas and in-depth comparative health history research).

4.1.4 King (2012)

A novel approach to estimate risk from chemicals associated with natural gas extraction was described by King (2012) in the US. The objective was to identify high risk elements of hydraulic fracturing activities.

Considering different scenarios that could result in environmental pollution and the probabilities that they may occur, a 'Risk Matrix' was created by plotting probable frequencies of occurrence of pollution events against the consequence, rated qualitatively from minimal to catastrophic. Probabilities of events occurring were estimated from historical analysis of hydraulic fracturing activities.

More than 20 potential pollution scenarios were considered and probable exposures (frequency of occurring) from these scenarios were calculated. These included transport of fracturing materials to the well, the specific process of fracturing, recovery of fracturing fluids

from the well prior to production and transport of fracturing materials from the well. Where information was not available, a worst-case scenario was used by imagining a route of transfer (e.g. cement channel, breach of casing etc.) and calculating the amount of fracturing fluid and the associated chemical in that fluid that could possibly be lost via that flow.

Fracturing activities associated with frequent spillages that resulted in unrecoverable toxic pollution were considered to be high-risk events. Activities were considered to be of low risk where the frequency of occurrence of spillages was low and spills were small and of chemicals that were non-toxic and quickly biodegradable.

A series of conclusions were drawn from this risk-matrix approach. For example, there was sufficient confidence that frequency of spills or leaks from high-risk events (transport, storage and well construction) could be reduced by more attention to the root cause of spills or leak events. Similarly, although the impact of spill and leak events were generally low, risks could be decreased further by reducing the number, amount (concentration and / or activity), toxicity and environmental permanence of chemicals used in fracturing. The author concluded that chemical rating systems that focus on these issues should be a part of the planning for any hydraulic fracture treatment. Separate risk analyses would be needed for drilling, production, abandonment and other operations.

4.1.5 Bishop (2011)

Another qualitative risk assessment approach was based on the hypothesis that recent historical performance of the gas industry could be used to predict future environmental and human health impacts (Bishop 2011). For the assessment, detailed information on spill incidents related to natural gas extraction activities in New York State in the period from January 2003 to March 2008 were sourced from official state, federal or industry reports. Chemical and biological hazards associated with chemicals used in extraction processes as well as geogenic contaminants were characterised against adverse health effects reported by people living near fracturing activities.

Based on information on incidents, the authors estimated that over the short term approximately 2 per cent of shale gas well projects in New York will pollute local groundwater and more than one of every six shale gas wells will leak fluids to surrounding rocks and to the surface over the next century.

An assessment of practices indicated that exposure of workers and public to toxic chemicals and noxious bacteria were exacerbated by certain common practices, such as air / foamlubricated drilling and the use of impoundments for flowback fluids. An assessment of chemical hazards noted that some chemicals in ubiquitous use for shale gas exploration and production, or consistently present in process wastes, constitute human health and environmental hazards when present even at extremely low concentrations.

The overall conclusion from this assessment was that further new projects in New York State using current practices were highly likely to negatively impact the environment and human health.

4.1.6 Rozell and Reaven (2012)

Rozell and Reaven (2012), using a probability bounds analysis, assessed the likelihood of water contamination from natural gas extraction in the Marcellus Shale. Probability bounds analyses are used when data are sparse and parameters highly uncertain. The study model identified five pathways of water contamination: transportation spills, well casing leaks, leaks through fractured rock, drilling site discharge and wastewater disposal. Probability boxes were generated for each pathway. The potential contamination risk and epistemic uncertainty (i.e. uncertainties that can be reduced by gathering more data or by refining models)

associated with hydraulic fracturing wastewater disposal were several orders of magnitude larger than other pathways. The epistemic uncertainty was also high for the rare, but serious, retention pond breach that could cause a large drilling site discharge and quite substantial for fluid migrating through fractures to an overlying aquifer.

However, the total uncertainty of fracture leaks was very small compared to the wastewater disposal potential risk and epistemic uncertainty. Even in a best-case scenario, it was very likely that an individual well would release at least 200 m³ of contaminated fluids. Using the best-case median risk determined above, this volume of contaminated water would equate to a few thousand Olympic-sized swimming pools. This potential substantial risk suggested that additional steps be taken to reduce the potential for contaminated fluid release from hydraulic fracturing of shale formations. To accomplish this, the authors have suggested that future research efforts should be focused primarily on wastewater disposal and specifically on the efficacy of contaminant removal by industrial and municipal wastewater treatment facilities.

