

Qualitative (screening) environmental risk assessment of drilling and hydraulic fracturing chemicals for the Isa 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 987-1-921069-28-4

Citation

Kirby JK, Golding L, Williams M, Apte S, Mallants D and Kookana R (2020) Qualitative (screening) environmental risk assessment of drilling and hydraulic fracturing chemicals for the Isa Superbasin. 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

The Burketown Bore, drilled in 1897 by the Queensland Government, is a naturally flowing bore that taps the artesian Gilbert River Formation aquifer at a depth of about 700 m below surface. Groundwater within this aquifer naturally contains a variety of dissolved chemical compounds that have deposited around the bore as the hot water (around 68 °C) has evaporated over the years, leading to the formation of a distinctive multi-coloured mound.

Credit: Steven Lewis, Geoscience Australia, July 2018 Element: GBA-ISA-2-264

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, nine were drilling chemicals, 99 were hydraulic fracturing chemicals and eight 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 tests were undertaken to provide an upper-bound estimate of geogenic chemical mobilisation from target formations in the Isa GBA region; this knowledge will help guide future field-based monitoring, management and treatment options. The leachate tests on powdered rock samples collected from geological formations in the Isa GBA region identified several elements that could be substantially mobilised into solutions by hydraulic fracturing fluids: aluminium, barium, cadmium, cerium, cobalt, copper, iron, lanthanum, manganese, neodymium, nickel, lead, yttrium, and zinc. Targeted polycyclic aromatic hydrocarbons (PAHs) were detected in six of nine sample extracts. Phenols were not detected (below reporting limits) in powdered rock sample extracts. The highest concentration of total recoverable hydrocarbons (TRHs) was found to be associated with the >C16–C34 National Environmental Protection Measure (NEPM) TRHs (54 to 134 mg/kg; 41% to 46% TRHs) and TRHs C15–C28 (26 to 105 mg/kg; 19% to 34% TRHs) fractions in sample extracts. 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 the: (i) geology and mineralogy of constituent rock units; (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).

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.

Contents

Ex	Executive summaryi						
Со	Contributors to the Programvii						
Ac	knowled	dgementsviii					
Ab	breviati	ons and acronymsix					
Ur	nits	х					
Th	e Geolo	gical and Bioregional Assessment Programxi					
1	Chemic	als associated with shale, tight and deep coal gas operations					
	1.1	Introduction1					
	1.2	Drilling chemicals1					
	1.3	Hydraulic fracturing chemicals2					
	1.4	Geogenic chemicals					
	1.5	Aim and objectives					
2	Qualitat	tive environmental risk assessment of chemicals5					
	2.1	Methods 5					
	2.2	Results and discussion8					
3		ory-based leachate and extraction tests on powdered rock samples from the Isa GBA					
re	gion – ge	eogenic chemicals					
	3.1	Methods					
	3.2	Results					
	3.3	Discussion					
4	Conclus	ions					
5	5 Knowledge gaps						
6	6 Recommendations						
Re	References						
GI	Glossary						

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 Basin3
Figure 2 Decision tree framework for Tier 1 qualitative (screening) environmental risk assessment of chemicals associated with shale, tight, and deep coal gas operations in Australia 9
Figure 3 Tier 1 qualitative ERA of chemicals associated with shale, tight and deep coal gas operations in Australia

