



Australian Government

**Department of Agriculture,
Water and the Environment**

Bureau of Meteorology

Geoscience Australia



Qualitative (screening) environmental risk assessment of drilling and hydraulic fracturing chemicals for the Beetaloo GBA region

Technical appendix for the Geological and Bioregional Assessment: Stage 2

2020



A scientific collaboration between the Department of Agriculture, Water and the Environment,
Bureau of Meteorology, CSIRO and Geoscience Australia

The Geological and Bioregional Assessment Program

The Geological and Bioregional Assessment Program will provide independent scientific advice on the potential impacts from development of selected unconventional hydrocarbon plays on water and the environment. The geological and environmental data and tools produced by the Program will assist governments, industry, landowners and the community to help inform decision making and enhance the coordinated management of potential impacts.

The Program is funded by the Australian Government Department of the Environment and Energy. The Department of the Environment and Energy, Bureau of Meteorology, CSIRO and Geoscience Australia are collaborating to undertake geological and bioregional assessments. For more information, visit <http://www.bioregionalassessments.gov.au>.

Department of the Environment and Energy

The Department designs and implements Australian Government policy and programs to protect and conserve the environment, water and heritage, promote climate action, and provide adequate, reliable and affordable energy. For more information visit <http://www.environment.gov.au>.

Bureau of Meteorology

The Bureau of Meteorology is Australia's national weather, climate and water agency. Under the *Water Act 2007*, the Bureau is responsible for compiling and disseminating Australia's water information. The Bureau is committed to increasing access to water information to support informed decision making about the management of water resources. For more information, visit <http://www.bom.gov.au/water/>.

CSIRO

Australia is founding its future on science and innovation. Its national science agency, CSIRO, is a powerhouse of ideas, technologies and skills for building prosperity, growth, health and sustainability. It serves governments, industries, business and communities across the nation. For more information, visit <http://www.csiro.au>.

Geoscience Australia

Geoscience Australia is Australia's national geoscience agency and exists to apply geoscience to Australia's most important challenges. Geoscience Australia provides geoscientific advice and information to the Australian Government to support current priorities. These include contributing to responsible resource development; cleaner and low emission energy technologies; community safety; and improving marine planning and protection. The outcome of Geoscience Australia's work is an enhanced potential for the Australian community to obtain economic, social and environmental benefits through the application of first-class research and information. For more information, visit <http://www.ga.gov.au>.

ISBN-PDF 978-1-76003-271-5

Citation

Kirby JK, Golding L, Williams M, Apte S, Mallants D, King J, Otalega I and Kookana R (2020) Qualitative (screening) environmental risk assessment of drilling and hydraulic fracturing chemicals for the Beetaloo GBA region. Technical appendix for the Geological and Bioregional Assessment: Stage 2. Department of the Environment and Energy, Bureau of Meteorology, CSIRO and Geoscience Australia, Australia.

Authorship is listed in relative order of contribution.

On 1 February 2020 the Department of the Environment and Energy and the Department of Agriculture merged to form the Department of Agriculture, Water and the Environment. Work for this document was carried out under the then Department of the Environment and Energy. Therefore, references to both departments are retained in this report.

Copyright



© Commonwealth of Australia 2020

With the exception of the Commonwealth Coat of Arms and where otherwise noted, all material in this publication is provided under a Creative Commons Attribution 4.0 International Licence <https://creativecommons.org/licenses/by/4.0/>. The Geological and Bioregional Assessment Program requests attribution as '© Commonwealth of Australia (Geological and Bioregional Assessment Program <http://www.bioregionalassessments.gov.au>)'.

Disclaimer

The information contained in this report is based on the best available information at the time of publication. The reader is advised that such information may be incomplete or unable to be used in any specific situation. Therefore, decisions should not be made based solely on this information or without seeking prior expert professional, scientific and technical advice.

The Geological and Bioregional Assessment Program is committed to providing web accessible content wherever possible. If you are having difficulties with accessing this document please contact bioregionalassessments@awe.gov.au.

Cover photograph

Mataranka Thermal Pools, Beetaloo GBA extended region, October 2018

Credit: Alf Larcher (CSIRO)

Element: GBA-BEE-2-381

Executive summary

A total of 116 chemicals have been identified as being associated with drilling and hydraulic fracturing at shale, tight and deep coal gas operations in the three regions (Cooper, Isa and Beetaloo) of the Geological and Bioregional Assessment (GBA) program between 2011 and 2016. Of the 116 chemicals, 9 were drilling chemicals, 99 were hydraulic fracturing chemicals and 8 were chemicals used for both drilling and hydraulic fracturing. Fifty-eight percent of the chemicals identified in the current study were not assessed in the National Assessment of Chemicals Associated with Coal Seam Gas (CSG) Extraction in Australia (NICNAS, 2017).

A Tier 1 qualitative (screening) environmental risk assessment (ERA) of these chemicals found: (i) 42 chemicals were of 'low concern' and considered to pose minimal risk to aquatic ecosystems, (ii) 33 chemicals were of 'potentially high concern' and (iii) 41 were of 'potential concern'. The identified chemicals of potential concern and potentially high concern would require further site-specific quantitative chemical assessments to be performed to determine risks from specific gas developments to aquatic ecosystems.

Natural rock formations contain elements and compounds (geogenic chemicals) that could be mobilised into flowback and produced waters during hydraulic fracturing. Laboratory-based leachate and extraction tests were undertaken to provide an upper-bound estimate of geogenic chemical mobilisation from target formations in the Beetaloo GBA region; and intended to guide future field-based monitoring, management and treatment options. Leachate tests on powdered rock samples identified several elements that could be substantially mobilised into solutions by hydraulic fracturing fluids: aluminium, cadmium, cesium, cobalt, iron, lanthanum, manganese, neodymium, nickel, lead, silver, yttrium, and zinc. Priority organic chemicals such as phenol, polycyclic aromatic hydrocarbon (PAHs) and total recoverable hydrocarbons (TRHs) were detected in extracts of powdered rock samples. Targeted analysis of PAHs represented a small fraction of the total organic geogenic compounds present in the sample extracts. Hence, the majority of organic compounds in sample extracts (as TRHs) were unidentified and their risk (individual and mixtures) to aquatic environments is unknown.

Companies undertake an environmental risk assessment (ERA) process of gas operations (in consultation with government agencies) that identifies potential hazards (e.g. chemical transport and storage, hydraulic fracturing fluid injection, flowback and produced water storage), determines the likelihood and consequence of a risk occurring, identifies and evaluates control and mitigation measures (e.g. what controls are in place or need to be in place to address the identified risk and how effective are these controls), and develops a monitoring program to ensure controls and management strategies are adequate/effective and for compliance. Despite undertaking these detailed ERAs, there is still public concern surrounding the potential environmental impacts of hydraulic fracturing – particularly, the threats posed by the mixture of industrial chemicals used and geogenic chemicals that could be mobilised and their impacts on water quality. The Stage 3 chemical assessment project will undertake water quality monitoring of future shale gas operations in the Beetaloo GBA region. The project will provide open and transparent reporting of water quality monitoring

data before, during and after hydraulic fracturing to improve community and government understanding in the ERA process (for chemical assessments), controls and monitoring of chemicals; and inform wastewater management and treatment options.

Contents

Executive summary	i
Contributors to the Program	vii
Acknowledgements	viii
Abbreviations and acronyms	ix
Units	x
The Geological and Bioregional Assessment Program	xi
1 Chemicals associated with shale, tight and deep coal gas operations	1
1.1 Introduction	1
1.2 Drilling chemicals	1
1.3 Hydraulic fracturing chemicals	2
1.4 Geogenic chemicals	3
1.5 Aim and objectives	3
2 Qualitative environmental risk assessment of chemicals	5
2.1 Methods	5
2.2 Results and discussion	8
3 Laboratory-based leachate and extraction tests on powdered rock samples from the Isa GBA region – geogenic chemicals	19
3.1 Methods	19
3.2 Results	25
3.3 Discussion	37
4 Conclusions	41
5 Knowledge gaps	43
6 Recommendations	45
References	47
Glossary	51

Figures

Figure 1 An example of overall percentages of water, proppant, and chemical additives in hydraulic fracturing fluid in a deep shale gas well fracturing operation in the Cooper Basin.....	3
Figure 2 Decision tree framework for Tier 1 qualitative (screening) ERA of chemicals associated with shale, tight, and deep coal gas operations (P = persistent; B = bioaccumulative; T = toxic; QSAR = quantitative structure-activity relationships)	9
Figure 3 Tier 1 qualitative ERA of chemicals associated with shale, tight and deep coal gas operations (Refer to Figure 2 for Screen 1 to 4 details; percentage of chemicals in each category are shown in each segment; further breakdown of chemicals of 'potential concern' and 'potentially high concern' are shown in the smaller coloured circles; P = persistent; B = bioaccumulative; T = toxic)	13

Tables

Table 1 Common hydraulic fracturing fluid chemical additives used in shale, tight, and deep coal gas operations.....	2
Table 2 Persistence and bioaccumulation methods and classifications for Tier 1 qualitative ERA	7
Table 3 Acute aquatic ecotoxicity data and classifications for Tier 1 qualitative ERA	8
Table 4 Chemicals identified associated with drilling and hydraulic fracturing at shale, tight, and deep coal gas operations	10
Table 5 Chemicals of ‘potentially high concern’ that are persistent (P) and bioaccumulative (B), and exhibit very high acute toxicity (T)	14
Table 6 Chemicals of ‘potentially high concern’ that are persistent (P) or bioaccumulative (B), and harmful to very toxic (T)	15
Table 7 Chemicals of ‘potentially high concern’ that are not persistent (P) or bioaccumulative (B), and very toxic (T).....	15
Table 8 Composition of the leachate and extraction solutions used in the geogenic chemical studies.....	20
Table 9 Rock samples sourced from drill cores in Beetaloo GBA region	20
Table 10 Limit of reporting for targeted organic compounds in powdered rock sample extracts	22
Table 11 In-house synthetic HFF composition	23
Table 12 Total particulate element concentrations of powdered rock samples (mg/kg).....	26
Table 13 Acid-extractable element (AEE) concentrations from powdered rock samples (mg/kg)	27
Table 14 Ratio (%) of AEE to particulate element concentration for selected elements in powdered rock samples.....	28
Table 15 Dissolved elemental concentrations in SGW leachate solutions	30
Table 16 Dissolved elemental concentrations in dilute HCl leachate solutions	32
Table 17 Dissolved elemental concentrations in HFF leachate solutions	34
Table 18 Effect of pressure on mobilisation of dissolved elemental concentrations in HFF leachate solutions from Tanumbirini-1 (Middle Velkerri; 3235m) powdered rock sample	36
Table 19 Solvent-extractable organic compound concentrations from powdered rock samples (µg/kg).....	38

Contributors to the Program

The following individuals have contributed to the Geological and Bioregional Assessment Program.

Role or team	Contributor(s)
Program Director	Department of the Environment and Energy: Anthony Swirepik
Program Implementation Board	Department of the Environment and Energy: Beth Brunoro, Nicholas Post Bureau of Meteorology: Kirsten Garwood, Kate Vinot CSIRO: Jane Coram, Warwick MacDonald Geoscience Australia: Stuart Minchin, Richard Blewett
Basin Leader	CSIRO: Kate Holland, Cameron Huddlestone-Holmes, Paul Wilkes Geoscience Australia: Steven Lewis
Program management	CSIRO: Karen Barry, Emanuelle Frery, Linda Merrin, Ruth Palmer Department of the Environment and Energy: Mitchell Bouma, Rod Dann, Andrew Stacey, David Thomas, Alex Tomlinson
Product integration and stakeholder engagement	CSIRO: Clare Brandon, Justine Lacey, Michelle Rodriguez, Sally Tetreault-Campbell
Analysis and visualisation	CSIRO: Dennis Gonzalez, Steve Marvanek Geoscience Australia: Adrian Dehelean, Chris Evenden, Chris Lawson, Bianca Reese, Nigel Skeers, Murray Woods
Basin geology and prospectivity	Geoscience Australia: Lisa Hall (Discipline Leader), Adam Bailey, George Bernardel, Barry Bradshaw, Donna Cathro, Merrie-Ellen Gunning, Amber Jarrett, Megan Lech, Meredith Orr, Ryan Owens, Tehani Palu, Martin Smith, Liuqu Wang
Chemical assessment	CSIRO: Jason Kirby (Discipline Leader), Simon Apte, Lisa Golding, Rai Kookana, Dirk Mallants, Michael Williams
Data management and transparency	Bureau of Meteorology: Andre Zerger (Discipline Leader), Derek Chen, Trevor Christie-Taylor, Donna Phillips CSIRO: Nicholas Car, Philip Davies, Stacey Northover, Matt Stenson Geoscience Australia: Matti Peljo
Hydrogeology	Geoscience Australia: Tim Ransley (Discipline Leader), Sam Buchanan, Scott Cook, Prachi Dixon-Jain, Bex Dunn, Tim Evans, Éamon Lai, Bruce Radke, Baskaran Sundaram
Impact analysis	CSIRO: David Post (Discipline Leader), Brent Henderson, Dane Kasperczyk, James Kear, Regina Sander
Impacts on protected matters	CSIRO: Anthony O'Grady (Discipline Leader), Alexander Herr, Craig MacFarlane, Justine Murray, Chris Pavey, Stephen Stewart
Spatial analysis	CSIRO: Dennis Gonzalez, Steve Marvanek Geoscience Australia: Adrian Dehelean, Murray Woods, Nigel Skeers
Water quantity	CSIRO: Russell Crosbie (Discipline Leader), Jorge Martinez Praveen Kumar Rachakonda, Matthias Raiber, Yongqiang Zhang, Hongxing Zheng

Acknowledgements

The Beetaloo Stage 2 baseline and technical products were reviewed by several groups:

- Internal Peer Review Group: Anu Kumar and Grant Douglas
- Technical Peer Review Group: Andrew Boulton, Peter McCabe, Catherine Moore and Jenny Stauber
- State and Territory Government Science Technical Review: This group includes scientists from the Northern Territory Government.

Abbreviations and acronyms

Abbreviation/acronym	Definition
AEE	acid extractable element
B	bioaccumulation
BCF	Bioconcentration factor
CSG	coal seam gas
ERA	environmental risk assessment
GBA	Geological and Bioregional Assessment
HFF	hydraulic fracturing fluid
HCl	hydrochloric acid
IMEA	Impact Modes and Effects Analysis
NEPM	National Environmental Protection Measure
NORM	Naturally occurring radioactive material
P	persistence
PAH	polycyclic aromatic hydrocarbon
SGW	synthetic groundwater
T	toxicity
TOC	total organic carbon
TRH	total recoverable hydrocarbon

Units

Unit	Description
d	days
hr	hours
µg/g	micrograms per gram
µg/kg	micrograms per kilogram
µg/L	micrograms per litre
µm	micrometer
g	gram
g/L	grams per litre
KPa	kiloPascal
min	minute
Molarity (M)	moles per litre
m/v	mass per volume
mg/L	milligrams per litre
mL	millilitres
°C	degrees Celsius
rpm	revolutions per minute
v/v	volume per volume

The Geological and Bioregional Assessment Program

The \$35.4 million Geological and Bioregional Assessment (GBA) Program is assessing the potential environmental impacts of shale and tight gas development to inform regulatory frameworks and appropriate management approaches. The geological and environmental knowledge, data and tools produced by the Program will assist governments, industry, landowners and the community by informing decision making and enabling the coordinated management of potential impacts.

In consultation with state and territory governments and industry, three geological basins were selected based on prioritisation and ranking in Stage 1: Cooper Basin, Isa Superbasin and Beetaloo Sub-basin. In Stage 2, geological, hydrological and ecological data were used to define 'GBA regions': the Cooper GBA region in Queensland, SA and NSW; the Isa GBA region in Queensland; and the Beetaloo GBA region in NT. In early 2018, deep coal gas was added to the assessment for the Cooper GBA region, as this play is actively being explored by industry.

The GBA Program will assess the potential impacts of selected shale and tight gas development on water and the environment and provide independent scientific advice to governments, landowners, the community, business and investors to inform decision making. Geoscience Australia and CSIRO are conducting the assessments. The Program is managed by the Department of the Environment and Energy and supported by the Bureau of Meteorology.

The GBA Program aims to:

- inform government and industry and encourage exploration to bring new gas supplies to the East Coast Gas Market within five to ten years
- increase understanding of the potential impacts on water and the environment posed by development of shale, tight and deep coal gas resources
- increase the efficiency of assessment and ongoing regulation, particularly through improved reporting and data provision/management approaches
- improve community understanding of the industry.

The GBA Program commenced in July 2017 and comprises three stages:

- **Stage 1 Rapid regional basin prioritisation** identified and prioritised geological basins with the greatest potential to deliver shale and/or tight gas to the East Coast Gas Market within the next five to ten years.
- **Stage 2 Geological and environmental baseline assessments** is compiling and analysing available data for the three selected regions to form a baseline and identify gaps to guide collection of additional baseline data where needed. This analysis includes a geological basin assessment to define structural and stratigraphic characteristics and an environmental data synthesis.
- **Stage 3 Impact analysis and management** will analyse the potential impacts to water resources and matters of environmental significance to inform and support Commonwealth and Territory management and compliance activities.

The PDF of this report and the supporting technical appendices are available at

<https://www.bioregionalassessments.gov.au/geological-and-bioregional-assessment-program>.

About this report

Presented in this technical appendix is a qualitative assessment of chemicals associated with drilling and hydraulic fracturing in the three GBA regions (Beetaloo, Cooper and Isa). More detailed information is presented regarding the chemicals associated with shale, tight and deep coal gas operations, a qualitative (screening) risk assessment of these chemicals, and investigations into the geogenic chemicals (naturally occurring contaminants) that may be mobilised into flowback and produced waters by hydraulic fracturing activities. The structure and focus of the synthesis report and technical appendices reflect the needs of government, industry, landowners and community groups.

Technical appendices

Other technical appendices that support the geological and environmental baseline assessment for the Beetaloo GBA region are:

- Orr ML, Bernardel G, Owens R, Hall LS, Skeers N, Reese B and Woods M (2020) Geology of the Beetaloo GBA region.
- Hall LS, Wang L, Bailey AHE, Orr ML, Owens R, Jarrett, A, Lech ME, Skeers N, Reese B and Woods M (2020) Petroleum prospectivity of the Beetaloo Sub-basin.
- Evans TJ, Radke BM, Martinez J, Buchanan S, Cook SB, Raiber M, Ransley TR, Lai ÉCS, Skeers N, Woods M, Evenden C, Cassel R and Dunn B (2020) Hydrogeology of the Beetaloo GBA region.
- Pavey C, Herr A, MacFarlane CM, Merrin LE and O'Grady AP (2020) Protected matters for the Beetaloo GBA region.
- Kear J and Kasperczyk D (2020) Hydraulic fracturing and well integrity review for the GBA regions.

All maps for the Beetaloo GBA region use the Map Grid of Australia (MGA) projection (zone 53) and the Geocentric Datum of Australia 1994 (GDA 1994).

1 Chemicals associated with shale, tight and deep coal gas operations

1.1 Introduction

Industrial chemicals are required in shale, tight and deep coal gas operations for activities such as drilling, cementing, well construction and completion, well clean-up, hydraulic fracturing, and waste treatment. The composition and concentration of chemicals will depend on site-specific conditions such as the geology and mineralogy of formations, environmental conditions such as temperature and pressure, and requirements to maintain well integrity and production. The managed use or accidental release of chemicals (industrial and geogenic (natural)) may have negative impacts on local and regional water quality (surface water and groundwater) and water-dependent ecosystems if not adequately controlled or managed.