4.2 Quantitative risk assessments

There are examples of quantitative assessments for unconventional gas where human risks associated with chemicals are quantified as hazard quotients. Hazard quotients are calculated by comparing estimated or measured chemical concentrations in environmental media with concentrations associated with adverse toxic effects.

4.2.1 Colorado Department of Public Health and Environment (2010)

The Colorado Department of Public Health and Environment conducted a risk assessment to investigate the basis for the concern that residents living in close proximity of oil and gas development activities were being exposed to airborne concentrations of toxics that may pose unacceptable health risk via inhalation (CDPHE and DCEED 2010).

For exposure assessment, data from ambient air toxics monitoring conducted previously were used for exposure assessment. The assumption was made that the air a person breathes, both while indoors and outdoors, contains the same concentrations of pollutants as monitored in the air monitoring study. The 95th upper confidence limit of the arithmetic mean concentration of a chemical was used as the Exposure Point Concentration (EPC) in calculating inhalation exposure, according to the US EPA recommendation (US EPA 1998).

Toxicity values for the chemicals were obtained from US EPA's Air Toxics website (US EPA 2017a) or from the Integrated Risk Information System (IRIS) (US EPA 2017b). Of the 86 contaminants reported in the air from previous monitoring studies, inhalation toxicity values were available for only 21 contaminants. Risk assessment was therefore conducted for these 21 contaminants.

Cancer risk was estimated by multiplying the EPC of a chemical by its respective inhalation unit risk (IUR). An IUR is defined as the upper-bound excess lifetime cancer risk estimated to result from continuous exposure to an agent at a concentration of 1 μ g/L in water, or 1 μ g/m³ in air. For example, a unit risk of 2 x 10⁻⁶ per μ g/L means two excess cancer cases are expected to develop per 1 000 000 people if exposed daily for a lifetime to 1 μ g of the chemical in 1 litre of drinking water. To estimate cumulative risk from multiple chemicals detected on a site, the individual risk from each chemical was added to estimate the total risk for the site.

The non-cancer hazard of chemicals was expressed as the hazard quotient (HQ) of the chemical. HQ for each contaminant was calculated as a ratio of its EPC to the reference concentration (RfC) of the substance (HQ = EPC / RfC).

For non-carcinogenic chemicals, HQ for each exposure pathway was summed to develop a hazard index (HI) for that exposure pathway. If the resulting HI was less than 1, it was concluded that no unacceptable risks were present. If the HI was greater than 1, it was deemed appropriate to segregate the chemicals by effect and by mechanism of action and to derive separate hazard indices for each group.

The results in this study indicated that the estimated cumulative lifetime cancer risks for six toxics (of the 21 contaminants whose toxicity values were available) found in the air around the sites were slightly above the high-end of US EPA's acceptable cancer range of 1 to 100 excess cancers per million $(1x10^{-6} \text{ to } 1x10^{-4})$ across all monitoring sites. The major contributors to this risk were formaldehyde and benzene.

Each of the 21 toxics assessed from the site had a chronic non-cancer hazard estimate well below the acceptable value of 1. However, when accounting for the cumulative chronic non-cancer hazards for all 21 toxics, the estimate was just below the acceptable level of 1. The major contributing chemicals to this risk were acetaldehyde, formaldehyde and benzene.

The data showed that concentrations of several COPCs, including benzene, in ambient air were significantly higher near the well pads during well development and completion activities than at other times and places.

The human health risk assessment concluded that:

- natural gas extraction processes release chemicals that are known to impact health
- chemicals emitted into the air from natural gas processes are more likely to impact health than chemicals released into the water or the soil
- exposures from air emissions are likely to be highest during well completion activities
- residents living near a well pad (defined as within half a mile) are more likely to experience health effects than residents living farther away from a well pad (defined as greater than half a mile).

The study recommended that since the risk assessment indicates that exposure to chemicals in the air is more likely to occur than exposure to chemicals in the water or soil, methods to reduce air pollution and monitor the air should be the focus of current and future pollution prevention.

4.2.2 Gradient Corporation (2012)

Gradient Corporation evaluated the human health risks associated with hydraulic fracturing fluid leaks or spills (Gradient 2012). Specifically, the study evaluated the potential for such spills from shale gas operations to impact groundwater and surface water and the human health implications of exposure to hydraulic fracturing constituents if such water is then used for drinking water. The study also examined potential health risks of constituents in flowback water and addressed concerns that hydraulic fracturing fluid constituents might migrate from shale reservoirs and contaminate shallow drinking water aquifers.