Companies undertake an ERA process of gas operations (in consultation with government agencies) that includes identifying potential hazards associated with (e.g. chemical transport and storage, hydraulic fracturing fluid injection, flowback and produced water storage), determines the likelihood and consequence of a risk event occurring, identifies and evaluates control and mitigation measures (e.g. what controls are in place or need to be in place to address the identified risk and how effective are these controls), and develops a monitoring program to ensure controls and management strategies are adequate/effective and for compliance.

1.2 Drilling chemicals

Shale, tight, and deep coal gas operations will require the construction of a well to access formations at depths to liberate the gas reserves. The wells are constructed to provide the necessary integrity and isolation (e.g. from groundwater) during the operational phase and post-decommissioning. As the well is being drilled, a series of metal casings are installed and cemented to provide the well stability, integrity, and isolation from aquifers and formations. The target formation(s) for gas production are accessed at specific well depths by perforating (creating small holes) the well casing and cement using small explosive charges or guns. Well pressure is tested at different stages during drilling and completion prior to hydraulic fracturing to monitor and confirm the well integrity.

Industrial chemicals are used to support the effectiveness and efficiency of drilling and maintenance of well integrity. The chemical additives are used for roles such as: (i) mobilise and remove cuttings; (ii) lubricate and support the drill bit and assembly; (iii) reduce friction; (iv) facilitate cementing; (v) minimise damage to formations; (vi) seal permeable formations; and (vii) prevent corrosion and bacterial growth.

Drilling wastes (e.g. muds and cuttings) are disposed of on-site in contained and often lined pits, used for beneficial purposes by the company (pending the necessary approvals and it being fit for purpose) and/or transported off-site to an approved treatment or disposal facility.

1.3 Hydraulic fracturing chemicals

Hydraulic fracturing involves the injection of fluids with chemical additives under high pressure into target formations to fracture the rock to create high-conductivity gas flow paths to the well. Common chemical additives in hydraulic fracturing fluids for shale, tight and deep coal gas operations are listed in Table 1.

Table 1 Common hydraulic fracturing fluid chemical additives used in shale, tight, and deep coal gas operations

Chemical additive	Purpose
Acid/solvent	Removes mineral scales and deposits, and cleans the wellbore prior to hydraulic fracturing stimulation; dissolves minerals and initiates fractures in formations
Buffer/acid	Adjusts pH to maintain the effectiveness of fluid components and iron control
Biocide	Prevents or limits bacterial growth that can result in clogging, unwanted gas production, and corrosion
Clay stabiliser	Prevents swelling or shifting in formations
Crosslinking agent	Used to link polymers or gelling agent to improve cohesion, adhesion and thermal stability, and maintain fluid viscosity
Inhibitor mineral scales and deposits	Prevents build-up of material on sides of well casing and surface equipment; iron control agent to prevent precipitation of metal oxides, such as iron oxides and hydroxides
Friction reducer	Minimises friction of the hydraulic fracturing fluid
Corrosion inhibitor	Prevents damage to the wellbore and corrosion of pipes
Surfactant	Allows for increased matrix penetration and aids in recovery of water used during hydraulic fracturing
Proppant	Holds open fractures to allow gas flow
Gelling agent/viscosifier	Adjusts fluid viscosity and thickens fluid in order to suspend the proppant
Breaker/deviscosifier	Degrades or breaks down the gelling agent/viscosifier

In general, the majority of hydraulic fracturing fluid consists of water (>97%), with smaller proportions of proppant (e.g. sand) and chemical additives (Figure 1).

The well pressure and volume of hydraulic fracturing fluids added and recovered are routinely monitored in wells during stimulation to assess well integrity and optimise gas production. Typically, flowback and produced water, and liquid from the gas separator, are directed to storage locations/ponds/tanks (above or below ground), which have specifications dependent on the environmental conditions and requirements at the well site. Depending on the water quality, environmental conditions and treatment/management costs, the stored wastewater could be: (i) treated on-site (e.g. reverse osmosis); (ii) reused, or recycled on-site (e.g. dust suppression); (iii) used for beneficial purposes by the company or a third party (e.g. irrigation pending the necessary approvals and it being fit for purpose); (iv) evaporated on-site in ponds to a solid waste or brine for storage in a controlled manner; (v) reinjected to deep aquifers (pending the necessary approvals); or (vi) transported and disposed off-site at an approved treatment/disposal facility.

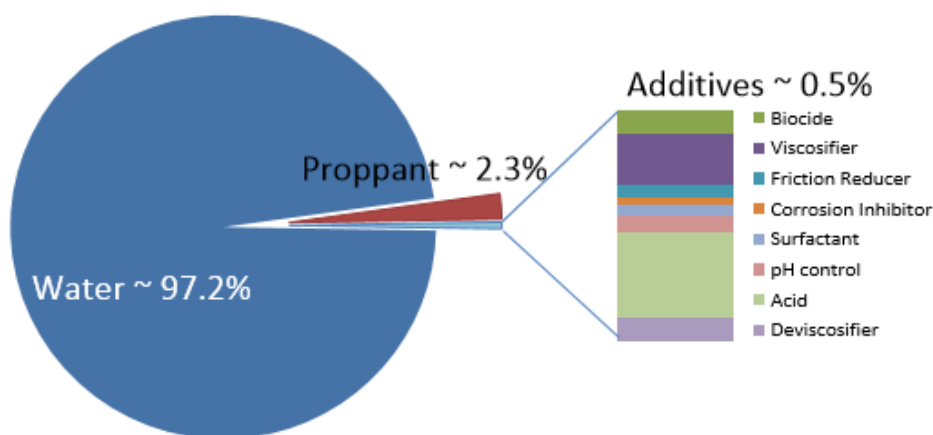


Figure 1 An example of overall percentages of water, proppant, and chemical additives in hydraulic fracturing fluid in a deep shale gas well fracturing operation in the Cooper Basin

Source: figure reproduced from Beach Energy and RPS (2012)

Element: GBA-BEE-2-282

1.4 Geogenic chemicals

Concerns surrounding the use of hydraulic fracturing have mainly centred on potential effects of a range of industrial chemicals that comprise, albeit an overall small percentage (Figure 1), of the fluids. However, shale, tight and deep coal gas rocks/formations are known to contain a number of geogenic (natural) occurring chemical constituents that could be mobilised into solutions during hydraulic fracturing (Ziemkiewicz and Thomas He, 2015; Harrison et al., 2017). These geogenic chemicals (compounds and elements) include nutrients, salinity (e.g. chlorides), carbonates, organics (e.g. PAHs and phenols), metals and metalloids (e.g. arsenic, manganese, barium, boron and zinc) and naturally occurring radioactive materials (NORMs) (e.g. isotopes of radium, thorium, and uranium). The composition and concentration of geogenic chemicals in flowback and produced waters will depend on many factors including: (i) geology and mineralogy of formations; (ii) surface area of the fracture network exposed to hydraulic fracturing fluids; (iii) composition and concentration of chemicals used in hydraulic fracturing; (iv) residence time of hydraulic fracturing fluids in formations; (v) operational and environmental conditions (e.g. volumes added and recovered, temperature, pressure); and (vi) chemical reactions (e.g. adsorption, complexation, precipitation, aggregation, degradation and transformations).

1.5 Aim and objectives

The aim of the Stage 2 chemical screening study was to gain a better understanding of risks of chemicals to surface water and groundwater quality and aquatic ecosystems from shale, tight, and deep coal gas operations in Australia. The assessment did not include chemicals used in shale oil development. The objectives were:

1. To conduct a Tier 1 qualitative (screening) ERA for chemicals identified associated with shale, tight and deep coal gas operations in the three GBA regions in Australia; and
2. To identify geogenic chemicals (compounds and elements) that could be mobilised into flowback and produced waters from powdered rock samples sourced from shale gas target formations in the Beetaloo GBA region due to hydraulic fracturing.

1 Chemicals associated with shale, tight and deep coal gas operations

2 Qualitative environmental risk assessment of chemicals

2.1 *Methods*

2.1.1 Framework for ERA of chemicals associated with shale, tight, and deep coal gas operations

An ERA provides for a systematic and transparent approach for evaluating the likelihood and consequences that adverse ecological effects may occur due to exposure to one or more stressors (e.g. chemicals) (USEPA, 1992; Norton et al., 1992). The Department of Environment and Energy has outlined a framework for performing an ERA of chemicals associated with CSG extraction in Australia (Department of the Environment and Energy, 2017). This framework provides a sound basis for undertaking an ERA of chemicals associated with shale, tight and deep coal gas operations in Australia.

There are two main approaches for undertaking an ERA depending on the availability of data, information, and resources (Department of the Environment and Energy, 2017; US EPA, 2004):

- Qualitative assessment: characterisation of hazards and effects, describes risk in terms of specific rank categories such as 'high', 'medium' or 'low' through an assessment of available data on persistence, bioaccumulation, and ecotoxicity; and is often based on expert judgement; and
- Quantitative assessment: measures risk on some defined scale, often expressed in terms of a numerical value such as a risk or hazard quotient and takes uncertainty and mitigation practices into account. Deterministic and probabilistic approaches can be used (USEPA, 2015):
 - Deterministic approaches use point estimates of exposure and effects to predict potential risks; and
 - Probabilistic approaches account for uncertainty in predicting risk by deriving probabilistic estimates of risk. The approaches use an observed range or statistical distribution of estimates of exposure and effects to predict potential risks.

A tiered approach to ERA is often used to provide a systematic way of evaluating risk that is proportional to resources, complexity, and cost (Department of the Environment and Energy, 2017; US EPA, 2004). The tiers progress in complexity and refinement from Tier 1 to Tier 3 and can be broadly described as:

- Tier 1: screening-level analysis using conservative assumptions (qualitative assessment);
- Tier 2: intermediate-level analysis using site-specific exposure assumptions and scenarios, with more sophisticated qualitative and quantitative uncertainty analysis; and
- Tier 3: advanced analysis using probabilistic exposure scenario analysis techniques, which incorporate quantitative assessment of variability and uncertainty.

A Tier 1 qualitative (screening) ERA generally has predetermined decision criteria to answer whether a potential environmental risk exists ('yes/no' questions). In higher tiers, the questions change to 'what', 'where', and 'how great' is the risk?

In this study, a Tier 1 qualitative chemical screening was undertaken as an initial step in the ERA chemical assessment process (on chemical data sourced at the time of the study) to determine if a potential risk exists from chemicals to aquatic ecosystems. If a potential risk was identified for chemicals, they would site-specific quantitative chemical assessments to be undertaken to determine risks from specific gas development to aquatic ecosystems.

2.1.2 Data sourcing

Chemicals used in drilling and hydraulic fracturing associated with shale, tight and deep coal gas operations in GBA regions in South Australia, Queensland and Northern Territory between 2011 and 2016 were identified from a range of sources; for example, industry environmental impact assessment reports (AECOM Australia Pty Ltd, 2017; Beach Energy and RPS, 2012), industry supplied data and information (Armour Energy Ltd; ICON Energy), drilling and hydraulic fracturing reports (Northern Territory Government, 2018 (<https://dpir.nt.gov.au/mining-and-energy/public-environmental-reports/chemical-disclosure-reports>)) and information and data provided to The Independent Scientific Inquiry into Hydraulic Fracturing of Onshore Unconventional Reservoirs in the Northern Territory (Northern Territory Government, 2018b). The chemicals were identified by their unique Chemical Abstracts Services Registry Numbers (CAS RN).

Specific chemical properties of interest for the Tier 1 ERA included water solubility, octanol-water partition coefficient ($\log K_{ow}$), volatility (Henry's constant), biodegradation (half-life), and bioconcentration factors (BCF =uptake of the chemical into aquatic organism from water only exposures) (Geological and Bioregional Assessment Program, 2018). Data for some chemical properties could be estimated using the US EPA Estimation Programme Interface (EPI Suite; (US EPA, 2018). Estimated properties were based on the Simplified Molecular Input Line-Entry System (SMILES), used to model the various physicochemical and fate parameters (Geological and Bioregional Assessment Program, 2018). For estimates of biodegradation (where biodegradation data could not be sourced from the literature), a number of models were used including Biowin 1 (linear model), Biowin 2 (non-linear model), Biowin 3 (ultimate biodegradability), Biowin 4 (ready biodegradability), Biowin 5 (Ministry of International Trade and Industry (MITI) linear model), Biowin 6 (MITI non-linear model) and Biowin 7 (anaerobic model) (Boethling et al., 1994; Meylan et al., 2007). The Biowin models 1, 2, 5 and 6 gave an indication of the ready biodegradability of chemicals based on similarity of structural fragments that were found to be important factors in training and validation datasets. Biowin models 3 and 4 gave an indication of the length of time for transformation and mineralisation of the parent compound based on expert opinion related to training datasets. Time for degradation was based on periods including hours, days, weeks, months and longer based on cumulative expert opinions. Biowin 7 gave an indication of the likelihood of rapid biodegradation under methanogenic conditions, based on similarity of fragments in a training dataset. Where there was an indication of a chemical not being readily biodegradable (under anaerobic and aerobic conditions) through available literature data or using Biowin models 1, 2, 5, 6 and 7 or being slowly biodegradable (weeks-months) based on Biowin

models 3 and 4, the Tier 1 ERA conservatively assessed the chemical as being potentially persistent.

The sourced ecotoxicology data for chemicals consisted mainly of acute effect concentrations (EC₅₀ values) or acute lethal concentrations (LC₅₀ values) which is the chemical concentration to cause a 50% effect or reduce survival by 50%, respectively (Geological and Bioregional Assessment Program, 2018). These data were collected for aquatic biota from at least three trophic levels represented by a freshwater alga, a water flea and a fish using standard testing protocols. The lowest effect concentration (i.e. highest toxicity) was used to represent toxicity for each chemical as a conservative approach to the Tier 1 ERA (Geological and Bioregional Assessment Program, 2018). Where no experimental toxicity data were available for organic compounds, ECOSAR 2.0 software (US EPA, 2017) was used to predict acute toxicity to aquatic biota based on quantitative structure activity relationships (QSAR). The assessment also utilised chronic ecotoxicity data where they could be sourced from the literature using standard testing protocols as a line of evidence when best professional judgement was required (Geological and Bioregional Assessment Program, 2018).

2.1.3 Qualitative environmental risk assessment

A Tier 1 qualitative (screening) ERA was performed on drilling and hydraulic fracturing fluid chemicals (data that could be sourced at the time of the study) identified being used in shale, tight, and deep coal gas activities in three GBA regions during 2011-2016. The Tier 1 assessment used a decision tree framework (Figure 2) that evaluates sourced data for chemicals in relation to their persistence (P), bioaccumulation (B) and toxicity (T) to aquatic organisms (Table 2; Table 3) (Department of the Environment and Energy, 2017). The main exposure pathway for chemicals if released during shale, tight and deep coal gas operations will likely occur through water (surface water and groundwater); hence, this assessment focused on the potential effects to aquatic organisms. A conservative (precautionary) approach (e.g. P, B, T data sourced only from standard testing protocols and international recognised ERA organisations/agencies and models, and assessments did not make assumptions based on chemical classes or groupings) was applied to the evaluation of chemical and ecotoxicity data and in the Tier 1 qualitative ERA.

Table 2 Persistence and bioaccumulation methods and classifications for Tier 1 qualitative ERA

Method	Result	Classification
Water/sediment: Test No.308: Aerobic and Anaerobic Transformation in Aquatic Sediment Systems (OECD TG 308)	> 60-d half-life in water	Persistent
Biodegradability tests (OECD301A-F)	Sufficient degradation over 10 d - 28 d window	Readily biodegradable – Not Persistent
Biodegradability tests (OECD302A-C)	< 20% degradation	Persistent
Bioconcentration factor (BCF)	> 2000	Bioaccumulative
In the absence of BCF	$\log K_{ow} \geq 4.2$	Bioaccumulative

Source: Department of the Environment and Energy (2017)

Table 3 Acute aquatic ecotoxicity data and classifications for Tier 1 qualitative ERA

Toxicity data*	Lowest acute toxicity value	Classification
3 trophic levels: Alga or other aquatic plants: 72- or 96- h EC50 Crustacea: 48- h EC50 Fish: 96 h LC50	> 100 mg/L	Low concern
3 trophic levels: Alga or other aquatic plants: 72- or 96- h EC50 Crustacea: 48 h EC50 Fish: 96 h LC50	> 10 but ≤100 mg/L	Harmful
3 trophic levels: Alga or other aquatic plants: 72- or 96- h EC50 Crustacea: 48- h EC50 Fish: 96- h LC50	> 1 but ≤ 10 mg/L	Toxic
3 trophic levels: Alga or other aquatic plants: 72- or 96 h EC50 Crustacea: 48- h EC50 Fish: 96- h LC50	≤ 1 mg/L	Very toxic

*Data may be experimental or predicted values from ECOSAR 2.0
Source: Department of the Environment and Energy (2017)

2.2 Results and discussion

2.2.1 Chemicals associated with shale, tight, and deep coal gas operations in GBA regions of Australia

A total of 116 chemicals were identified for use in drilling and hydraulic fracturing at shale, tight and deep coal gas operations between 2011 and 2016 (Table 4) (Geological and Bioregional Assessment Program, 2018). Of the 116 chemicals identified, 9 were drilling chemicals, 99 were hydraulic fracturing chemicals, and 8 were chemicals used for both activities. An additional 32 proprietary chemicals (in products) were identified as being used for drilling and hydraulic fracturing but are not assessed further due to imitations in public disclosure of information.

A similar number of chemicals (n=113) were identified as associated with CSG extraction in Australia (NICNAS, 2017). Fifty-eight percent of the chemicals (n=67) identified in the current study were not assessed in the National Assessment of Chemicals Associated with CSG extraction (NICNAS, 2017) (Table 4). Of the 67 chemicals not previously assessed, a Tier 1 qualitative ERA found 16 chemicals were of ‘low concern’, 28 chemicals were of ‘potential concern’ and 23 chemicals were of ‘potentially high concern’. The additional chemicals identified in this study for shale, tight and deep coal gas operations may be due to site-specific requirements needed for higher temperatures and pressure, geology and mineralogy of the formations, scale and biofilm build-up, fluid stability and viscosity, proppant transport, improved gas extraction and efficiency, and a move by industry towards ‘greener-safer’ options.