To determine chemical concentrations in drinking water, the authors determined dilution attenuation factors (DAF) by modelling soil to groundwater pathways to account for the dilution and attenuation of the chemical constituents as they leach from a spill or leak through the soil to reach a shallow aquifer or mix with steam water. DAFs were calculated using a modified method developed by the US EPA (1996). DAFs were then used to calculate chemical concentrations.

For the upward migration of hydraulic fracturing constituents from shale reservoirs to shallower groundwater, the authors argued that the rate of migration would be extremely

slow and the resulting DAF would be greater than a million-fold because, after the initial fracturing phase and during flowback, any fluid within the gas zone will preferentially move towards the gas well rather than upward. Additionally, any fluid beyond the capture zone of the gas will remain hydraulically isolated at depth.

The following separate scenarios were considered:

- diffuse spills to shallow groundwater
- diffuse spills to surface water (streams)
- sudden spills to shallow groundwater (water wells)
- sudden spills to surface water
- upward migration of fracturing fluid to shallow fresh water aquifers.

For hazard characterisation of the hydraulic fracturing and flowback constituents, a tiered approach was used to identify their risk-based concentrations (RBCs). Preference was given to chemical-specific drinking water maximum concentration levels (MCLs) as these represented federally established acceptable drinking water concentrations for public water supplies. Where MCLs were not available, other criteria such as chronic toxicity data or inhalation standards were used.

The human health risk characterisation for individual chemicals was presented as a hazard quotient (HQ), relating the estimated concentration in drinking water (hydraulic fracturing chemical concentration (C) divided by the dilution attenuation factor (DAF) and the chemical's risk based concentration (RBC):

$$HQ = C \div DAF \div RBC$$
 [Equation 1]

Calculated HQ values less than 1 (i.e. exposure concentration in drinking water is less than the chemical's RBC) indicate that no adverse health effects are anticipated. The study concluded that the potential health risks posed by constituents of hydraulic fracturing fluid and flowback waters in drinking water are insignificant.

4.3 Knowledge gaps

This review of existing literature indicated significant gaps in the understanding of the impact of chemicals associated with coal seam gas (drilling and fracturing fluids) on human health. This is not unexpected because, although hydraulic fracturing has been in use for over four decades, large-scale operations for coal seam gas extraction started only about a decade ago in the USA and much more recently in Australia.

The following major gaps in knowledge about the impacts of unconventional gas are listed below.

- There were no epidemiological studies conducted in coal seam gas workers or in the general populations living close to coal seam gas activity that could be used for risk assessment.
- Limited peer-reviewed studies were available on the relationship between exposure to fracturing chemicals and adverse health effects noted in residents living close to fracturing activities. Most available information was from anecdotal reports of exposure and health effects. More research based on atmospheric monitoring studies is required to establish the links, if any, between coal seam gas activities and public health effects. Data on baseline measurement of ambient air concentrations for air toxics are lacking (CDPHE 2011), as well as baseline studies on the health status of relevant

communities. Concentrations of several chemicals in ambient air that may be directly or indirectly associated with natural gas development and production activities are not known.

- The effects of chemicals on the endocrine system needs to be further investigated (European Commission 2011). Many physiological systems, most notably the endocrine system, are extremely sensitive to very low levels of chemicals; in parts-perbillion or less. The damage may not be evident at the time of exposure but can have unpredictable delayed, life-long effects on the individual and / or their offspring (Colborn et al. 2012). It is possible that, for many of the chemicals used, the methods to monitor their presence at very low concentrations in the wastewater may not be available.
- Exposure assessment is an integral part of a risk characterisation of chemicals or techniques. There is a lack of monitoring information on dermal and inhalation exposure to chemicals at different stages of gas extraction. As a result, a majority of the risk assessments conducted to date have been qualitative, using only the hazard characteristics available for some chemicals and the potential exposures.
- Monitoring of ongoing air, groundwater, surface water and soil levels of contaminants around well pads and centralised water storage facilities will assist in validating modelled exposure assessments.

5 Summary and Conclusions

Coal seam gas (also called coal bed methane) is methane-rich gas sourced from coal seams. It is a type of 'unconventional' gas resource, meaning that the resource has porosity, permeability or other characteristics that differ from those of 'conventional' reservoirs and typically requires stimulation or flow enhancement, such as from hydraulic fracturing, to provide gas flows at economically productive levels.

Coal seam gas is currently the main form of unconventional gas production in Australia. Coal seam gas activities are located mainly in Queensland and NSW with the predominance of Australian on-shore coal seam gas reserves located in the Queensland Bowen and Surat Basins.