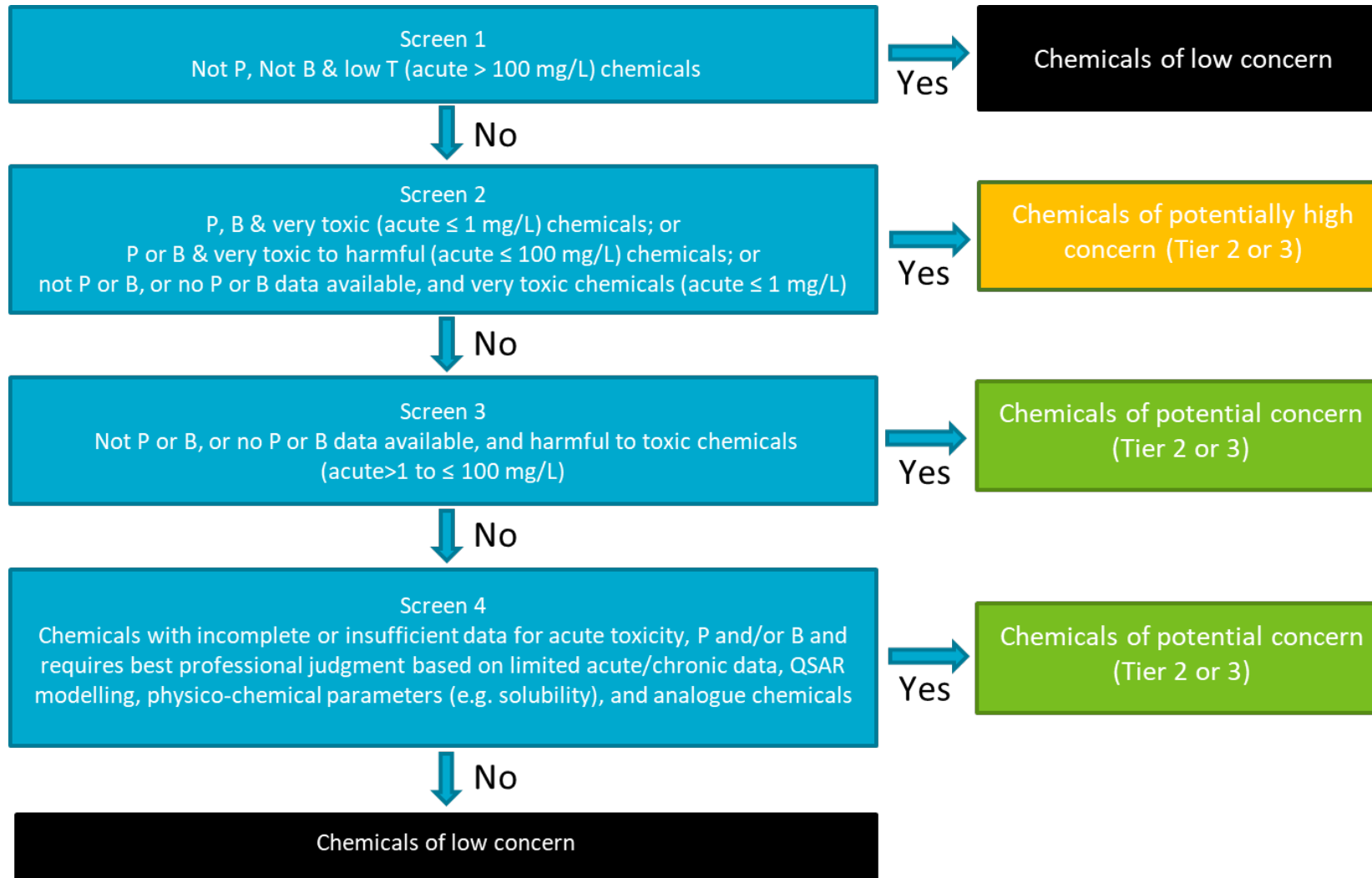


Figure 2 Decision tree framework for Tier 1 qualitative (screening) ERA of chemicals associated with shale, tight, and deep coal gas operations (P = persistent; B = bioaccumulative; T = toxic; QSAR = quantitative structure-activity relationships)

Source: Geological and Bioregional Assessment Program (2018)

Element: GBA-BEE-2-283

Table 4 Chemicals identified associated with drilling and hydraulic fracturing at shale, tight, and deep coal gas operations

#	Chemical name	CAS RN	#	Chemical name	CAS RN
1	1-Benzyl quinolinium chloride	15619-48-4	59	Glyoxal	107-22-2*
2	1-Benzyl methyl pyridinium chloride	68909-18-2	60	Guar gum	9000-30-0*
3	1,2,4-Trimethylbenzene	95-63-6	61	Heavy aromatic solvent naphtha (petroleum)	64742-94-5
4	2,6-Octadien-1-ol, 3,7-dimethyl-, (2E)-	106-24-1	62	Hemicellulase	9025-56-3*
5	2,6-Octadien-1-ol, 3,7-dimethyl-, (2Z)-	106-25-2	63	Hexamethylene glycol (1,6-Hexanediol)	629-11-8
6	2-Bromo-2-nitro-1,3-propanediol	52-51-7*	64	Hydrochloric acid	7647-01-0*
7	2-hydroxy-N,N,N-trimethylethanaminium chloride (choline chloride)	67-48-1*	65	Hydrotreated light distillate (C13-C14 isoparaffin)	64742-47-8*
8	2-Mercaptoethyl alcohol	60-24-2	66	Hydroxypropyl guar	39421-75-5
9	2-Methyl-4-isothiazol-3-one	2682-20-4*	67	Isopropanol	67-63-0*
10	2-Propenoic acid, polymer with sodium phosphinate	129898-01-7	68	Kyanite (Al ₂ O(SiO ₄))	1302-76-7
11	2-Propenoic acid, 2-methyl-, polymer with 2-methyl-2-((1-oxo-2-propenyl)amino)-1-propanesulfonic acid monosodium salt	136793-29-8	69	Magnesium chloride	7786-30-3*
12	5-Chloro-2-methyl-4-isothiazolol-3-one	26172-55-4*	70	Magnesium nitrate	10377-60-3*
13	Acetic acid	64-19-7*	71	Maltodextrin	9050-36-6
14	Acrylamide	79-06-1	72	Methanol	67-56-1*
15	Acrylamide, 2-acrylamido-2-methylpropanesulfonic acid, sodium salt polymer	38193-60-1	73	Monosodium fumarate	7704-73-6
16	Acrylonitrile	107-13-1	74	Mullite (SiO ₂ /Al ₂ O ₃)	1302-93-8
17	Alcohols, C6-12, ethoxylated propoxylated	68937-66-6	75	Naphthalene	91-20-3
18	Alcohols C9-11, ethoxylated	68439-46-3	76	Naphthenic acids, ethoxylated	68410-62-8
19	Alcohols, C10-16, ethoxylated propoxylated	69227-22-1	77	Octamethylcyclotetrasiloxane	556-67-2
20	Alcohols, C12-C16, ethoxylated	68551-12-2	78	Orthoboric acid with 2-aminoethanol	26038-87-9*
21	Alkyl polyglycol ether	31726-34-8	79	Poly(ethylene glycol)	25322-68-3
22	Almandite garnet (Al ₂ Fe ₃ (SiO ₄) ₃)	1302-62-1	80	Pontacyl carmine 2B (acid violet 12)	6625-46-3
23	Aluminium oxide (Al ₂ O ₃)	1344-28-1	81	Portland cement	65997-15-1
24	Amaranth (acid red 27)	915-67-3	82	Potassium carbonate	584-08-7*

#	Chemical name	CAS RN	#	Chemical name	CAS RN
25	Amines, coco alkyl, ethoxylated	61791-14-8	83	Potassium chloride	7447-40-7*
26	Amines, tallow alkyl, ethoxylated	61791-26-2	84	Potassium hydroxide	1310-58-3
27	Ammonium phosphate	7722-76-1	85	Reaction products of dimethyl siloxanes and silicones with silica	67762-90-7
28	Ammonium sulfate	7783-20-2*	86	Silica dioxide	14464-46-1*
29	Azophloxine (acid red 1)	3734-67-6	87	Silica dioxide (sand)	14808-60-7*
30	Barium sulfate (Barite)	7727-43-7*	88	Silica gel	112926-00-8*
31	Boric acid	10043-35-3*	89	Silicon dioxide	7631-86-9*
32	C12-18-alkyldimethylbenzyl ammonium chlorides	68391-01-5	90	Silicone oil (poly(dimethyl siloxane))	63148-62-9
33	Calcium carbonate (Limestone)	1317-65-3*	91	Sodium acryloyldimethyltaurate	5165-97-9
34	Calcium chloride	10043-52-4*	92	Sodium bisulfite	7631-90-5
35	Calcium sulfate	7778-18-9	93	Sodium bicarbonate	144-55-8*
36	Chromium (VI)	18540-29-9	94	Sodium bromate	7789-38-0
37	Cinnamaldehyde	104-55-2	95	Sodium calcium borate (ulexite)	1319-33-1
38	Citric acid	77-92-9*	96	Sodium carbonate	497-19-8*
39	Citronellol	106-22-9	97	Sodium chloride	7647-14-5*
40	Coffee bean oil	8001-67-0	98	Sodium chlorite (NaClO ₂)	7758-19-2*
41	Coco alkyldimethyl oxide	61788-90-7	99	Sodium hydroxide	1310-73-2*
42	Corundum (Al ₂ O ₃)	1302-74-5	100	Sodium hypochlorite	7681-52-9*
43	Copper (II) sulfate	7758-98-7	101	Sodium iodide	7681-82-5
44	Decamethylcyclotrisiloxane	541-02-6	102	Sodium persulfate	7775-27-1*
45	Diatomaceous earth, calcined powder	91053-39-3*	103	Sodium pyrophosphate	7447-40-7*
46	Dicoco dimethyl ammonium chloride	61789-77-3	104	Sodium sulfate	7757-82-6*
47	Diethylene glycol	111-46-6	105	Sodium sulfite	7757-83-7*
48	Dipentene terpene hydrocarbon byproducts	68956-56-9	106	Sodium tetraborate	1330-43-4
49	Disodium octaborate tetrahydrate	12008-41-2*	107	Sodium thiosulfate	7772-98-7*
50	Diutan gum	595585-15-2	108	Tall oil (fatty acids)	61790-12-3
51	Dodecamethylcyclotrisiloxane	540-97-6	109	Tar bases, quinoline derivatives, benzyl chloride-quaternized	72480-70-7
52	Ethylene glycol	107-21-1*	110	Tetrakis(hydroxymethyl) phosphonium sulfate	55566-30-8*
53	Ethylene glycol butyl ether	111-76-2*	111	Tetrasodium ethylenediaminetetraacetate	64-02-8*

#	Chemical name	CAS RN	#	Chemical name	CAS RN
54	Ferric oxide	1309-37-1	112	Tributyl-tetradecylphosphonium chloride	81741-28-8*
55	Formic acid	64-18-6	113	Titanium dioxide	13463-67-7
56	Fumaric acid	110-17-8	114	Urea	57-13-6
57	Glutaraldehyde	111-30-8*	115	Water	7732-18-5*
58	Glycerol	56-81-5*	116	Xanthan gum	11138-66-2*

* Chemical was assessed in the National Assessment of Chemicals Associated with CSG extraction in Australia (NICNAS, 2017)

In the United States of America (USA) more than 300 industrial chemicals were identified (randomly selected 100 wells from operations across the USA) as being used between January 2016 and January 2018 for hydraulic fracturing at shale gas operations (FracFocus Chemical Disclosure Registry, extracted 16 March 2018) (Ground Water Protection Council et al., 2018). The large number of chemicals recently being used in USA likely illustrates the dynamic nature of the industry to adapt to site-specific conditions, improve gas extraction efficiency and well integrity, improve environmental performance, and reduce costs.

2.2.2 Qualitative environmental risk assessment of chemicals

The Tier 1 screening of 116 chemicals identified 42 of ‘low concern’ (Screen 1 (13) and Screen 4 (29)), 33 of ‘potentially high concern’ (Screen 2), and 41 of ‘potential concern’ (Screen 3 (18) and Screen 4 (23)) (Figure 3) (Geological and Bioregional Assessment Program, 2018).

Of the 33 chemicals identified as being of ‘potentially high concern’, 5 chemicals (1 biocide and 4 defoaming agents) are not likely to be easily degraded (persistent), are bioaccumulative (potentially can accumulate in organisms), and exhibit very high acute toxicity to aquatic organisms (P, B, T chemicals) (Table 5; Figure 3). Such chemicals are considered a high concern/risk to the environment, as they can pose serious harm to aquatic ecosystems if released and require specific controls to prevent their release into the environment.

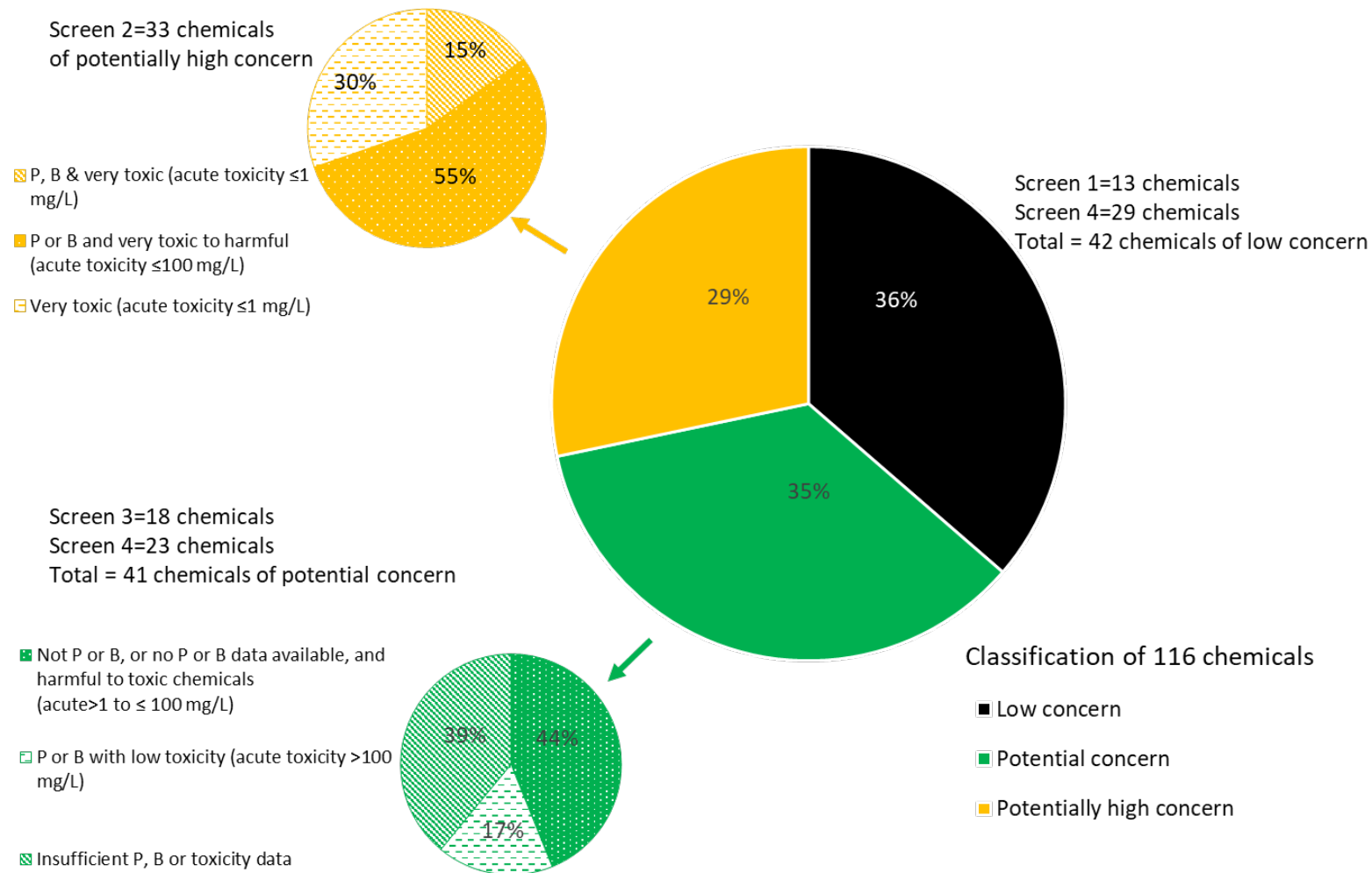


Figure 3 Tier 1 qualitative ERA of chemicals associated with shale, tight and deep coal gas operations (Refer to Figure 2 for Screen 1 to 4 details; percentage of chemicals in each category are shown in each segment; further breakdown of chemicals of 'potential concern' and 'potentially high concern' are shown in the smaller coloured circles; P = persistent; B = bioaccumulative; T = toxic)

Source: Geological and Bioregional Assessment Program (2018)

Element: GBA-BEE-2-284

Table 5 Chemicals of ‘potentially high concern’ that are persistent (P) and bioaccumulative (B), and exhibit very high acute toxicity (T)

Chemical	CAS RN	Use	P ¹	B ²	T ³
Dicoco dimethyl ammonium chloride	61789-77-3	Biocide/surfactant	##	‡‡	***
Decamethylcyclopentasiloxane (D5)	541-02-6	Defoaming agent/surfactant	##	‡‡	***
Silicone oil (poly(dimethyl siloxane))	63148-62-9	Defoaming agent/surfactant	##	‡‡	***
Dodecamethylcyclohexasiloxane (D6)	540-97-6	Defoaming agent/surfactant	##	‡‡	***
Octamethylcyclotetrasiloxane (D4)	556-67-2	Defoaming agent/surfactant	##	‡‡	***

¹Persistence = half-life > 60 d (##); ²Bioconcentration factor = BCF > 2000 or octanol/water partition coefficient = Log Kow ≥ 4.2 (‡‡); ³Toxicity = ≤1 mg/L (***); CAS RN = Chemical Abstracts Services Registry Number

The remaining 28 chemicals identified as being of ‘potentially high concern’ are persistent or bioaccumulative and harmful to very toxic chemicals (n=18) (Table 6; Figure 3), or not persistent or bioaccumulative (or no data available) and very toxic (n=10) chemicals (Table 7; Figure 3) (Geological and Bioregional Assessment Program, 2018). These chemicals can pose serious harm to aquatic ecosystems if released and require specific controls to prevent their release into the environment. Persistent and bioaccumulative chemicals are generally considered of high concern in the environment due to the potential for organisms to be exposed for longer time periods (chronic effects). There were limited aquatic chronic data available (using standard tests) for most of the 116 chemicals associated with shale, tight and deep coal gas operations in Australia.

The 41 chemicals identified as ‘potential concern’ are not persistent and not bioaccumulative (or no persistence and bioaccumulative data could be sourced), but are toxic or harmful chemicals (n=18) (Screen 3), and are chemicals with incomplete data that require professional judgement (n=23) (Screen 4) (Figure 3) (Geological and Bioregional Assessment Program, 2018). These chemicals have the potential to harm aquatic ecosystems if released and may require specific control and management measures to prevent their release into the environment.

For Screen 4 (Figure 3), seven of the 52 chemicals identified were found to be persistent or bioaccumulative, and have low toxicity (Geological and Bioregional Assessment Program, 2018). These seven chemicals are: (i) 1-benzyl quinolinium chloride; (ii) sodium acryloyldimethyltaurate; (iii) Amaranth (acid red 27); (iv) alcohols, C6-12 ethoxylated propoxylated; (v) ethylene glycol butyl ether; (vi) poly(ethylene glycol); and (vii) Tall oil (fatty acids). Since the Tier 1 ERA used mainly acute toxicity data, these chemicals are considered to be of ‘potential concern’ due to their unknown effects on organisms that may occur due to long-term exposure (chronic toxicity).

Table 6 Chemicals of ‘potentially high concern’ that are persistent (P) or bioaccumulative (B), and harmful to very toxic (T)

Chemical	CAS RN	Use	P ¹	B ²	T ³
1,2,4-Trimethylbenzene	95-63-6	Solvent	##	‡	**
1-Benzyl methyl pyridinium chloride	68909-18-2	Corrosion inhibitor	##	‡	***
5-Chloro-2-methyl-4-isothiazolol-3-one	26172-55-4	Biocide	##	‡	***
2-Mercaptoethyl alcohol	60-24-2	Surfactant	##	‡	***
2-Methyl-4-isothiazol-3-one	2682-20-4	Biocide	##	‡	***
Acrylamide	79-06-1	Friction reducer/gelling agent	##	‡	*
Alcohols, C10-16, ethoxylated propoxylated	69227-22-1	Surfactant	##	‡	***
Alcohols, C12-C16, ethoxylated	68551-12-2	Surfactant	##	‡	***
Amines, tallow alkyl, ethoxylated	61791-26-2	Surfactant	##	‡	***
C12-18-alkyldimethylbenzyl ammonium chlorides	68391-01-5	Biocide	##	‡	***
Coco alkyldimethyl oxide	61788-90-7	Surfactant	#	‡‡	***
Dipentene terpene hydrocarbon byproducts	68956-56-9	Friction reducer/gelling agent	#	‡‡	**
Naphthalene	91-20-3	Friction reducer/gelling agent	##	‡	***
Naphthenic acids, ethoxylated	68410-62-8	Friction reducer/gelling agent	##	‡	*
Polyethylene glycol monohexyl ether	31726-34-8	Non emulsifier	##	‡	*
Pontacyl carmine 2B (acid violet 12)	6625-46-3	Tracking dye	##	‡	*
Heavy aromatic solvent naphtha (petroleum)	64742-94-5	Friction reducer/gelling agent	##	‡	**
Hydrotreated light distillate (C13-C14 isoparaffin)	64742-47-8	Friction reducer/gelling agent	##	‡	***

¹Persistence = half-life >60 d (##), half-life ≤60 d (#); ²Bioconcentration factor = BCF >2000 or octanol/water partition coefficient = Log Kow ≥4.2 (‡‡), BCF ≤2000 or Log Kow <4.2 (‡); ³Toxicity = ≤1 mg/L (***) , >1 to ≤10 mg/L (**), >10 to ≤100 mg/L (*); CAS RN = Chemical Abstracts Services Registry Number

Table 7 Chemicals of ‘potentially high concern’ that are not persistent (P) or bioaccumulative (B), and very toxic (T)

Chemical	CAS RN	Use	P ¹	B ²	T ³
2-Bromo-2-nitro-1,3-propanediol	52-51-7	Biocide	#	‡	***
Chromium (VI)	18540-29-9	Breaker	na	na	***
Cupric sulfate	7758-98-7	Biocide/breaker	na	na	***
Glutaraldehyde	111-30-8	Biocide	#	‡	***
Hydrochloric acid	7647-01-0	Scale remover	na	na	***
Sodium chlorite (NaClO ₂)	7758-19-2	Biocide/breaker	na	na	***
Sodium hypochlorite	7681-52-9	Biocide/breaker	na	na	***
Sodium iodide	7681-82-5	Breaker/breaker	na	na	***
Tetrakis(hydroxymethyl) phosphonium sulfate	55566-30-8	Biocide	#	‡	***
Tributyl-tetradecylphosphonium chloride	81741-28-8	Biocide	na	na	***

¹Persistence = half-life ≤60 d (#), not applicable (na); ²Bioconcentration = BCF ≤2000 or octanol/water partition coefficient = Log Kow <4.2 (‡); not applicable or no data (na); ³Toxicity = ≤1 mg/L (***)

2.2.3 Biocides and siloxanes (P,B,T chemicals)

Biocides are used in drilling and hydraulic fracturing to prevent excess biofilm production in wells and formations, which may lead to clogging, unwanted gas production (e.g. hydrogen sulfide gas), and corrosion of underground casing/tubing and equipment (Kahrilas et al., 2016; Kahrilas et al., 2015). Biocide selection will depend on factors including: (i) the mineralogy and biogeochemistry of the formation; (ii) compatibility with environmental conditions (e.g. temperature, pressure, salinity, and organic matter contents); (iii) abiotic transformations; (iv) sorption reactions; (v) performance against specific microbial species (mode of action); and (vi) cost.

Biocides are inherently toxic and are, therefore, of 'potentially high concern' if released into the environment. Four biocides identified are water-soluble, persistent, and highly toxic to aquatic organisms (Geological and Bioregional Assessment Program, 2018): (i) dicoco dimethyl ammonium chloride (CAS RN 61789-77-3); (ii) 2-methyl-4-isothiazol-3-one (CAS RN 2682-20-4); (iii) 5-chloro-2-methyl-4-isothiazol-3-one (CAS RN 26172-55-4); and (iv) C12-18-alkyldimethylbenzyl ammonium chlorides (CAS RN 68391-01-5). The effect on biota in the receiving aquatic environment is likely to be dependent on the release scenario (e.g. surface spills, pond overflow to soil and surface water, or well leakage to groundwater, etc.); exposure concentrations; fate and behaviour in environments (e.g. rate of degradation and transformation, partitioning, and complexation); bioavailability and sensitivity of aquatic organisms.

Biocides such as glutaraldehyde (CAS RN 111-30-8) and tetrakis (hydroxymethyl) phosphonium sulfate (CAS RN 55566-30-8), which are very toxic to aquatic organisms, may pose a lower risk to aquatic organisms due to their expected rapid (i.e. ≤ 60 d) degradation in aquatic environments (Geological and Bioregional Assessment Program, 2018). However, degradation products of some biocides have been reported to be more toxic and/or persistent than their parent compounds (Kahrilas et al., 2016; Kahrilas et al., 2015), and highlights the need for the development of sensitive and selective analytical methods to detect parent and transformation products in wastewaters and receiving waters to assess impacts on aquatic ecosystems.

Siloxanes can be added to hydraulic fracturing fluids as defoaming agents and surfactants. These chemicals have low water-solubility (soluble/miscible in solvents), are hydrophobic and, in the case of cyclic siloxanes, are volatile. The siloxanes are of 'potentially high concern' to aquatic organisms due to their persistence and bioaccumulative and highly toxic nature (Geological and Bioregional Assessment Program, 2018). The three cyclic siloxanes: octamethylcyclotetrasiloxane (CAS RN 556-67-2), decamethylcyclopentasiloxane (CAS RN 541-02-6) and dodecamethylcyclohexasiloxane (CAS RN 540-97-6), are likely to volatilise or degrade in water (via hydrolysis) but, due to their hydrophobic nature, are also likely to strongly associate with sediments/suspended solids where they can persist. Furthermore, there are currently conflicting ERAs on the cyclic siloxanes due to difficulties in conducting aquatic toxicity tests because of their volatility, making the toxicity assessments highly uncertain (ECHA, 2018; Environment Canada Health Canada, 2008; Fairbrother et al., 2015; Fairbrother and Woodburn, 2016; Government of Canada, 2012b, 2012a). The National Industrial Chemicals Notification and Assessment Scheme (NICNAS, (2018) conducted a Tier 2 ERA on these chemicals and found all three to be persistent, two to be bioaccumulative (octamethylcyclotetrasiloxane and decamethylcyclopentasiloxane), and one (octamethylcyclotetrasiloxane) to have 'uncertain toxicity'. These chemicals, therefore, if used

at shale, tight and deep coal gas operations, will require a more detailed quantitative ERA to be undertaken with realistic exposure scenarios in which the quantitative ERA assesses and models the likelihood and consequence of a risk event occurring, identifies and evaluates control and mitigation measures (e.g. what controls are in place to address the identified risk and how effective are these controls), and monitors to ensure controls and management strategies are adequate to prevent impacts on the environment.

2.2.4 Fate and behaviour of chemicals in the environment

The ecotoxicity of chemicals released during shale, tight and deep coal gas operations will likely be affected by reactions and processes in environments that can modify their fate and bioavailability (e.g. exposure concentrations) (Adriano, 2001; ANZECC/ARMCANZ, 2000; Neilson, 1994). Organic chemicals can be volatilised, photodegrade, undergo abiotic and biotic degradation and transformations, and complex/adsorb to a range of solid phases (e.g. organic matter). Inorganic chemicals can undergo neutralisation, displacement, ionisation, redox and precipitation reactions, and undergo biotransformation (e.g. arsenic methylation), and complex/partition to a range of solid phases (e.g. clays, oxides/hydroxides and organic matter). These reactions and processes will be influenced by the physical and chemical properties of the receiving environment such as pH, salinity, redox conditions, microbial populations and organic matter content.

Chemical additives used in hydraulic fracturing fluids may also be lost in wells and formations to solid surfaces and/or degrade or be transformed leading to lower concentrations than what was initially added. For example, polymers can degrade/decompose, biocides can degrade and complex/adsorb onto solid surfaces, and surfactants can be adsorbed onto solid surfaces in formations. In addition, chemical concentrations from source zones can be attenuated in surface water and groundwater through dilution and volatilisation processes.

The Tier 1 qualitative (screening) ERA used aquatic acute ecotoxicity data representing three trophic levels – a freshwater alga, water flea and a fish species using standard testing protocols (Geological and Bioregional Assessment Program, 2018). Acute toxicity data may not be sufficient in assessing the environmental risk of persistent and bioaccumulative chemicals that could result in effects on biota due to long-term exposure (chronic effects) in the environment. Chronic toxicity data on aquatic organisms from a range of trophic positions (and sensitive species) are needed to accurately assess effects due to long-term exposure of these chemicals to aquatic organisms. In addition, the approach of single-chemical acute toxicity test data provides a highly uncertain assessment when there is limited detailed knowledge on the interactions that modify toxicity, and on the modes of toxicity of the chemicals to aquatic biota. A direct toxicity approach where aquatic biota are exposed to dilutions of a complex chemical mixture (e.g. a hydraulic fracturing fluid, flowback and produced water) would provide a more relevant environmental exposure assessment that incorporates chemical interactions/mixtures. Further, these assessments do not consider pulse discharges and dispersion of chemicals (individual and mixtures) into aquatic ecosystems.

2.2.5 Limitations of Tier 1 qualitative ERA of chemicals

The limitations of the Tier 1 qualitative ERA are:

- The assessment focused on aquatic organisms as there is limited standard ecotoxicity testing data for the 116 chemicals identified in soils and sediments.
- Physicochemical, biodegradation and bioaccumulation data were often limited or did not exist for the assessed chemicals and, in these cases, QSARs were used to estimate some of these parameters.
- Biodegradation data were limited to organic chemicals and are not applicable to inorganic chemicals. Studies on biodegradation are not routinely conducted for mixtures and polymers, under varying environmental parameters (e.g. oxygen concentrations, redox potential, salinity, and temperatures), exposure concentrations, and the presence of degradation and transformation products considered.
- Bioconcentration factor (e.g. fish) data were limited for the 116 chemicals and appear to be not routinely conducted using standard protocols. In the absence of BCF data, the potential for a chemical to bioaccumulate was predicted from its chemical's hydrophobicity, typically determined using its octanol-water partition coefficient (Log K_{ow} ; hydrophilic: hydrophobic nature).
- Assessments were conducted using mainly acute toxicity data for three trophic levels (fish, invertebrates, and algae) as only limited chronic data could be sourced using standard testing protocols.
- There were limited ecotoxicity data available for Australian species.
- Ecotoxicity endpoint data for groundwater organisms are currently not available.
- Tier 1 ERA did not consider chemical mixtures.
- Qualitative assessment used conservative exposure assumptions and scenarios that did not account for existing control or mitigation measures that would substantially reduce the likelihood and consequence of the risk to aquatic organisms. A conservative (precautionary) approach (e.g. P, B, T data was sourced only from standard testing protocols and international recognised ERA organisations/agencies and models, and assessments did not make assumptions based on chemical classes or groups) was applied to the evaluation of chemical and ecotoxicity data and Tier 1 qualitative ERA.

3 Laboratory-based leachate and extraction tests on powdered rock samples from the Isa GBA region – geogenic chemicals

3.1 *Methods*

3.1.1 Overview of the experimental approach

The study involved the application of leach and extraction tests which were designed to assess the mobilisation (release) of geogenic chemicals (compounds and elements) due to exposure to hydraulic fracturing fluids (HFFs). The laboratory-based tests were designed to provide an upper-bound estimate of geogenic chemical mobilisation from target formations in the Beetaloo GBA region; and intended to guide future field-based monitoring, management and treatment options.

The specific aims of the study were to:

- Apply laboratory batch leachate and extraction tests that allow the chemical screening of geogenic chemicals (compounds and elements) mobilised from target formations for shale gas development in the Beetaloo GBA region during hydraulic fracturing; and
- Identify potential inorganic and organic chemicals that could be mobilised into solution from powdered rock samples from formations in the Beetaloo GBA region to guide future field-based monitoring, management, and treatment options.

The leach tests were based on previous investigations relating to coal seam gas extraction (Apte et al., 2017). The logic of this approach was that if geogenic chemicals were not detected during these laboratory batch tests (under upper-bound conditions), then they are unlikely to be detected in environmental samples. The leaching test solutions applied during this study are summarised in Table 8. Leachate tests were conducted at 80°C (inorganics) in order to examine elevated temperature conditions that could be present during hydraulic fracturing operations at deep shale gas operations (median aquifer temperature at 1000-2500 m drill hole ~ 80°C; after removal of unknown, uncorrected, and unidentified data and methodologies in the dataset) (<https://ecat.ga.gov.au/geonetwork/srv/eng/catalog.search#/metadata/70604>). Exploratory studies were also conducted on the effect of pressure (inorganics) that would be present in wells of shale gas operations on geogenic chemical (element) mobilisation into solution from powdered rock samples.

Table 8 Composition of the leachate and extraction solutions used in the geogenic chemical studies

Leach solution	Components	Leach test conditions	Substances analysed
Dilute hydrochloric acid (HCl)	1 M HCl	80 °C, 17 hr, atmospheric pressure	Elements, inorganics
Synthetic groundwater (SGW)	750 mg/L sodium chloride 750 mg/L sodium bicarbonate	80 °C, 17 hr, atmospheric pressure	Elements, inorganics
Hydraulic fracturing fluid (HFF)	See Table 11	80 °C, 17 hr, 100 KPa and 18,400 KPa	Elements, inorganics
Organic solvents	Methanol: acetone: dichloromethane (1:2.5:2.5)	100 °C, 10,000 KPa	Organics

As previously stated, the composition and concentration of geogenic chemicals in flowback and produced waters will depend on many factors including: (i) geology and mineralogy of formations; (ii) surface area of the fracture network exposed to HFFs; (iii) composition and concentration of chemicals used in hydraulic fracturing; (iv) residence time of HFFs in formations; (v) operational and environmental conditions (e.g. volumes added and recovered, temperature, pressure); and (vi) chemical reactions (e.g. adsorption, complexation, precipitation, aggregation, degradation and transformations).

3.1.2 Powdered rock samples

Rock samples from formations in the Beetaloo GBA region were sourced from Dr Tonguc Uysal, CSIRO. These formations (Kyalla and Velkerri) are representative of potential targets for shale gas developments in the Beetaloo GBA region. Seven rock sections were sourced from Tanumbirini-1, Aلتree-2 and Shenandoah-1/1A drill cores (Table 9). The samples were stored under dry, non-climate controlled conditions. The rock samples were fine ground to <70 µm to a uniform particle size (as an upper bound for potential chemical mobilisation into solution).

Table 9 Rock samples sourced from drill cores in Beetaloo GBA region

Drillhole	Formation	Depth (m)
Tanumbirini-1	Middle Velkerri	3235
Tanumbirini-1	Middle Velkerri	3272.88
Altreetree-2	Upper Velkerri	671
Altreetree-2	Middle Velkerri	709.15
Altreetree-2	Middle Velkerri	764
Shenandoah-1/1A	Lower Kyalla Shale	1595
Shenandoah-1/1A	Velkerri B Shale	2513

3.1.3 Analytical procedures

3.1.3.1 Particulates

Total recoverable particulate elements were determined using microwave-assisted, reverse aqua regia digestion (based on USEPA method 3051A). Portions (0.5 g) of powdered rock samples were weighed into acid-washed perfluoroalkoxy digestion vessels, to which 9 mL concentrated nitric acid and 3 mL concentrated HCl were added, then heated in a microwave oven (MARS Xpress 6, CEM) to 175°C for 16.5 min. Sample digests were then diluted with ultra-pure deionised water and analysed for inorganic elements by a combination of inductively coupled plasma-atomic emission spectrometry (ICP-AES) (Varian 730-ES, Australia) and inductively coupled plasma-mass spectrometry (ICP-MS) (8800, Agilent Technologies, Japan) using matrix-matched standards. The results are reported on a dry weight basis. Certified reference materials (ERM-CC018, European Reference Materials; OREAS-25a, Ore Research and Exploration Australia) were included in each digestion batch. Replicate analyses and spike recoveries were carried out on selected samples.

It should be noted that the analytical method applied does not measure all forms of particulate elements; rather, the portion of an element that is released into solution (recoverable) during the acid-digestion procedure. Metals associated with silicates and refractory elements such as chromium are likely to be underestimated; however, for many metals (e.g. copper and zinc) near-full recovery from particulates can be expected. For environmental studies which focus on trace element mobilisation under typical environmental conditions, the fraction of metals not mobilised by acid digestion is not likely to play a significant role and can be regarded as being inert. For the purposes of simplification, the term ‘particulate metals’ is used in this technical appendix to denote the total recoverable metals.

Acid-extractable element (AEE) concentrations were also determined on powdered rock samples. The acid-extractable metal fraction gives an indication of the fraction of particulate metals that may be amenable to mobilisation under environmental conditions. An approximate 0.5 g sub-sample of powdered rock was weighed into a 50 mL centrifuge tube and 30 mL of 1 M HCl was added. The sample was mixed for 1 hr at room temperature, and then syringe-filtered through 0.45 µm filter cartridges (Sartorius Minisart). The acid extracts were then diluted ten-fold and analysed by ICP-MS and ICP-AES using matrix-matched standards. Results are reported on a dry weight basis. Replicate analyses and spike recoveries were carried out on selected samples.

Dissolved (<0.45 µm) organic carbon (DOC) was analysed using a Shimadzu TOC-LCSH Total Organic Carbon Analyser. Prior to analysis, 300 µL of 6 M HCl was added to each sample, followed by purging with oxygen gas for 20 min to remove inorganic carbon. Water pH was measured on unfiltered samples using an Orion Versa Star Pro meter, with an Orion Ross Ultra pH probe. The pH meter was calibrated using pH buffer solutions daily on use.

3.1.3.2 Inorganic element analysis

A wide range of inorganic elements (> 60) were quantified in solutions using ICP-AES and ICP-MS. Limits of detection were calculated as three times the standard deviation (3 Sigma) of the analytical blank measurements. The CSIRO laboratory is a National Association of Testing Authorities (NATA) accredited facility for trace element analysis.

The ICP-AES was calibrated with matrix-matched (2% v/v nitric acid) standards (AccuStandard, US) for the analysis of the 0.01 M HCl leach solutions (which were acidified to 2% v/v nitric acid). Analysis of the other solutions for inorganic elements was carried out using the method of standard additions to overcome analyte suppression caused by the high concentrations of total dissolved solids (TDS). Quality control procedures included analysis of certified reference materials (where feasible), replicate analyses and spike recoveries. The levels of reporting (LORs) can be found in results tables and data repository (Geological and Bioregional Assessment Program, 2019).

3.1.3.3 Organics analysis

Extracts were analysed for a range of priority (targeted) organic compounds: 14 substituted phenols, 15 PAHs, and TRH fractions (C10 to C40) (Table 10) at the National Measurement Institute (a NATA-accredited facility). Results are reported on a dry weight basis. Replicate analyses and spike recoveries were carried out on selected samples.

Table 10 Limit of reporting for targeted organic compounds in powdered rock sample extracts

PAHs	LOR (µg/kg)	Phenols	LOR (µg/kg)	TRH	LOR (µg/kg)
Acenaphthene	5	2-Chlorophenol	5	C10-C14	100
Acenaphthylene	5	4-Chloro-3-methylphenol	5	C15-C28	100
Anthracene	5	2,4-Dichlorophenol	5	C29-C36	100
Benz(a)anthracene	2	2,6-Dichlorophenol	5	C10-C16*	100
Benzo(a)pyrene	5	2,4-Dimethylphenol	5	C10-C16 (-Naphthalene)*	100
Benzo(b)&(k)fluoranthene	5	2-Methylphenol	5	C16-C34*	100
Benzo(ghi)perylene	5	3-& 4-Methylphenols	5	C34-C40*	100
Chrysene	5	2-Nitrophenol	5		
Dibenz(ah)anthracene	5	4-Nitrophenol	5		
Fluoranthene	2	Pentachlorophenol	5		
Fluorene	5	Phenol	5		
Indeno(1,2,3-cd)pyrene	5	2,3,4,6-Tetrachlorophenol	5		
Naphthalene	5	2,4,5-Trichlorophenol	5		
Phenanthrene	5	2,4,6-Trichlorophenol	5		
Pyrene	5				

* National Environmental Protection Measures (NEPM) TRH reporting values; LOR = limits of reporting

3.1.4 Leachate test protocol – inorganics

3.1.4.1 General test conditions

The leachate test solutions used to examine geogenic inorganic element mobilisation from powdered rock samples can be found in Table 8.