The life of a coal seam gas project involves separate stages of exploration, well construction, gas production and well decommissioning. Well construction involves stages of drilling and installation of well infrastructure to prepare for long-term gas production. Gas production requires extracting water from the well (de-watering) to lower the hydrostatic pressure within the coal seam to allow gas to flow.

Drilling requires the use of specialised drilling fluids. During drilling, fluids are circulated and recirculated down the drill string and up the space between the drill string and the hole to clear cuttings, cool and lubricate the drill string and bit, and to apply hydraulic pressure to subsurface formations to prevent fluid and gas from flowing into the well. Drilling fluids consist of a base liquid supplemented with chemical additives, either liquid or solid. Chemical additives in drilling fluids serve various purposes such as to stabilise clay, control pH, inhibit bacterial growth, adjust viscosity and to control fluid losses.

Hydraulic fracturing is a well stimulation (flow enhancement) technique used to increase the flow area for hydrocarbons and water in underground formations by creating or enhancing conductive pathways (fractures) extending outward from the wellbore into the hydrocarbonbearing formation. It is a common stimulation technique in the petroleum industries. For coal seam gas, the technique involves injecting a fluid (commonly water) or foam containing an inert, granular material called a proppant (commonly sand), under high pressure into the coal seam via the wellbore through perforations created in the wellbore casing.

Chemicals are added to hydraulic fracturing fluids for specific purposes. Although exact percentages vary, water and sand (or other types of engineered ceramics) are reported to typically comprise 97 to 99 per cent and chemical additives 1 to 3 per cent of the hydraulic fracturing fluid. Other than water and sand, other specific chemicals serve a variety of functions such as to dissolve minerals, enhance or reduce viscosity or maintain viscosity at elevated temperatures, inhibit bacterial growth, adjust pH, prevent scale formation, reduce friction and prevent metal oxide precipitation.

In addition to gas and water, other chemicals occurring naturally in coal seams may be mobilised from drilling and hydraulic fracturing. Naturally occurring or 'geogenic' chemicals found in produced water include brines, trace metals, naturally occurring radioactive material (NORM), and various liquid hydrocarbons including heterocyclic compounds, aromatic amines, polycyclic aromatic hydrocarbons (PAHs) and other organic materials.

Human exposures to drilling and hydraulic fracturing chemicals can occur at worksites or at more distant locations via environmental contamination. At worksites, the extent of exposures is largely dependent on the use of manual versus automated processes. Workers can be exposed from spill incidents during transport, storage and handling, including mixing

of fluids and during equipment cleaning. Public exposure to drilling and hydraulic fracturing chemicals is possible from transportation incidents, fugitive emissions or releases from storage. The main routes of public exposure are contamination of ambient air and drinking water sources. Both worker and public exposures to drilling and hydraulic fracturing chemicals is also possible via contact with flowback/produced water containing residual chemicals.

Overseas, as well as in Australia, a number of unconventional gas-related chemical release incidents have been reported. However, documented incidents of human exposures to drilling or hydraulic fracturing chemicals are sparse. Some overseas studies have measured water and ambient air contaminants around hydraulic fracturing sites and attempted to link exposures to health complaints. Other studies have assessed the toxicity of drilling and hydraulic fracturing chemicals and compiled profiles of possible health effects.

The literature review identified some knowledge gaps in the understanding of the impact of chemicals associated with coal seam gas (drilling and fracturing fluids) on human health – in particular, the lack of epidemiological and peer reviewed experimental studies on the effects on human health from exposure to hydraulic fracturing chemicals.

Limited peer-reviewed studies are available on the relationship between exposure to fracturing chemicals and adverse health effects noted in residents living close to fracturing activities. There were no epidemiological studies conducted in coal seam gas workers or in the general populations living close to coal seam gas activity that could be used for risk assessment. Most available information is from anecdotal reports of exposure and health effects. Data on baseline measurement of ambient air concentrations for air toxics are lacking. Concentrations of several chemicals in ambient air that may be directly or indirectly associated with natural gas development and production activities are not known.

More research based on well conducted atmospheric monitoring studies is required to establish the links, if any, between coal seam gas activities and public health effects. Exposure assessment is an integral part of a risk characterisation of chemicals or techniques. There is a lack of monitoring information on dermal and inhalation exposure to chemicals at different stages of gas extraction. As a result, a majority of the risk assessments conducted to date have been qualitative, using only the hazard characteristics available for some chemicals and the potential exposures.

Ongoing monitoring of air, groundwater, surface water and soil levels of contaminants around well pads and centralised water storage facilities would provide actual data for exposure assessment and assist in validating modelled exposures.

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