Ultrapure deionised water was sourced from a Milli-Q system (18 MΩ.cm conductivity, Millipore, Australia). Plastic ware used for element analyses were acid-washed prior to use by soaking for a minimum of 24 hr in 10% (v/v) analytical reagent (AR) nitric acid (Merck Tracepur) followed by rinsing with Milli-Q water.

Synthetic groundwater (SGW) was composed of sodium chloride (NaCl) and sodium bicarbonate (NaHCO₃) both at concentrations of 750 mg/L (total dissolved solids of 1500 mg/L) and pH of 8.0. This SGW composition has previously been identified as being typical of groundwaters associated with unconventional gas extraction (Apte et al., 2017; Worley Parsons, 2010) as they are usually dominated by sodium, chloride and bicarbonate ions. Aside from use as a leachate solution in its own right, the SGW was used as a background matrix for the preparation of the HFF.

A thorough literature search was undertaken of HFF composition, and advice was also obtained from Schlumberger Research Centre, Cambridge, UK. Based on this information, an in-house synthetic HFF solution was developed (Table 11). The formulation was based largely on the work of Prud'homme and co-workers (Kesavan and Prud'homme, 1992). The HFF was prepared using SGW as the base fluid and contained representative chemicals of the key components. Guar gum was not added to the formulation in order to alleviate analytical problems that can arise from elevated carbon concentrations. It was assumed that the constituents of guar would not significantly mobilise (greater than the presence of acid, solvents and surfactants in HFF) geogenic chemicals into solution from the powdered rock samples.

Table 11 In-house synthetic HFF composition

Test solutions	Role in hydraulic fracturing	Amount/concentration in 1 L ultrapure deionised water
Synthetic groundwater	Base solution	750 mg NaCl & 750 mg NaHCO ₃
Sodium diacetate		1.2 g
Potassium chloride		20 g
Glutaraldehyde solution (25%)	Biocide	0.25 mL
Ethylenediaminetetraacetic acid (EDTA)		0.034 g
Citric acid		0.012 g
Isopropyl alcohol/Tyzor AA titanate solution 9:1 (v/v)	Cross-linker	4 mL
Ammonium persulfate solution (6% m/v)	Breaker	67 mL

Source: Apte et al. (2017); Worley Parsons (2010); Kesavan and Prud'homme (1992)

The leach tests were based on those developed by CSIRO for the investigation of the mobilisation of geogenic chemicals from coals during hydraulic fracturing operations (Apte et al., 2017).

Leaching experiments were undertaken by weighing a known mass of rock sample (typically 0.6 to

1 g) into 50 mL polypropylene centrifuge tubes, followed by addition of the required volume of leach solution to achieve the desired powdered rock (solids) concentration (unless otherwise stated, 1:50 m/v solids to solution ratio). The suspensions were shaken on a hot block heater at 80°C for 17 hr. The suspensions were then centrifuged at 3000 rpm for 3 min, and then syringe-filtered through 0.45 µm filter cartridges (Minisart, Sartorius Stedim, Germany). If sample masses permitted, duplicate leach tests were performed. The tests also included a blank treatment (no solids added).

3.1.4.2 Synthetic groundwater

Leach tests were conducted using SGW in order to determine the concentration of easily mobilised elements from powdered rock samples. By comparison with the HFF leach test findings, it is possible to determine which elements were mobilised specifically as a consequence of the presence of hydraulic fracturing chemicals.

3.1.4.3 Dilute HCl

The purpose of the dilute 1M HCl leach test was to equilibrate the rock samples in an acidic environment under conditions in which there would be some mineral dissolution and potential release of geogenic chemicals into solution. Hydrochloric acid is used in hydraulic fracturing for bore clean-up after drilling and to help open up fractures in formations.

3.1.4.4 Hydraulic fracturing fluid

Leach tests were performed using the in-house synthetic HFF at 80°C and 100 KPa. A leachate test on the Tanumbirini-1 (Middle Velkerri; 3235 m) powdered rock sample was also conducted at 80°C and elevated pressure (18,400 KPa) in order to ascertain if pressure had an effect on geogenic chemical mobilisation. The pressure experiment was conducted in a Berghof DB300 pressure reactor equipped with a polytetrafluoroethylene reaction chamber of approximately 300 mL capacity. The reactor was gas-pressurised and had a maximum operating pressure of 20,000 KPa. The reactor was pressurised with nitrogen doped with oxygen in order to maintain aerobic conditions.

3.1.5 Extract protocol – organics

Powdered rock samples were extracted using an accelerated solvent-extraction (ASE) system (ThermoFisher) with a combination of hydrophilic and hydrophobic solvents. This study used a mixture of strong polar and non-polar solvents to gain an understanding (upper-bound conditions) of potential mobilisation of geogenic organic compounds from powdered rocks samples due to hydraulic fracturing. An extraction of powdered rock samples using hydraulic fracturing fluid was not undertaken due to unknown risks of fluids under high pressure and temperature in the ASE system. Approximately 1 g of sample was weighed in a 10 mL stainless steel ASE extraction cell in which cleaned sand had been added (acid/solvent-washed and baked for 2 hr at 400°C). A 1:10 m/v ratio was selected based on its common use in solids and mineral phase extraction and solid-solution partitioning studies. Approximately 10 mL of a mixture of acetone, dichloromethane and methanol (2:2:1 (v/v/v)) was added into the ASE cells and held at 100°C and 10,000 KPa for 5 min. Approximately 10 mL of the solvent mixture was collected from each extraction vial and blown to

dryness under a gentle stream of nitrogen gas. The dried sample extracts were analysed for a range of priority (targeted) organics compounds (Table 10) at the National Measurement Institute. The results are reported on a dry weight basis.

3.2 Results

The detailed results of all tests performed including duplicates (when applicable) and quality control data can be found in (Geological and Bioregional Assessment Program, 2019).

3.2.1 Trace element concentrations in powdered rock samples

The particulate concentrations of commonly occurring elements are summarised in Table 12 . The concentrations of many elements were quite variable and typically ranged by over one order of magnitude across the rock samples. Comparisons of the elemental data with the mean global crustal abundance values (Taylor, 1964) and/or the ANZECC/ARMCANZ sediment quality guidelines ((ANZECC/ARMCANZ, 2000) indicated that the rock samples from Tanumbirini-1 and Altree-2 were enriched in elements such as antimony, arsenic, cadmium, copper, mercury, molybdenum, nickel, selenium, silver, sulfur, and zinc (Table 12). Powdered rock samples from Shenandoah 1/1A were enriched in elements such as copper, sulfur, mercury, nickel (Velkerri B Shale) and selenium (Velkerri B Shale) (Table 12).

The AEE concentrations of commonly occurring elements are summarised in Table 13 (and less common trace elements are presented in Geological and Bioregional Assessment Program (2019). The AEE concentrations are a better indication of potential environmental mobility than total particulate metal concentrations. The elements showing enrichment in AEE extracts relative to global crustal abundance values (Taylor, 1964) and/or the ANZECC sediment quality guidelines (ANZECC/ARMCANZ 2000) were cadmium (Altree-2), copper (Tanumbirini-1; Altree-2 (Upper Velkerri); Shenandoah 1/1A (Velkerri B shale)), nickel (Tanumbirini-1, Altree-2 (Upper and Middle Velkerri)), sulfur (Tanumbirini-1; Altree-2 (Upper and Middle Velkerri)), antimony (Tanumbirini-1), and zinc (Altree-2). The percentage of elements extracted in AEE are summarised in Table 14. The ratios provide an indication of the extent to which elements could be mobilised from powdered rock samples into solution: Tanumbirini-1 (e.g. barium, calcium, copper, manganese, molybdenum, nickel, phosphorus, lead, sodium and uranium); Altree-2 (e.g. calcium, cadmium, manganese, nickel, phosphorus, uranium, and zinc) and Shenandoah-1/1A (e.g. barium, calcium, manganese, sodium, phosphorus, lead, uranium, and zinc) had the highest mean percentages (mean >50%).

Table 12 Total particulate element concentrations of powdered rock samples (mg/kg)

Drillhole	Tanumbirini-1		Aldree-2			Shenandoah-1/1A	
Formation	Middle Velkerri	Middle Velkerri	Upper Velkerri	Middle Velkerri	Middle Velkerri	Lower Kyalla Shale	Velkerri B Shale
Depth (m)	3235	3272.88	671	709.15	764	1595	2513
Ag	0.76	0.79	1.9	0.81	0.95	0.03	0.27
Al	10500	20600	17700	14100	23100	20400	15300
As	42	33	39	51	33	3.6	9.6
B	43	57	53	48	58	26	35
Ba	157	238	94	212	176	177	229
Ca	10800	6070	9190	5450	10300	712	8210
Cd	3.6	3.6	13	8.8	5.7	<0.01	0.2
Co	26	22	18	18	17	11	13
Cr	28	21	26	15	24	21	16
Cu	116	114	206	95	224	36	181
Fe	41200	45300	35300	41400	50100	24200	24900
Hg	0.73	0.49	0.72	0.68	0.62	0.07	0.34
K	4200	6500	7500	5800	6900	7100	5800
Mg	3860	4220	4340	3210	5040	5240	3700
Mn	103	112	68	82	70	70	110
Mo	92	60	55	74	74	0.71	3.7
Na	950	1600	900	790	1600	1400	1200
Ni	318	124	233	163	118	18	76
P	2710	1580	3170	1500	3960	33	2560
Pb	37	39	45	26	39	8.8	34
S	38700	33400	31400	34600	33200	2210	14200
Sb	4.5	6.1	7.6	5.1	4.0	0.09	0.39
Se	2.8	2.2	6.3	2.7	2.9	<0.1	1.2
U	3.0	4.9	4.0	4.3	4.4	0.56	1.1
V	128	81	259	124	168	25	38
Zn	362	218	763	751	471	29	104

Black bold numbers: exceed x10 mean global crustal abundance; Red bold numbers: exceed x10 mean global crustal abundance & exceed the ANZECC/ARCMCANZ sediment quality guideline value; Red numbers (not bold) exceed the ANZECC/ARCMCANZ sediment quality guideline value.

Source: Geological and Bioregional Assessment Program (2019)

Table 13 Acid-extractable element (AEE) concentrations from powdered rock samples (mg/kg)

Drillhole	Tanumbirini-1		Atree-2			Shenandoah-1/1A	
Formation	Middle Velkerri	Middle Velkerri	Upper Velkerri	Middle Velkerri	Middle Velkerri	Lower Kyalla Shale	Velkerri B Shale
Depth (m)	3235	3272.88	671	709.15	764	1595	2513
Ag	0.034	0.026	0.54	0.12	0.11	0.005	0.026
Al	1720	1820	2160	2210	2370	1720	2220
As	14	11	13	18	12	0.97	4.4
B	<10	<10	<10	<10	<10	<10	<10
Ba	106	137	34	76	56	149	172
Ca	11000	5840	8880	5240	9290	700	8320
Cd	1.4	1.3	7.9	3.7	1.8	0.006	0.082
Co	4.8	3.2	6.5	6.3	5.6	4.2	3.3
Cr	1.9	1.2	2.2	1.6	2.5	1.0	1.7
Cu	77	88	89	38	97	16	84
Fe	3560	2450	2460	2450	2710	1420	2160
Hg	0.04	0.04	0.04	<0.02	<0.02	<0.02	0.04
K	1300	1600	1500	1200	1100	2100	1800
Mg	1810	925	1530	1250	1150	485	823
Mn	74	68	29	47	17	12	72
Mo	62	45	12	9.7	12	0.3	1.8
Na	740	1300	330	99	300	1300	960
Ni	165	27	119	80	39	2.5	17
P	2860	1570	3070	1340	3540	<10	2570
Pb	20	26	8.2	3.5	3.0	5.3	24
S	2680	1460	3060	4340	2320	186	486
Sb	2.1	3.0	1.8	1.1	0.89	<0.04	0.18
Se	0.7	0.5	0.9	0.3	0.3	<0.1	0.2
U	2.1	2.6	2.3	1.8	2.9	0.036	0.81
V	21	7.1	23	13	20	1.6	5.4
Zn	173	93	497	463	258	8	53

Black bold numbers: exceed x10 mean global crustal abundance; Red bold numbers: exceed x10 mean global crustal abundance & exceed the ANZECC/ARCMCANZ sediment quality guideline value; Red numbers (not bold): exceed the ANZECC/ARCMCANZ sediment quality guideline value.

Source: Geological and Bioregional Assessment Program (2019)

Table 14 Ratio (%) of AEE to particulate element concentration for selected elements in powdered rock samples

Drillhole	Tanumbirini-1		Aldree-2			Shenandoah-1/1A	
Formation	Middle Velkerri	Middle Velkerri	Upper Velkerri	Middle Velkerri	Middle Velkerri	Lower Kyalla Shale	Velkerri B Shale
Depth (m)	3235	3272.88	671	709.15	764	1595	2513
Ag	4	3	28	15	12	17	10
Al	16	9	12	16	10	8	15
As	33	33	33	35	36	27	46
B	<12 ^a	<9 ^a	<9 ^a	<9 ^a	<9 ^a	<19 ^a	<14 ^a
Ba	68	58	36	36	32	84	75
Ca	102	96	97	96	90	98	101
Cd	39	36	61	42	32	<12 ^a	41
Co	18	15	36	35	33	38	25
Cr	7	6	8	11	10	5	11
Cu	66	77	43	40	43	44	46
Fe	9	5	7	6	5	6	9
Hg	5	8	6	<1 ^a	<2 ^a	<14 ^a	12
K	31	25	20	21	16	30	31
Mg	47	22	35	39	23	9	22
Mn	72	61	43	57	24	17	65
Mo	67	75	22	13	16	42	49
Na	78	81	37	13	19	93	80
Ni	52	22	51	49	33	14	22
P	106	99	97	89	89	<15 ^a	100
Pb	54	67	18	13	8	60	71
S	7	4	10	13	7	8	3
Sb	47	49	24	22	22	<22 ^a	46
Se	25	23	14	11	10	na	17
U	70	53	58	42	66	6	74
V	16	9	9	10	12	6	14
Zn	48	43	65	62	55	28	51

^a values calculated using half detection limit; na = not applicable/could not be calculated. Bold = ratio of AEE to particulate element concentration > 50%

Source: Geological and Bioregional Assessment Program (2019)

3.2.2 Leachate tests – inorganics

3.2.2.1 SGW tests

The concentrations of elements mobilised into solution by SGW (17 hr equilibration time) are summarised in Table 15 (Geological and Bioregional Assessment Program, 2019). In general, the concentration of elements in solution were relatively low. The following elements showed increased mobilisation into SGW (compared to SGW blank): aluminium, antimony, arsenic, barium, calcium, cadmium, chromium, iron, lithium, magnesium, molybdenum, neodymium, phosphorus, rubidium, sulfur, selenium, strontium, and vanadium (>10-fold median increase compared to SGW blank). It should be noted that leachate solution pH became alkaline by the end of the tests (typically 7-8) and this may have contributed to the mobilisation of some elements such as arsenic, antimony, selenium and vanadium into solution.

3.2.2.2 Dilute HCl tests

The mean concentration of elements leached into solution by dilute HCl (17 hr equilibration time) are summarised in Table 16 (Geological and Bioregional Assessment Program, 2019). Acidification of the rock samples led to substantial mobilisation (>50-fold median increase compared to SGW) of a range of elements into solution including: aluminium, barium, cadmium, cesium, cobalt, iron, lanthanum, manganese, neodymium, nickel, phosphorus, lead, silver, thorium, titanium, uranium, yttrium, and zinc.

3.2.2.3 Synthetic hydraulic fracturing fluid tests

The concentration of elements mobilised into solution by HFF (17 hr equilibration time) are summarised in Table 17 (Geological and Bioregional Assessment Program, 2019). The HFF data were compared to the SGW leachate data to assess which elements were preferentially mobilised under hydraulic fracturing. The concentrations of elements released into solution were generally much higher in HFF than in the SGW treatment indicating the role in mobilisation of industrial chemicals present in the HFF. The elements showing substantial mobilisation (>50-fold median increase compared to SGW) in HFF included: aluminium, cadmium, cesium, cobalt, iron, lanthanum, manganese, neodymium, nickel, lead, silver, yttrium, and zinc.

Increased pressure from 100 to 18400 KPa for the leachate tests using HFF resulted in higher mobilisation of elements such as thorium (4.5x), cobalt (3.9x), uranium (3.3), lithium (1.8x), copper (1.7x), silver (1.7x), calcium (1.6x), and zinc (1.6x); and decreased mobilisation for elements such as vanadium (0.4x), boron (0.3x), antimony (0.3x), molybdenum (0.02x), barium (0.01x), and lead (0.003x) (Table 18) (Geological and Bioregional Assessment Program, 2019).

Table 15 Dissolved elemental concentrations in SGW leachate solutions

Drillhole		Blank	Tanumbirin-1		Atree-2			Shenandoah-1/1A	
Formation			Middle Velkerri	Middle Velkerri	Upper Velkerri	Middle Velkerri	Middle Velkerri	Lower Kyalla Shale	Velkerri B Shale
Depth (m)			3235	3272.88	671	709.15	764	1595	2513
Final pH	Units	8.7	7.8	7.9	7.5	5.8	7.1	8.5	8.5
Ag	µg/L	<0.01	0.01	0.01	0.04	0.14	0.03	<0.01	<0.01
Al	mg/L	0.01	0.12	0.17	0.06	0.04	0.05	0.38	0.70
As	µg/L	<0.2	6.3	7.4	27	7.3	12	7.1	18
B	mg/L	0.05	0.09	0.09	0.09	0.09	0.08	0.06	0.09
Ba	µg/L	<0.3	40	69	1	2	<0.3	54	58
Ca	mg/L	0.09	34	19	19	40	12	2.5	5.0
Cd	µg/L	<0.1	0.6	0.3	5.1	52	1.2	<0.1	<0.1
Ce	µg/L	<0.02	<0.02	0.02	0.07	0.1	0.08	0.09	0.08
Co	µg/L	<0.1	<0.1	<0.1	1.1	7.0	0.3	0.2	0.2
Cr	µg/L	<1	7	5	10	1	13	5	6
Cu	µg/L	<0.4	0.5	1	10	0.7	0.9	1	3
Fe	mg/L	0.002	0.002	0.003	0.03	0.04	0.04	0.038	0.037
Hg	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Li	µg/L	0.11	16	30	36	76	63	23	25
Mg	mg/L	0.02	14	6.6	10	16	7.5	0.72	1.0
Mn	µg/L	<0.3	<0.3	<0.3	0.4	10	2	1.5	0.7
Mo	µg/L	0.2	749	644	470	78	629	9.5	41

Nd	µg/L	<0.01	<0.01	<0.01	0.04	0.08	0.06	0.07	0.06
Ni	µg/L	2	12	5	46	260	8	2	2
P	mg/L	0.1	0.2	0.4	0.8	0.1	0.2	1.1	1.0
Pb	µg/L	<0.1	0.7	0.7	0.3	0.2	<0.1	<0.1	<0.1
Rb	µg/L	0.08	26	30	17	21	14	43	33
S	mg/L	3.6	96	72	91	156	81	8.9	37
Sb	µg/L	0.09	11	16	27	4.9	14	0.94	1.9
Se	µg/L	<0.2	14	15	27	5.2	8.5	0.8	11
Sr	µg/L	<1	188	270	5	12	2	45	132
Th	µg/L	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
Ti	mg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
U	µg/L	<0.2	0.98	1.3	0.73	0.23	0.41	0.30	1.4
V	µg/L	1.5	57	19	116	9.0	45	16	42
Y	µg/L	<0.03	<0.03	<0.03	0.07	0.25	0.19	0.11	0.16
Zn	µg/L	2	4	7	33	1100	12	8	6

Source: Geological and Bioregional Assessment Program (2019)

Table 16 Dissolved elemental concentrations in dilute HCl leachate solutions

Drillhole	Units	Blank	Tanumbirin-1		Atree-2			Shenandoah-1/1A	
Formation			Middle Velkerri	Middle Velkerri	Upper Velkerri	Middle Velkerri	Middle Velkerri	Lower Kyalla Shale	Velkerri B Shale
Depth (m)			3235	3272.88	671	709.15	764	1595	2513
Final pH			<1	<1	<1	<1	<1	<1	<1
Ag	µg/L	<0.01	4.4	4.0	27	9.4	12	0.41	2.4
Al	mg/L	0.007	181	237	208	198	311	341	233
As	µg/L	<0.1	355	287	481	760	509	36	110
B	mg/L	0.05	0.39	0.47	0.55	0.53	0.68	0.53	0.45
Ba	µg/L	<1	2600	3000	1400	3400	2900	2900	3500
Ca	mg/L	0.05	190	112	156	94	169	14	148
Cd	µg/L	<0.02	62	59	218	149	74	0.20	3.6
Ce	µg/L	0.008	243	181	490	284	527	336	301
Co	µg/L	<0.03	148	121	194	197	218	189	131
Cr	µg/L	<1	317	300	351	249	436	399	279
Cu	mg/L	<0.01	1.7	1.7	3.5	1.5	4.2	0.61	3.4
Fe	mg/L	0.002	208	322	243	350	497	445	257
Hg	µg/L	<0.2	0.8	0.4	8.0	5.5	5.6	0.5	1.1
La	µg/L	0.042	103	71	204	117	207	139	110
Li	µg/L	<0.1	139	316	175	201	409	536	297
Mg	mg/L	0.008	77	78	71	56	87	102	70
Mn	µg/L	<1	1900	2000	1100	1400	1200	1400	2000

Mo	µg/L	0.4	1470	972	504	657	737	5.5	38
Nd	µg/L	<0.002	259	159	436	247	475	149	314
Ni	µg/L	<10	4400	1300	2800	2100	1200	300	940
P	mg/L	<0.04	55	32	60	28	73	0.34	51
Pb	µg/L	0.03	582	621	703	406	676	154	551
Rb	µg/L	<0.2	329	331	541	564	580	868	427
S	mg/L	<0.1	71	43	118	184	163	5.8	20
Sb	µg/L	<0.1	24	20	31	19	13	0.3	1.8
Se	µg/L	<0.1	9.5	9.2	16	3.7	13	<0.1	3.3
Sr	µg/L	<1	1070	893	515	541	1020	326	995
Th	µg/L	0.005	79	51	90	61	91	44	81
Ti	mg/L	<0.01	0.59	0.61	1.8	1.8	1.6	2.9	0.67
U	µg/L	<0.001	52	69	59	52	70	5.7	19
V	µg/L	<10	2370	1030	3220	1930	2900	539	655
Y	µg/L	<0.01	455	254	520	237	577	30	374
Zn	µg/L	<10	6000	3500	13000	13000	8900	640	2000

Source: Geological and Bioregional Assessment Program (2019)

Table 17 Dissolved elemental concentrations in HFF leachate solutions

Drillhole		Blank	Tanumbirin-1		Aldree-2			Shenandoah-1/1A	
Formation			Middle Velkerri	Middle Velkerri	Upper Velkerri	Middle Velkerri	Middle Velkerri	Lower Kyalla Shale	Velkerri B Shale
Depth (m)			3235	3272.88	671	709.15	764	1595	2513
Final pH		2.1	2.6	2.6	2.5	2.3	2.5	2.6	2.6
Ag	µg/l	0.01	2.9	2.7	19	5.8	8.1	0.34	2.0
Al	mg/l	0.03	18	27	19	22	27	43	30
As	µg/l	<0.2	34	24	73	115	51	1.3	14
B	mg/l	0.21	0.29	0.32	0.29	0.22	0.23	0.23	0.21
Ba	µg/l	<1	250	230	70	90	80	100	220
Ca	mg/l	0.26	91	62	95	81	70	12	63
Cd	µg/l	<0.1	52	51	179	108	68	0.3	2.8
Ce	µg/l	0.1	79	59	158	71	145	2.2	105
Co	µg/l	0.16	112	86	126	128	107	108	89
Cr	µg/l	0.5	31	30	23	21	49	44	27
Cu	mg/l	<0.01	0.90	1.0	2.1	0.82	2.3	0.40	2.3
Fe	mg/l	0.04	54	77	25	30	43	76	53
Hg	µg/l	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
La	µg/l	0.013	33	19	64	22	58	0.52	33
Li	µg/l	0.2	35	95	68	110	193	168	89
Mg	mg/l	0.03	32	22	27	21	22	18	18
Mn	µg/l	1	1300	1300	510	760	270	320	1300

Mo	µg/l	0.05	190	117	109	106	119	0.11	5.0
Nd	µg/l	0.06	88	67	192	120	181	2.4	132
Ni	µg/l	<10	3000	700	2200	1400	700	100	450
P	mg/l	0.05	1.6	0.75	10	6.4	5.5	<0.04	1.1
Pb	µg/l	2.1	53	184	8.2	5.8	2.1	50	147
S	mg/l	---	---	---	---	---	---	---	---
Sb	µg/l	0.26	6.0	6.7	9.3	7.4	4.3	0.25	0.74
Se	µg/l	6.8	23	24	22	16	18	11	18
Sr	µg/l	2.4	615	582	191	177	193	196	537
Th	µg/l	0.01	0.17	0.23	0.07	0.04	0.05	0.07	0.22
Ti	mg/l	0.28	0.18	0.26	0.10	0.18	0.14	0.19	0.22
U	µg/l	0.04	11	19	20	18	27	0.5	5.0
V	µg/l	<0.3	294	117	310	197	342	20	67
Y	µg/l	0.17	235	151	308	177	336	6.3	186
Zn	µg/l	10	3700	2500	10000	8900	5500	300	1400

Source: Geological and Bioregional Assessment Program (2019)

Table 18 Effect of pressure on mobilisation of dissolved elemental concentrations in HFF leachate solutions from Tanumbirini-1 (Middle Velkerri; 3235m) powdered rock sample

Drillhole	Units	Tanumbirini-1	Tanumbirini-1	Ratio	Trajectory
Pressure (KPa)		100	18400		
Final pH		2.6	1.8		
Th	µg/l	0.17	0.77	4.5	↑
Co	µg/l	112	439	3.9	↑
U	µg/l	11	36	3.3	↑
Li	µg/l	35	64	1.8	↑
Cu	mg/l	0.9	1.5	1.7	↑
Ag	µg/l	2.9	4.8	1.7	↑
Ca	mg/l	91	143	1.6	↑
Zn	µg/l	3.7	5.8	1.6	↑
As	µg/l	34	52	1.5	↑
Ni	µg/l	3	4.5	1.5	↑
Al	mg/l	18	26	1.4	↑
Mg	mg/l	32	41	1.3	↑
Mn	mg/l	1.3	1.6	1.2	↑
Se	µg/l	23	28	1.2	↑
Cd	µg/l	52	60	1.2	↑
Ti	Mg/l	0.18	0.2	1.1	↔
Sr	µg/l	615	661	1.1	↔
Hg	µg/l	<0.3	<0.3	1.0 ^a	↔
Fe	mg/l	54	51	0.9	↔
P	mg/l	1.6	1.5	0.9	↔
Cr	µg/l	31	29	0.9	↔
V	µg/l	294	132	0.4	↓
B	mg/l	0.29	0.1	0.3	↓
Sb	µg/l	6	1.9	0.3	↓
Mo	µg/l	190	4.3	0.02	↓
Ba	mg/l	0.25	0.003	0.01	↓
Pb	µg/l	53	<0.3	0.003 ^a	↓

^a half detection limit used to calculate difference; na = not applicable; Green = increased metal mobilisation with increased pressure; Red = decreased metal mobilisation with increased pressure; black = similar metal concentrations with increasing pressure

Source: Geological and Bioregional Assessment Program (2019)

3.2.3 Extracts – organics

Phenol were detected only in powdered rock sample extracts from Shenandoah-1/1A drill core (Lower Kyalla and Velkerri B Shale) (2 of 7 sample extracts) (Table 19) (Geological and Bioregional Assessment Program, 2019). Targeted PAHs were detected only in powdered rock sample extracts from Atree-2 drill core (Upper and Middle Velkerri) (3 of 7 sample extracts) (Table 19) (Geological and Bioregional Assessment Program, 2019). Other targeted phenols and PAHs were below their respective concentrations of reporting in sample extracts (Table 10). The most common identified PAHs in sample extracts were benzo(ghi)perylene, chrysene, indeno-(1,2,3-cd)-pyrene, and phenanthrene (3 of 7 extracts) (Table 19). The Atree-2 Upper Velkerri sample contained the highest number of PAHs (n=5) and concentrations in sample extracts e.g. anthracene = 10.5 µg/kg, benzo(ghi)perylene = 7.2 µg/kg, indeno-(1,2,3-cd)-pyrene = 7.2 µg/kg, and phenanthrene = 45.9 µg/kg (except chrysene = 64.8 µg/kg in the Middle Velkerri sample (764m) from Atree-2) (Table 19).

The highest concentration of TRHs were found to be associated with the >C16-C34 NEPM TRH (21 to 277 mg/kg; 39 to 43% TRHs) and TRH C15-C28 (17 to 225 mg/kg; 32 to 35% TRHs) fractions for powdered rock samples (Table 19) (Geological and Bioregional Assessment Program, 2019). Targeted analysis of phenols and PAHs represented a small fraction of the total organic geogenic compounds identified in the sample extracts (i.e. 0.02-0.07%) (Table 19). The absence of volatile compounds in sample extracts from this study may be due to the long-term storage of the sourced rocks in dry, non-climate controlled conditions. Hence, most geogenic organic compounds (as TRHs) in sample extracts were unidentified and their potential risk (individuals and mixtures) to aquatic environments is unknown. A study by Maguire-Boyd and Barron (2014) found that the composition of chemicals based on their carbon content varied between shale gas regions and the majority of organic chemicals were present in the > C6 fractions. Similarly, solvent-extracted shale samples from the United Kingdom were found to have organic chemicals predominantly in the C14-C29 fraction, reflecting both the maturity of the shales as well as their algal origins (Wright et al., 2015).

3.3 Discussion

The leachate tests conducted with dilute HCl and HFF mobilised the highest element concentrations into solutions compared to SGW. This demonstrates the role that acidity and chemical constituents of HFFs (e.g. chelating agents, surfactants, solvents, etc.) can play in mobilising elements from powdered rocks in formations. The elements showing substantial mobilisation (>50-fold median increase compared to SGW) in HFF included: aluminium, cadmium, cesium, cobalt, iron, lanthanum, manganese, neodymium, nickel, lead, silver, yttrium, and zinc. It was noted that there was variability between rock types in formations both in terms of the total content of elements and concentrations of elements mobilised into solution. Further studies are needed to determine the underlying relationships between element content and physico-chemical properties of the formations and fate of chemicals in the hydraulic fracturing fluid.

Table 19 Solvent-extractable organic compound concentrations from powdered rock samples (µg/kg)

	Tanumbirin 1		Atree-2			Shenandoah 1/1A	
Formation	Middle Velkerri	Middle Velkerri	Upper Velkerri	Middle Velkerri	Middle Velkerri	Lower Kyalla Shale	Velkerri B Shale
Depth (m)	3235	3272.88	671	709.15	764	1595	2513
PAHs							
Anthracene	<5	<5	10.5	<5	<5	<5	<5
Benzo(ghi)perylene	<5	<5	7.2	5.9	6.5	<5	<5
Chrysene	<5	<5	52.6	31.2	64.8	<5	<5
Indeno-(1,2,3-cd)-pyrene	<5	<5	7.2	5.9	6.5	<5	<5
Phenanthrene	<5	<5	45.9	9.4	39.4	<5	<5
Phenols							
Phenol	<5	<5	<5	<5	<5	31	22.9
TRHs							
TRH C10 - C14	<100	<100	<100	<100	<100	<100	<100
TRH>C10 - C16*	<100	<100	2438	594	1065	<100	<100
TRH C15 - C28	40,514	17,274	224,665	123,762	120,370	38,878	17,544
TRH >C16 - C34*	47,431	21,113	277,247	163,366	157,407	54,134	24,366
TRH C29 - C36	17,787	9,117	90,822	69,307	64,815	25,098	13,645
TRH >C34 - C40*	11,364	6,718	52,581	45,050	43,981	20,177	13,158

*NEPM TRH reporting values

Source: Geological and Bioregional Assessment Program (2019)

Higher pressure led to increased mobilisation into solutions using HFFs of elements such as thorium, cobalt, uranium, lithium, copper, silver, calcium and zinc; and decreased mobilisation for elements such as vanadium, boron, antimony, molybdenum, barium, and lead. The findings highlight the important role pressure can play in the mobilisation of geogenic chemicals from powdered rocks in formations during hydraulic fracturing. Further work is required to determine the relationship between pressure (and temperature) on the HFFs and mobilisation of geogenic chemicals from powdered rocks in shale gas formations in the Beetaloo GBA region.

Targeted priority organic chemicals such as phenols, PAHs and TRHs were detected in extracts of powdered rock samples from formation in Beetaloo GBA region. However, the majority of the organic geogenic compounds extracted (as TRHs) were unidentified and would require further 'forensic' analysis for their identification and quantification. Analytical methodology used to assess unknown organic compounds have previously included gas chromatography-mass spectrometry (GC-MS) (combined with library searches), pyGC-MS, GCxGC-time-of-flight mass spectrometry (TOFMS) and liquid chromatography-TOFMS (Maguire-Boyle and Barron, 2014; Hoelzer et al., 2016; Huang et al., 2019; Luek and Gonsior, 2017; Orem et al., 2014; Piotrowski et al., 2018; Wright et al., 2015). This study used a mixture of polar and non-polar solvents to gain an understanding (under upper bound conditions) of the mobilisation of geogenic organic compounds from powdered rock samples due to hydraulic fracturing. Further research is needed to determine the composition and concentration of industrial chemicals (and their degradation/transformational products) and targeted/unknown geogenic organic compounds mobilised during hydraulic fracturing at shale, tight and deep coal gas operations to assess potential environmental risks and guide future field-based monitoring, management, and treatment options. This study did not consider attenuation processes occurring in natural systems (attenuation processes) that could reduce the concentrations of industrial and geogenic chemicals in the environment.

3 Laboratory-based leachate and extraction tests on powdered rock samples from the Isa GBA region – geogenic chemicals

4 Conclusions

A total of 116 chemicals were identified for use in drilling and hydraulic fracturing at shale, tight and deep coal gas operations between 2011 and 2016. A Tier 1 qualitative (screening) ERA of the identified chemicals found: 42 chemicals were of 'low concern' and considered to pose minimal risk to surface water and groundwater aquatic ecosystems; 33 chemicals are of 'potentially high concern'; and 41 are of 'potential concern'. The identified chemicals of potential concern and potential high concern would require further site-specific quantitative chemical assessments to be performed to determine risks from specific gas operations to aquatic ecosystems.

The chemicals used in drilling and hydraulic fracturing are expected to change with time as the gas industry adapts to site-specific conditions, improves gas extraction efficiency, and endeavours to use 'greener-safer' options. A Tier 1 qualitative (screening) ERA should be undertaken on new chemicals (and chemical not previously assessed) used in shale, tight and deep coal operations in Australia to determine if a potential environmental risk exists ('yes/no'). If a risk exists, the questions will change to 'what', 'where' and 'how great' is the risk (i.e. Tier 2 and 3 quantitative ERAs)?

Laboratory-based leachate tests on powdered rock samples collected from formations in the Beetaloo GBA region identified several elements that could be substantially mobilised into solutions by HFFs including aluminium, cadmium, cesium, cobalt, iron, lanthanum, manganese, neodymium, nickel, lead, silver, yttrium, and zinc. Priority organic chemicals such as phenol, PAHs and TRHs were detected in extracts of powdered rock samples. Targeted analysis of PAHs represented a small fraction of the total organic geogenic compounds present in the sample extracts. Hence, the majority of organic compounds in sample extracts (as TRHs) were unidentified and their risk (individual and mixtures) to aquatic environments is unknown. The composition and concentration of geogenic chemicals in flowback and produced waters will depend on many factors including: (i) geology and mineralogy of formations; (ii) surface area of the fracture network exposed to hydraulic fracturing fluids; (iii) composition and concentration of chemicals used in hydraulic fracturing; (iv) residence time of hydraulic fracturing fluids in formations; (v) operational and environmental conditions (e.g. volumes added and recovered, temperature, pressure); and (vi) chemical and physical reactions (e.g. adsorption, complexation, precipitation, aggregation, degradation and transformations).

Companies undertake an ERA process of gas operations (in consultation with government agencies) that identifies potential hazards (e.g. chemical transport and storage, hydraulic fracturing fluid injection, flowback and produced water storage), determines the likelihood and consequence of a risk occurring, identifies and evaluates control and mitigation measures (e.g. what controls are in place or need to be in place to address the identified risk and how effective are these controls), and develops a monitoring program to ensure controls and management strategies are adequate/effective and for compliance. Despite undertaking these detailed ERAs, there is still public concern surrounding the potential environmental impacts of hydraulic fracturing – particularly, the threats posed by the mixture of industrial chemicals used and geogenic chemicals that could be mobilised and their impacts on water quality.

5 Knowledge gaps

The chemical assessment identified the following knowledge gaps:

- Chemicals used in drilling and hydraulic fracturing are expected to change with time as industry adapts to site-specific conditions, improves gas extraction efficiency and endeavours to use 'greener-safer' options. A Tier 1 qualitative (screening) ERA should be undertaken on new chemicals (and chemicals not previously assessed) used in shale, tight and deep coal operations in Australia to determine if a potential environmental risk exists ('yes/no'). If a potential risk exists, the questions should change to 'what', 'where' and 'how great' is the risk (Tier 2 and 3 quantitative ERAs)? The chemical assessments should be undertaken in the context of the risk management framework that determines the likelihood and consequence of a risk event occurring, identifies and evaluates control and mitigation measures (e.g. what controls are in place or need to be in place to address the identified risk and how effective are these controls), and develops a monitoring program to ensure controls and management strategies are adequate/effective and for compliance.
- The Tier 1 qualitative ERA relied mainly on aquatic acute ecotoxicity data representing three trophic levels – a freshwater alga, a water flea and a fish species. Acute toxicity data may not be sufficient for assessing the environmental risks of persistent and bioaccumulative chemicals that could have effects on aquatic organisms due to long-term exposure. Chronic toxicity data using a range of aquatic organisms and trophic levels are needed to accurately assess the effects of long-term exposure of chemicals to aquatic organisms. In addition, ecotoxicity data on drilling and hydraulic fracturing chemicals for Australian species are limited and ecotoxicity endpoints are currently not available for groundwater organisms (e.g. stygofauna).
- Comprehensive baseline surface water and groundwater quality data used for targeted aquifers, irrigation and drinking water, and ground water dependent ecosystems should be collected prior to shale, tight and deep coal gas developments.
- Publicly available data on the composition and concentration of chemicals in hydraulic fracturing fluids, flowback and produced water, and wastes (e.g. muds, brines) from shale, tight and deep coal operations in Australia are limited. The fate, transformations and toxicity of chemicals present in hydraulic fracturing fluids, and flowback and produced water (individual chemicals and mixtures) in the environment are also unknown.
- Leachate tests did not include analysis for naturally occurring radioactive materials (NORMs). Further research needs to be undertaken into understanding the mobilisation of NORMs from formations in the Beetaloo GBA region and their fate and behaviour during hydraulic fracturing, storage, and treatment.
- The majority of organic compounds present in sample extracts from powdered rock samples were unidentified and their potential risk (if present in flowback and produced waters) to aquatic environments is unknown.
- Despite the very low likelihood of a well integrity failure or failure of surface infrastructure (ponds, tanks, pipelines, etc.) associated with shale, tight and deep coal gas operations in Australia (i.e. constructed to highest industry standards, high level of government regulation

and compliance), there is still public concern about the consequences to water quality (drinking, livestock, aquatic ecosystems and cultural) if fluids are released. Surface water and groundwater monitoring and modelling using site-specific conditions and exposure scenarios would improve public understanding of potential impacts and consequences to water quality (i.e. localised event) and the adequacy of control and management plans to prevent environmental impacts.

6 Recommendations

The following are recommendations to improve chemical ERAs at shale, tight and deep coal operations in Australia:

- Chemicals identified in a Tier 1 chemical screening as ‘potentially high concern’ and ‘potential concern’ should undergo further site-specific assessments under realistic environmental conditions and exposure scenarios to determine ‘what’, ‘where’ and ‘how great’ is the risk (Tier 2 and 3 quantitative ERAs)? The chemical assessments should be undertaken in the context of the risk management framework that determines the likelihood and consequence of a risk event occurring, identifies and evaluates control and mitigation measures (e.g. what controls are in place or need to be in place to address the identified risk and how effective are these controls), and develops a monitoring program to ensure controls and management strategies are adequate/effective and for compliance.
- Comprehensive baseline surface water and groundwater quality data in targeted aquifers, used for irrigation and drinking water, and for ground water dependent ecosystems collected prior to shale, tight and deep coal gas developments.
- Consideration of site-specific groundwater-related risks of chemicals due to hydraulic fracturing in the event of unlikely release of fluids due to well integrity failure and pond/tank leakage (residual risk reduction).
- Public disclosure of chemicals and water quality monitoring data before, during and after hydraulic fracturing would provide greater community and government understanding in drilling and hydraulic fracturing (Development of National Register of Chemicals for Shale, Tight and Deep-Coal Gas Operations in Australia).
- Research needs to be undertaken into determining the composition and concentration of unknown organic compounds present in flowback and produced waters and their potential effects on aquatic organisms, management and treatment.
- Direct toxicity assessments of hydraulic fracturing fluids, flowback and produced water would, in conjunction with chemical analyses, provide information on no-effect concentrations and for safe dilutions/treatment options.

Public concern about potential environmental impacts on water quality from hydraulic fracturing remains heightened. In particular, the community is concerned about potential impacts on water quality from the mixture of industrial chemicals and geogenic chemicals that could be mobilised during shale, tight and deep coal gas resource developments. The independent collection and open and transparent reporting of water quality data at future gas operations before, during and after hydraulic fracturing would improve community and government understanding in the ERA process, controls and monitoring of chemicals; and inform wastewater management and treatment options. The Stage 3 chemical assessment project will undertake water quality monitoring before, during and after hydraulic fracturing at future shale gas developments in the Beetaloo GBA region. Specifically, the project aims to:

1. Assess the concentration of industrial and geogenic chemicals in flowback and produced waters resulting from hydraulic fracturing operations to determine safe dilutions/treatment options.
2. Check compliance of chemical concentrations in nearby surface water and groundwater bores with relevant Australian water quality guideline values (i.e. Australian drinking water quality criteria, Australian livestock watering quality criteria, ANZECC/ARMCANZ (2000) criteria for the protection of aquatic ecosystems).
3. Quantify the site-specific surface water and groundwater-related risks of chemicals used in hydraulic fracturing in the event of unlikely release of fluids, for example, due to compromised well integrity or leakage from storage dams. Residual risk reduction that unlikely event will have minimal consequence on water quality (localised event) and treatment, remediation and management plans are adequate to prevent impacts.

References

- Adriano DC (2001) Trace elements in terrestrial environments: biogeochemistry, bioavailability, and risk of metals. Springer-Verlag, New York, NY, USA.
- AECOM Australia Pty Ltd (2017) Beetaloo Project Hydraulic Fracturing Risk Assessment. Amungee NW-1H. Prepared for: Origin Energy Resources Limited. 08-Sep-2017. Job No. 60542121. Viewed 16 November 2018, <https://frackinginquiry.nt.gov.au/submission-library>.
- ANZECC/ARMCANZ (2000) Australian and New Zealand guidelines for fresh and marine water quality. Australia and New Zealand Environment and Conservation Council / Agricultural and Resource Management Council of Australia and New Zealand, Canberra, Australia. Viewed 15 January 2019, <https://www.waterquality.gov.au/anz-guidelines/resources/previous-guidelines/anzecc-armcanz-2000>.
- Apte SC, Williams M, Kookana RS, Batley GE, King JJ, Jarolimek CV and Jung RF (2017) Release of geogenic contaminants from Australian coal seams: experimental studies, Project report, report prepared by the Land & Water, Commonwealth Scientific and Industrial Research Organisation (CSIRO) as part of the National Assessment of Chemicals Associated with Coal Seam Gas Extraction in Australia, Commonwealth of Australia, Canberra. Viewed 17 December 2018, <https://publications.csiro.au/rpr/download?pid=csiro:EP143463&dsid=DS1>.
- Beach Energy and RPS (2012) Environmental Impact Report. Fracture stimulation of deep shale gas and tight gas targets in the Nappamerri Trough (Cooper Basin), Queensland. A269B-Queensland Cooper Basin shale gas fracture stimulation EIR; Rev 0 / September 2012. Beach Energy, Adelaide.
- Boethling RS, Howard PH, Meylan W, Stiteler W, Beauman J and Tirado N (1994) Group contribution method for predicting probability and rate of aerobic biodegradation. Environmental Science & Technology 28(3), 459-465. Doi: 10.1021/es00052a018.
- Department of the Environment and Energy (2017) Chemical risk assessment guidance manual: for chemicals associated with coal seam gas extraction. Guidance manual prepared by Hydrobiology and ToxConsult Pty Ltd for the Department of the Environment and Energy. Commonwealth of Australia, Canberra. Viewed 05 March 2019, <http://www.environment.gov.au/system/files/consultations/81536a00-45ea-4aba-982c-5c52a100cc15/files/risk-assessment-guidance-manual-chemicals-associated-csg-extraction-australia-exposure-draft.pdf>.
- ECHA (2018) Current SVHC intentions. European Chemicals Agency, Helsinki, Finland. Viewed 03 September 2018, <https://echa.europa.eu/registry-of-intentions>.
- Environment Canada Health Canada (2008) Screening assessment for the challenge. Dodecamethylcyclohexasiloxane (D6): Chemical Abstracts Service Registry Number 540-97-6. Environment and Climate Change Canada, Government of Canada. Viewed 04 September 2018, https://www.ec.gc.ca/ese-ees/FC0D11E7-DB34-41AA-B1B3-E66EFD8813F1/batch2_540-97-6_en.pdf.

References

- Fairbrother A, Burton GA, Klaine SJ, Powell DE, Staples CA, Mihaich EM, Woodburn KB and Gobas FAPC (2015) Characterization of ecological risks from environmental releases of decamethylcyclopentasiloxane (D5). *Environmental Toxicology and Chemistry* 34(12), 2715–2722. Doi: 10.1002/etc.3041.
- Fairbrother A and Woodburn KB (2016) Assessing the aquatic risks of the cyclic volatile methyl siloxane D4. *Environmental Science and Technology Letters* 3(10), 359–363. Doi: 10.1021/acs.estlett.6b00341.
- Geological and Bioregional Assessment Program (2018) Chemical properties and ecotoxicity database. [tabular]. Viewed 26 November 2018, <https://repo.bioregionalassessments.gov.au/metadata/FAC2728A-81BC-466F-A430-909A371D1187>. GBA data repository GUID: FAC2728A-81BC-466F-A430-909A371D1187.
- Geological and Bioregional Assessment Program (2019) Elemental and compound concentrations from laboratory-based leachate tests: Beetaloo GBA region. [tabular]. Viewed 17 July 2019. GBA data repository GUID: F586FC62-A8BE-4B81-B011-845A80461F58.
- Government of Canada (2012a) Siloxane D4 (Cyclotetrasiloxane, octamethyl-) CAS Registry Number 556-67-2. Viewed 03 September 2018, <https://www.canada.ca/en/health-canada/services/chemical-substances/challenge/batch-2/cyclotetrasiloxane-octamethyl.html>.
- Government of Canada (2012b) Siloxane D5 (Cyclopentasiloxane, decamethyl-): CAS Registry Number 541-02-6. Viewed 03 September 2018, <https://www.canada.ca/en/health-canada/services/chemical-substances/challenge/batch-2/cyclopentasiloxane-decamethyl.html>.
- Ground Water Protection Council, Interstate Oil and Gas Compact Commission (2018) Fracfocus chemical data from 100 shale gas wells in USA. [tabular]. Viewed 28 November 2018, <http://fracfocus.org/>. GBA data repository GUID: 00F41402-0D60-44D4-822E-8864AA77564E.
- Harrison AL, Jew AD, Dustin MK, Thomas DL, Joe-Wong CM, Bargar JR, Johnson N, Brown GE and Maher K (2017) Element release and reaction-induced porosity alteration during shale-hydraulic fracturing fluid interactions. *Applied Geochemistry* 82, 47–62. Doi: <https://doi.org/10.1016/j.apgeochem.2017.05.001>.
- Hoelzer K, Sumner AJ, Karatum O, Nelson RK, Drollette BD, O'Connor MP, D'Ambro EL, Getzinger GJ, Ferguson PL, Reddy CM, Elsner M and Plata DL (2016) Indications of transformation products from hydraulic fracturing additives in shale-gas wastewater. *Environmental Science & Technology* 50(15), 8036–8048. Doi: 10.1021/acs.est.6b00430.
- Huang KZ, Xie YF and Tang HL (2019) Formation of disinfection by-products under influence of shale gas produced water. *Science of The Total Environment* 647, 744–751. Doi: 10.1016/j.scitotenv.2018.08.055.

- Kahrilas GA, Blotevogel J, Stewart PS and Borch T (2015) Biocides in hydraulic fracturing fluids: a critical review of their usage, mobility, degradation, and toxicity. *Environmental Science and Technology* 49(1), 16–32. Doi: 10.1021/es503724k.
- Kahrilas GA, Blotevogel J, Corrin ER and Borch T (2016) Downhole transformation of the hydraulic fracturing fluid biocide glutaraldehyde: implications for flowback and produced water quality. *Environmental Science and Technology* 50(20), 11414–11423. Doi: 10.1021/acs.est.6b02881.
- Kesavan S and Prud'homme RK (1992) Rheology of guar and (hydroxypropyl) guar crosslinked by borate. *Macromolecules* 25(7), 2026–2032. Doi: 10.1021/ma00033a029.
- Luek JL and Gonsior M (2017) Organic compounds in hydraulic fracturing fluids and wastewaters: A review. *Water Research* 123, 536–548. Doi: 10.1016/j.watres.2017.07.012.
- Maguire-Boyle SJ and Barron AR (2014) Organic compounds in produced waters from shale gas wells. *Environmental Science: Processes & Impacts* 16(10), 2237–2248. Doi: 10.1039/C4EM00376D.
- Meylan W, Boethling R, Aronson D, Howard P and Tunkel J (2007) Chemical structure-based predictive model for methanogenic anaerobic biodegradation potential. *Environmental Toxicology and Chemistry* 26(9), 1785–1792. Doi: 10.1897/06-579R.1.
- Neilson AH (1994) *Organic chemicals in the aquatic environment: distribution, persistence, and toxicity*. CRC Press, Inc., Boca Raton.
- NICNAS (2017) Identification of chemicals associated with coal seam gas extraction in Australia. Project report prepared by the National Industrial Chemicals Notification and Assessment Scheme (NICNAS) as part of the National Assessment of Chemicals Associated with Coal Seam Gas Extraction in Australia, Commonwealth of Australia, Canberra.
- NICNAS (2018) Cyclic volatile methyl siloxanes: environment tier II assessment. National Industrial Chemicals Notification and Assessment Scheme, Sydney, Australia. Viewed 03 September 2018, <https://www.nicnas.gov.au/chemical-information/imap-assessments/imap-assessments/tier-ii-environment-assessments/cvms>.
- Northern Territory Government (2018) Department of Primary Industry and Resources. Chemical disclosure reports. Viewed 15 December 2018, <https://dpir.nt.gov.au/mining-and-energy/public-environmental-reports/chemical-disclosure-reports>.
- Norton SB, Rodier DJ, van der Schalie WH, Wood WP, Slimak MW and Gentile JH (1992) A framework for ecological risk assessment at the EPA. *Environmental Toxicology and Chemistry* 11(12), 1663–1672. Doi: 10.1002/etc.5620111202.
- Orem W, Tatu C, Varonka M, Lerch H, Bates A, Engle M, Crosby L and McIntosh J (2014) Organic substances in produced and formation water from unconventional natural gas extraction in coal and shale. *International Journal of Coal Geology* 126, 20–31. Doi: 10.1016/j.coal.2014.01.003.

References

- Piotrowski PK, Weggler BA, Barth-Naftilan E, Kelly CN, Zimmermann R, Saiers JE and Dorman FL (2018) Non-Targeted chemical characterization of a Marcellus shale gas well through GC × GC with scripting algorithms and high-resolution time-of-flight mass spectrometry. *Fuel* 215, 363–369. Doi: 10.1016/j.fuel.2017.11.026.
- Taylor SR (1964) Abundance of chemical elements in the continental crust: a new table. *Geochimica et Cosmochimica Acta* 28(8), 1273–1285. Doi: [https://doi.org/10.1016/0016-7037\(64\)90129-2](https://doi.org/10.1016/0016-7037(64)90129-2).
- US EPA (1992) Framework for ecological risk assessment. Risk assessment forum. EPA/630/R-92/001. Washington, DC, USA.
- US EPA (2004) An examination of EPA risk assessment principles and practices. Office of the Science Advisor EPA/100/B-04/001. US Environmental Protection Agency, Washington, DC, USA. Viewed 16 November 2018, <https://semspub.epa.gov/work/10/500006305.pdf>.
- US EPA (2015) Risk Toolbox. United States Environmental Protection Agency. Washington, DC. Viewed 16 November 2018, <http://www2.epa.gov/risk>.
- US EPA (2017) Operation Manual for the ECOlogical Structure-Activity Relationship Model (ECOSAR) Class Program. Estimating toxicity of industrial chemicals to aquatic organisms using the ECOSAR (ecological structure activity relationship) class program. Risk Assessment Division. US Environmental Protection Agency, Washington DC, USA. October 2017. Viewed 27 November 2018, https://www.chemsafetypro.com/Topics/CRA/How_to_Use_US_EPA_ECOSAR_to_Predict_Aquatic_Toxicity.html.
- US EPA (2018) Estimation Programs Interface Suite™ for Microsoft® Windows, v 4.11. US Environmental Protection Agency, Washington, DC, USA. Viewed 27 November 2018, <https://www.epa.gov/tsca-screening-tools/epi-suite™-estimation-program-interface>.
- Worley Parsons (2010) Spatial analysis of coal seam water chemistry. Report for Department of Environment and Resource Management (DERM), Queensland.
- Wright MC, Court RW, Kafantaris F-CA, Spathopoulos F and Sephton MA (2015) A new rapid method for shale oil and shale gas assessment. *Fuel* 153, 231–239. Doi: 10.1016/j.fuel.2015.02.089.
- Ziemkiewicz PF and Thomas He Y (2015) Evolution of water chemistry during Marcellus Shale gas development: A case study in West Virginia. *Chemosphere* 134, 224–231. Doi: <https://doi.org/10.1016/j.chemosphere.2015.04.040>.

Glossary

The register of terms and definitions used in the Geological and Bioregional Assessment Program is available online at <http://registry.it.csiro.au/def/gba/glossary> (note that terms and definitions are respectively listed under the 'Name' and 'Description' columns in this register). This register is a list of terms, which are the preferred descriptors for concepts. Other properties are included for each term, including licence information, source of definition and date of approval. Semantic relationships (such as hierarchical relationships) are formalised for some terms, as well as linkages to other terms in related vocabularies. Many of the definitions for these terms have been sourced from external glossaries – several from international sources; spelling variations have been preserved to maintain authenticity of the source.

accumulation: in petroleum geosciences, an 'accumulation' is referred to as an individual body of moveable petroleum

activity: for the purposes of Impact Modes and Effects Analysis (IMEA), a planned event associated with unconventional gas resource development. For example, activities during the exploration life-cycle stage include drilling and coring, ground-based geophysics and surface core testing. Activities are grouped into ten major activities, which can occur at different life-cycle stages.

adsorption: the capability of all solid substances to attract to their surfaces molecules of gases or solutions with which they are in contact

anticline: an arch-shaped fold in rock in which rock layers are upwardly convex. The oldest rock layers form the core of the fold and, outward from the core, progressively younger rocks occur.

aquifer: rock or sediment in a formation, group of formations, or part of a formation that is saturated and sufficiently permeable to transmit quantities of water to bores and springs

aquitard: a saturated geological unit that is less permeable than an aquifer, and incapable of transmitting useful quantities of water. Aquitards commonly form a confining layer over an artesian aquifer.

artesian aquifer: an aquifer that has enough natural pressure to allow water in a bore to rise to the ground surface

asset: an entity that has value to the community and, for the purposes of geological and bioregional assessments, is associated with a GBA region. An asset is a store of value and may be managed and/or used to maintain and/or produce further value. An asset may have many values associated with it that can be measured from a range of perspectives; for example, the values of a wetland can be measured from ecological, sociocultural and economic perspectives.

bed: in geosciences, the term 'bed' refers to a layer of sediment or sedimentary rock, or stratum. A bed is the smallest stratigraphic unit, generally a centimetre or more in thickness. To be labeled a bed, the stratum must be distinguishable from adjacent beds.

bioaccumulation: a process by which chemicals are taken up by a plant or animal either directly through exposure to a contaminated medium (soil, sediment, water) or by consuming food or water containing the chemical

biogenic gas: hydrocarbon gases (which are overwhelmingly (greater than or equal to 99%) methane) produced as a direct consequence of bacterial activity

bore: a narrow, artificially constructed hole or cavity used to intercept, collect or store water from an aquifer, or to passively observe or collect groundwater information. Also known as a borehole or piezometer.

casing: a pipe placed in a well to prevent the wall of the hole from caving in and to prevent movement of fluids from one formation to another

cementing: the application of a liquid slurry of cement and water to various points inside and outside the casing

charge: in petroleum geoscience, a 'charge' refers to the volume of expelled petroleum available for entrapment

cleat: the vertical cleavage of coal seams. The main set of joints along which coal breaks when mined.

coal: a rock containing greater than 50 wt.% organic matter

coal seam gas: coal seam gas (CSG) is a form of natural gas (generally 95% to 97% pure methane, CH₄) extracted from coal seams, typically at depths of 300 to 1000 m. Also called coal seam methane (CSM) or coalbed methane (CBM).

compression: lateral force or stress (e.g. tectonic) that tends to decrease the volume of, or shorten, a substance

conceptual model: an abstraction or simplification of reality that describes the most important components and processes of natural and/or anthropogenic systems, and their response to interactions with extrinsic activities or stressors. They provide a transparent and general representation of how complex systems work, and identify gaps or differences in understanding. They are often used as the basis for further modelling, form an important backdrop for assessment and evaluation, and typically have a key role in communication. Conceptual models may take many forms, including descriptive, influence diagrams and pictorial representations.

confined aquifer: an aquifer saturated with confining layers of low-permeability rock or sediment both above and below it. It is under pressure so that when the aquifer is penetrated by a bore, the water will rise above the top of the aquifer.

consequence: synonym of impact

context: the circumstances that form the setting for an event, statement or idea

contingent resources: those quantities of petroleum which are estimated, on a given date, to be potentially recoverable from known accumulations but which are not currently considered to be commercially recoverable

conventional gas: conventional gas is obtained from reservoirs that largely consist of porous sandstone formations capped by impermeable rock, with the gas trapped by buoyancy. The gas can often move to the surface through the gas wells without the need to pump.

Cooper Basin: the Cooper Basin geological province is an Upper Carboniferous – Middle Triassic geological sedimentary basin that is up to 2500 m thick and occurs at depths between 1000 and 4400 m. It is overlain completely by the Eromanga and Lake Eyre basins. Most of the Cooper Basin is in south-west Queensland and north-east SA, and includes a small area of NSW at Cameron Corner. It occupies a total area of approximately 130,000 km², including 95,740 km² in Queensland, 34,310 km² in SA and 8 km² in NSW.

crude oil: the portion of petroleum that exists in the liquid phase in natural underground reservoirs and remains liquid at atmospheric conditions of pressure and temperature. Crude oil may include small amounts of non-hydrocarbons produced with the liquids.

crust: the outer part of the Earth, from the surface to the Mohorovicic discontinuity (Moho)

current economic conditions: establishment of current economic conditions should include relevant historical petroleum prices and associated costs and may involve an averaging period that is consistent with the purpose of the reserve estimate, appropriate contract obligations, corporate procedures and government regulations involved in reporting these reserves

dataset: a collection of data in files, in databases or delivered by services that comprise a related set of information. Datasets may be spatial (e.g. a shape file or geodatabase or a Web Feature Service) or aspatial (e.g. an Access database, a list of people or a model configuration file).

deep coal gas: gas in coal beds at depths usually below 2000 m are often described as 'deep coal gas'. Due to the loss of cleat connectivity and fracture permeability with depth, hydraulic fracturing is used to release the free gas held within the organic porosity and fracture system of the coal seam. As dewatering is not needed, this makes deep coal gas exploration and development similar to shale gas reservoirs.

deformation: folding, faulting, shearing, compression or extension of rocks due to the Earth's forces

development: a phase in which newly discovered oil or gas fields are put into production by drilling and completing production wells

discovered: the term applied to a petroleum accumulation/reservoir whose existence has been determined by its actual penetration by a well, which has also clearly demonstrated the existence of moveable petroleum by flow to the surface or at least some recovery of a sample of petroleum. Log and/or core data may suffice for proof of existence of moveable petroleum if an analogous reservoir is available for comparison.

dome: a type of anticline where rocks are folded into the shape of an inverted bowl. Strata in a dome dip outward and downward in all directions from a central area.

drill bit: a drilling tool that cuts through rock by a combination of crushing and shearing

ecosystem: a dynamic complex of plant, animal, and micro-organism communities and their non-living environment interacting as a functional unit. Note: ecosystems include those that are human-influenced such as rural and urban ecosystems.

effect: for the purposes of Impact Modes and Effects Analysis (IMEA), a change to water or the environment, such as changes to the quantity and/or quality of surface water or groundwater, or to the availability of suitable habitat. An effect is a specific type of an impact (any change resulting from prior events).

endpoint: for the purposes of geological and bioregional assessments, an endpoint is a value pertaining to water and the environment that may be impacted by development of unconventional gas resources. Endpoints include assessment endpoints – explicit expressions of the ecological, economic and/or social values to be protected; and measurement endpoints – measurable characteristics or indicators that may be extrapolated to an assessment endpoint as part of the impact and risk assessment.

exploration: the search for new hydrocarbon resources by improving geological and prospectivity understanding of an area and/or play through data acquisition, data analysis and interpretation. Exploration may include desktop studies, field mapping, seismic or other geophysical surveys, and drilling.

extraction: the removal of water for use from waterways or aquifers (including storages) by pumping or gravity channels. In the oil and gas industry, extraction refers to the removal of oil and gas from its reservoir rock.

fault: a fracture or zone of fractures in the Earth's crust along which rocks on one side were displaced relative to those on the other side

field: in petroleum geoscience, a 'field' refers to an accumulation, pool, or group of pools of hydrocarbons or other mineral resources in the subsurface. A hydrocarbon field consists of a reservoir with trapped hydrocarbons covered by an impermeable sealing rock, or trapped by hydrostatic pressure.

flowback: the process of allowing fluids and entrained solids to flow from a well following a treatment, either in preparation for a subsequent phase of treatment or in preparation for cleanup and returning the well to production. The flowback period begins when material introduced into the well during the treatment returns to the surface following hydraulic fracturing or refracturing. The flowback period ends when either the well is shut in and permanently disconnected from the flowback equipment or at the startup of production.

fold: a curve or bend of a formerly planar structure, such as rock strata or bedding planes, that generally results from deformation

formation: rock layers that have common physical characteristics (lithology) deposited during a specific period of geological time

formation water: water that occurs naturally in sedimentary rocks

fracking: see hydraulic fracturing

fracture: a crack or surface of breakage within rock not related to foliation or cleavage in metamorphic rock along which there has been no movement. A fracture along which there has been displacement is a fault. When walls of a fracture have moved only normal to each other, the fracture is called a joint. Fractures can enhance permeability of rocks greatly by connecting pores together, and for that reason, fractures are induced mechanically in some reservoirs in order to boost hydrocarbon flow. Fractures may also be referred to as natural fractures to distinguish them from fractures induced as part of a reservoir stimulation or drilling operation. In some shale reservoirs, natural fractures improve production by enhancing effective permeability. In other cases, natural fractures can complicate reservoir stimulation.

free gas: the gaseous phase present in a reservoir or other contained area. Gas may be found either dissolved in reservoir fluids or as free gas that tends to form a gas cap beneath the top seal on the reservoir trap. Both free gas and dissolved gas play important roles in the reservoir-drive mechanism.

gas cap: part of a petroleum reservoir that contains free gas

geogenic chemical: a naturally occurring chemical originating from the earth – for example, from geological formations

geological formation: stratigraphic unit with distinct rock types, which is able to mapped at surface or in the subsurface, and which formed at a specific period of geological time

groundwater: water occurring naturally below ground level (whether stored in or flowing through aquifers or within low-permeability aquitards), or water occurring at a place below ground that has been pumped, diverted or released to that place for storage there. This does not include water held in underground tanks, pipes or other works.

hazard: an event, or chain of events, that might result in an effect (change in the quality and/or quantity of surface water or groundwater)

hydraulic fracturing: also known as ‘fracking’, ‘fraccing’ or ‘fracture simulation’. This is a process by which geological formations bearing hydrocarbons (oil and gas) are ‘stimulated’ to increase the flow of hydrocarbons and other fluids towards the well. In most cases, hydraulic fracturing is undertaken where the permeability of the formation is initially insufficient to support sustained flow of gas. The process involves the injection of fluids, proppant and additives under high pressure into a geological formation to create a conductive fracture. The fracture extends from the well into the production interval, creating a pathway through which oil or gas is transported to the well.

hydraulic fracturing fluid: the fluid injected into a well for hydraulic fracturing. Consists of a primary carrier fluid (usually water or a gel), a proppant such as sand and chemicals to modify the fluid properties.

hydrocarbons: various organic compounds composed of hydrogen and carbon atoms that can exist as solids, liquids or gases. Sometimes this term is used loosely to refer to petroleum.

hydrogeology: the study of groundwater, including flow in aquifers, groundwater resource evaluation, and the chemistry of interactions between water and rock

hydrostatic pressure: equal pressure in all direction, equivalent to the pressure which is exerted on a portion of a column of water as a result of the weight of the fluid above it

impact: the difference between what could happen as a result of activities and processes associated with extractive industries, such as shale, tight and deep coal gas development, and what would happen without them. Impacts may be changes that occur to the natural environment, community or economy. Impacts can be a direct or indirect result of activities, or a cumulative result of multiple activities or processes.

impact cause: an activity (or aspect of an activity) that initiates a hazardous chain of events

impact mode: the manner in which a hazardous chain of events (initiated by an impact cause) could result in an effect (change in the quality and/or quantity of surface water or groundwater). There might be multiple impact modes for each activity or chain of events.

Impact Modes and Effects Analysis: a systematic hazard identification and prioritisation technique based on Failure Modes and Effects Analysis

injection: the forcing or pumping of substances into a porous and permeable subsurface rock formation. Examples of injected substances can include either gases or liquids.

kerogen: insoluble (in organic solvents) particulate organic matter preserved in sedimentary rocks that consists of various macerals originating from components of plants, animals, and bacteria. Kerogen can be isolated from ground rock by extracting bitumen with solvents and removing most of the rock matrix with hydrochloric and hydrofluoric acids.

known accumulation: the term accumulation is used to identify an individual body of moveable petroleum. The key requirement to consider an accumulation as known, and hence contain reserves or contingent resources, is that each accumulation/reservoir must have been penetrated by a well. In general, the well must have clearly demonstrated the existence of moveable petroleum in that reservoir by flow to surface or at least some recovery of a sample of petroleum from the well. However, where log and/or core data exist, this may suffice, provided there is a good analogy to a nearby and geologically comparable known accumulation.

life-cycle stage: one of five stages of operations in unconventional gas resource development considered as part of the Impact Modes and Effects Analysis (IMEA). These are exploration, appraisal, development, production, and rehabilitation. Each life-cycle stage is further divided into major activities, which are further divided into activities.

likelihood: probability that something might happen

lithology: the description of rocks, especially in hand specimen and in outcrop, on the basis of characteristics such as colour, mineralogic composition and grain size

material: pertinent or relevant

metamorphic rock: a rock formed from pre-existing rock due to high temperature and pressure in the Earth's crust, but without complete melting

methane: a colourless, odourless gas, the simplest paraffin hydrocarbon, formula CH₄. It is the principal constituent of natural gas and is also found associated with crude oil. Methane is a greenhouse gas in the atmosphere because it absorbs long-wavelength radiation from the Earth's surface.

migration: the process whereby fluids and gases move through rocks. In petroleum geoscience, 'migration' refers to when petroleum moves from source rocks toward reservoirs or seep sites. Primary migration consists of movement of petroleum to exit the source rock. Secondary migration occurs when oil and gas move along a carrier bed from the source to the reservoir or seep. Tertiary migration is where oil and gas move from one trap to another or to a seep.

Moho: the Mohorovicic discontinuity (seismic reflector) at the base of the crust

natural gas: the portion of petroleum that exists either in the gaseous phase or is in solution in crude oil in natural underground reservoirs, and which is gaseous at atmospheric conditions of pressure and temperature. Natural gas may include amounts of non-hydrocarbons.

naturally occurring radioactive materials: radioactive elements and their decay products found in the environment that have been generated from natural processes

oil: a mixture of liquid hydrocarbons and other compounds of different molecular weights. Gas is often found in association with oil. Also see petroleum.

oil-prone: organic matter that generates significant quantities of oil at optimal maturity

organic matter: biogenic, carbonaceous materials. Organic matter preserved in rocks includes kerogen, bitumen, oil and gas. Different types of organic matter can have different oil-generative potential.

outcrop: a body of rock exposed at the surface of the Earth

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 and spaces in the ground.

petroleum: a naturally occurring mixture consisting predominantly of hydrocarbons in the gaseous, liquid or solid phase

petroleum system: the genetic relationship between a pod of source rock that is actively producing hydrocarbon, and the resulting oil and gas accumulations. It includes all the essential elements and processes needed for oil and gas accumulations to exist. These include the source, reservoir, seal, and overburden rocks, the trap formation, and the hydrocarbon generation, migration and accumulation processes. All essential elements and processes must occur in the appropriate time and space in order for petroleum to accumulate.

play: a conceptual model for a style of hydrocarbon accumulation used during exploration to develop prospects in a basin, region or trend and used by development personnel to continue exploiting a given trend. A play (or group of interrelated plays) generally occurs in a single petroleum system.

porosity: the proportion of the volume of rock consisting of pores, usually expressed as a percentage of the total rock or soil mass

potential effect: specific types of impacts or changes to water or the environment, such as changes to the quantity and/or quality of surface water or groundwater, or to the availability of suitable habitat

produced water: a term used in the oil industry to describe water that is produced as a by-product along with the oil and gas. Oil and gas reservoirs often have water as well as hydrocarbons, sometimes in a zone that lies under the hydrocarbons, and sometimes in the same zone with the oil and gas. The terms 'co-produced water' and 'produced water' are sometimes used interchangeably by government and industry. However, in the geological and bioregional assessments, 'produced water' is used to describe water produced as a by-product of shale and tight gas resource development, whereas 'co-produced water' refers to the large amounts of water produced as a by-product of coal seam gas development.

producing: a well or rock formation from which oil, gas or water is produced

production: in petroleum resource assessments, 'production' refers to the cumulative quantity of oil and natural gas that has been recovered already (by a specified date). This is primarily output from operations that has already been produced.

production well: a well used to remove oil or gas from a reservoir

proppant: a component of the hydraulic fracturing fluid system comprising sand, ceramics or other granular material that 'prop' open fractures to prevent them from closing when the injection is stopped

reserves: quantities of petroleum anticipated to be commercially recoverable in known accumulations from a given date forward under defined conditions. Reserves must further satisfy four criteria: they must be discovered, recoverable, commercial and remaining (as of the evaluation date) based on the development project(s) applied.

reserves, proved: those quantities of petroleum, which by analysis of geological and engineering data, can be estimated with reasonable certainty (greater than 90% probability) to be commercially recoverable, from a given date forward, from known reservoirs and under current economic conditions, operating methods, and government regulations. Often referred to as P1.

reservoir: a subsurface body of rock having sufficient porosity and permeability to store and transmit fluids and gases. Sedimentary rocks are the most common reservoir rocks because they have more porosity than most igneous and metamorphic rocks and form under temperature conditions at which hydrocarbons can be preserved. A reservoir is a critical component of a complete petroleum system.

reservoir rock: any porous and permeable rock that contains liquids or gases (e.g. petroleum, water, CO₂), such as porous sandstone, vuggy carbonate and fractured shale

ridge: a narrow, linear geological feature that forms a continuous elevated crest for some distance (e.g. a chain of hills or mountains or a watershed)

risk: the effect of uncertainty on objectives (AS/NZ ISO 3100). This involves assessing the potential consequences and likelihood of impacts to environmental and human values that may stem from an action, under the uncertainty caused by variability and incomplete knowledge of the system of interest.

sandstone: a sedimentary rock composed of sand-sized particles (measuring 0.05–2.0 mm in diameter), typically quartz

seal: a relatively impermeable rock, commonly shale, anhydrite or salt, that forms a barrier or cap above and around reservoir rock such that fluids cannot migrate beyond the reservoir. A seal is a critical component of a complete petroleum system.

sediment: various materials deposited by water, wind or glacial ice, or by precipitation from water by chemical or biological action (e.g. clay, sand, carbonate)

sedimentary rock: a rock formed by lithification of sediment transported or precipitated at the Earth's surface and accumulated in layers. These rocks can contain fragments of older rock transported and deposited by water, air or ice, chemical rocks formed by precipitation from solution, and remains of plants and animals.

seismic survey: a method for imaging the subsurface using controlled seismic energy sources and receivers at the surface. Measures the reflection and refraction of seismic energy as it travels through rock.

sensitivity: the degree to which the output of a model (numerical or otherwise) responds to uncertainty in a model input

shale: a fine-grained sedimentary rock formed by lithification of mud that is fissile or fractures easily along bedding planes and is dominated by clay-sized particles

shale gas: generally extracted from a clay-rich sedimentary rock, which has naturally low permeability. The gas it contains is either adsorbed or in a free state in the pores of the rock.

shear: a frictional force that tends to cause contiguous parts of a body to slide relative to each other in a direction parallel to their plane of contact

source rock: a rock rich in organic matter which, if heated sufficiently, will generate oil or gas. Typical source rocks, usually shales or limestones, contain about 1% organic matter and at least 0.5% total organic carbon (TOC), although a rich source rock might have as much as 10% organic matter. Rocks of marine origin tend to be oil-prone, whereas terrestrial source rocks (such as coal) tend to be gas-prone. Preservation of organic matter without degradation is critical to creating a good source rock, and necessary for a complete petroleum system. Under the right conditions, source rocks may also be reservoir rocks, as in the case of shale gas reservoirs.

spring: a naturally occurring discharge of groundwater flowing out of the ground, often forming a small stream or pool of water. Typically, it represents the point at which the watertable intersects ground level.

stress: the force applied to a body that can result in deformation, or strain, usually described in terms of magnitude per unit of area, or intensity

stressor: chemical or biological agent, environmental condition or external stimulus that might contribute to an impact mode

structure: a geological feature produced by deformation of the Earth's crust, such as a fold or a fault; a feature within a rock, such as a fracture or bedding surface; or, more generally, the spatial arrangement of rocks

surface water: water that flows over land and in watercourses or artificial channels and can be captured, stored and supplemented from dams and reservoirs

tight gas: tight gas is trapped in reservoirs characterised by very low porosity and permeability. The rock pores that contain the gas are minuscule, and the interconnections between them are so limited that the gas can only migrate through it with great difficulty.

total organic carbon: the quantity of organic matter (kerogen and bitumen) is expressed in terms of the total organic carbon (TOC) content in mass per cent. The TOC value is the most basic measurement for determining the ability of sedimentary rocks to generate and expel hydrocarbons.

toxicity: inherent property of an agent to cause an adverse biological effect

trap: a geologic feature that permits an accumulation of liquid or gas (e.g. natural gas, water, oil, injected CO₂) and prevents its escape. Traps may be structural (e.g. domes, anticlines), stratigraphic (pinchouts, permeability changes) or combinations of both.

unconfined aquifer: an aquifer whose upper water surface (watertable) is at atmospheric pressure and does not have a confining layer of low-permeability rock or sediment above it

unconventional gas: unconventional gas is generally produced from complex geological systems that prevent or significantly limit the migration of gas and require innovative technological solutions for extraction. There are numerous types of unconventional gas such as coal seam gas, deep coal gas, shale gas and tight gas.

watertable: the upper surface of a body of groundwater occurring in an unconfined aquifer. At the watertable, pore water pressure equals atmospheric pressure.

well: typically a narrow diameter hole drilled into the earth for the purposes of exploring, evaluating, injecting or recovering various natural resources, such as hydrocarbons (oil and gas), water or carbon dioxide. Wells are sometimes known as a 'wellbore'.

well barrier: envelope of one or several dependent barrier elements (including casing, cement, and any other downhole or surface sealing components) that prevent fluids from flowing unintentionally between a bore or a well and geological formations, between geological formations or to the surface.

well integrity: maintaining full control of fluids (or gases) within a well at all times by employing and maintaining one or more well barriers to prevent unintended fluid (gas or liquid) movement between formations with different pressure regimes, or loss of containment to the environment

well integrity failure: when all well barriers have failed and there is a pathway for fluid to flow in or out of the well



www.bioregionalassessments.gov.au



Australian Government

**Department of Agriculture,
Water and the Environment**

Bureau of Meteorology

Geoscience Australia