Tables

Table 1 Common hydraulic fracturing fluid chemical additives used in shale, tight, and deep coalgas operations
Table 2 Persistence and bioaccumulation methods and classifications for Tier 1 qualitativeenvironmental risk assessments7
Table 3 Acute aquatic ecotoxicity data and classifications for Tier 1 qualitative environmentalrisk assessments
Table 4 Chemicals identified associated with drilling and hydraulic fracturing at shale, tight, anddeep coal gas operations in GBA regions of Australia10
Table 5 Chemicals of 'potentially high concern' that are persistent (P) and bioaccumulative (B), and exhibit very high acute toxicity (T)
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)
Table 8 Composition of the leach and extraction solutions used in the geogenic chemical studies
Table 9 Rock samples sourced from drill cores in Isa Superbasin 20
Table 10 Limit of reporting for targeted organic compounds in powdered rock sample extracts
Table 11 In-house synthetic HFF composition 23
Table 12 Total particulate element concentrations in powdered rock samples (mg/kg)
Table 13 Acid extractable element (AEE) concentrations from powdered rock samples (mg/kg)
Table 14 Ratio (%) of AEE to particulate element concentration for selected elements in powdered rock samples
Table 15 Dissolved elemental concentrations in SGW leachate solutions
Table 16 Dissolved elemental concentrations in dilute HCl leachate solutions 33
Table 17 Dissolved elemental concentrations in HFF leachate solutions 35
Table 18 Effect of pressure on mobilisation of dissolved elemental concentrations in HFF leachate solutions 37

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

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 stake holder engagement	CSIRO: Clare Brandon, Justine Lacey, Michelle Rodriquez, 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, 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, YongqiangZhang, Hongxing Zheng			

Acknowledgements

This technical product was reviewed by several groups:

- Internal Peer Review Group: Steven Lewis
- Technical Peer Review Group: Andrew Boulton, Jenny Stauber, Graeme Batley
- State Government Science Technical Review: This group includes scientists from the Queensland 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 fracturingfluid			
HCI	hydrochloric acid		
NEPM	National Environmental Protection Measure		
Р	persistence		
РАН	polycyclic aromatic hydrocarbon		
SGW synthetic groundwater			
т	toxicity		
TRH	total recoverable hydrocarbon		

Units

Unit	Description
d	days
hr	hours
µg/g	micrograms pergram
μg/kg	micrograms per kilogram
μg/L	micrograms per litre
μm	micrometer
g	gram
g/L	grams per litre
КРа	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.

The 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 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 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 State 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 Isa GBA region are:

- Orr ML, Bradshaw BE, Bernardel G, Palu TJ, Hall LS, Bailey AHE, Skeers N, Dehelean A, Reese B and Woods M (2020) Geology of the Isa GBA region.
- Bailey AHE, Bradshaw BE, Palu T, Wang L, Jarrett AJM, Orr M, Lech M, Evenden C, Arnold D, Reese B, Skeers N, Woods M, Dehelean A, Lawson C and Hall L (2020) Shale gas prospectivity of the Isa GBA region.
- Buchanan S, Dixon-Jain P, Martinez J, Raiber M, Kumar P, Woods M, Arnold D, Dehelean A and Skeers N (2020) Hydrogeology and groundwater systems of the Isa GBA region.
- MacFarlane CM, Herr A, Merrin LE, O'Grady AP and Pavey C (2020) Protected matters for the Isa GBA region.
- Kear J and Kasperczyk D (2020) Hydraulic fracturing and well integrity review for the GBA regions.

All maps for the Isa GBA region use the Map Grid of Australia (MGA) projection (zone 54) 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 environmental risk assessment (ERA) process of gas operations (in consultation with government agencies) that includes identifying 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 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 to: (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 commonly 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 (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 can 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.

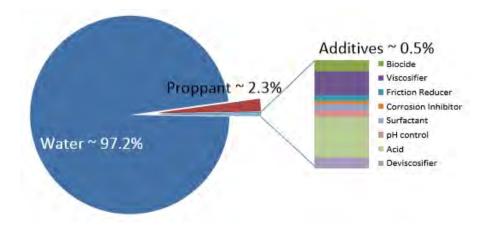


Figure 1 An example of overall percentages of water, proppant, and chemical additives in hydraulic fracturing fluid in a deep shale gas well fracturing operation in the Cooper Basin

Source: figure reproduced from Beach Energy and RPS (2012) Element: GBA-ISA-245

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 an overall small percentage (Figure 1) of the fluids. However, shale rocks are known to naturally contain a number of geogenic (natural) chemical constituents that could be mobilised into flowback and produced waters during hydraulic fracturing activities (Ziemkiewicz and Thomas He, 2015; Harrison et al., 2017). These geogenic chemicals (compounds and elements) include nutrients, 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 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 this 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 objectives were to:

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

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

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

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) (US EPA, 1992; Norton et al., 1992). The Department of the 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 judgment; 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 (US EPA, 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 of drilling and hydraulic fracturing chemicals (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, site-specific quantitative chemical assessments would then ideally be undertaken to determine risks from specific shale gas developments 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 SA, Queensland and the NT 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 and information and data provided to The Independent Scientific Inquiry into Hydraulic Fracturing of Onshore Unconventional Reservoirs in the Northern Territory (2018). 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 Kow), 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 judgment 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 as being used in shale, tight, and deep coal gas activities in the three GBA regions from 2011 to 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.

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 (OECD 301A-F)	Sufficient degradation over 10 d - 28 d window	Readily biodegradable – Not Persistent
Biodegradability tests (OECD 302A-C)	< 20% degradation	Persistent
Bioconcentration factor (BCF)	> 2000	Bioaccumulative
In the absence of BCF	$\log K_{ow} \ge 4.2$	Bioaccumulative

 Table 2 Persistence and bioaccumulation methods and classifications for Tier 1 qualitative environmental risk assessments

Source: Department of the Environment and Energy (2017)

Table 3 Acute aquatic ecotoxicity data and classifications for Tier 1 qualitative environmental risk assessments

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, nine were drilling chemicals, 99 were hydraulic fracturing chemicals, and eight 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.

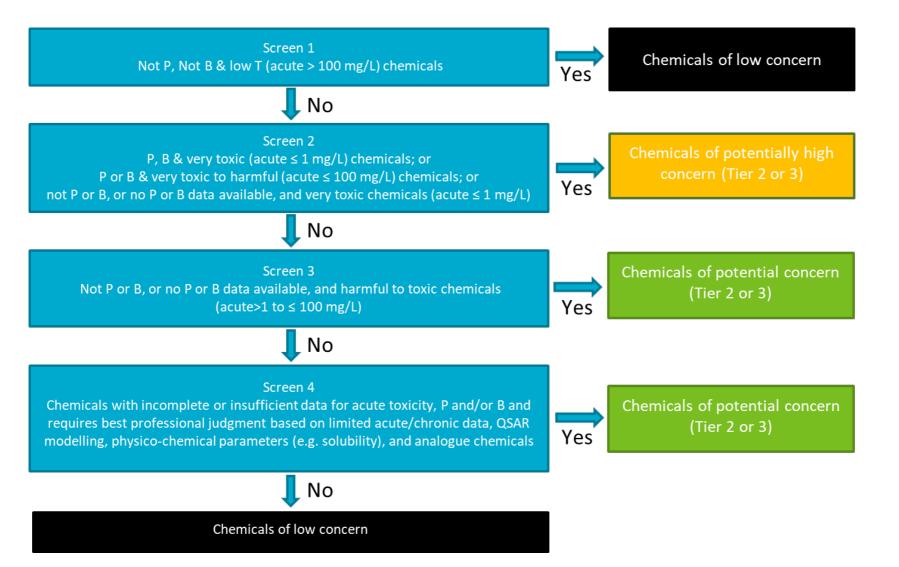


Figure 2 Decision tree framework for Tier 1 qualitative (screening) environmental risk assessment of chemicals associated with shale, tight, and deep coal gas operations in Australia

P = persistent; B = bioaccumulative; T = toxic; QSAR = quantitative structure-activity relationships Element: GBA-ISA-246

Table 4 Chemicals identified associated with drilling and hydraulic fracturing at shale, tight, and deep coal gas operations in GBA regions of Australia

	operations in GBA regions of Australia						
#	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	Hydrochloricacid	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, cocoalkyl, 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 acryloyldimethytaurate	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 carbon <i>a</i> te	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	Decamethylcyclopentasiloxane	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	Diethyleneglycol	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	Dodecamethylcyclohexasiloxane	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*

2 Qualitative environmental risk assessment of chemicals

#	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', five chemicals (one biocide and four 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.

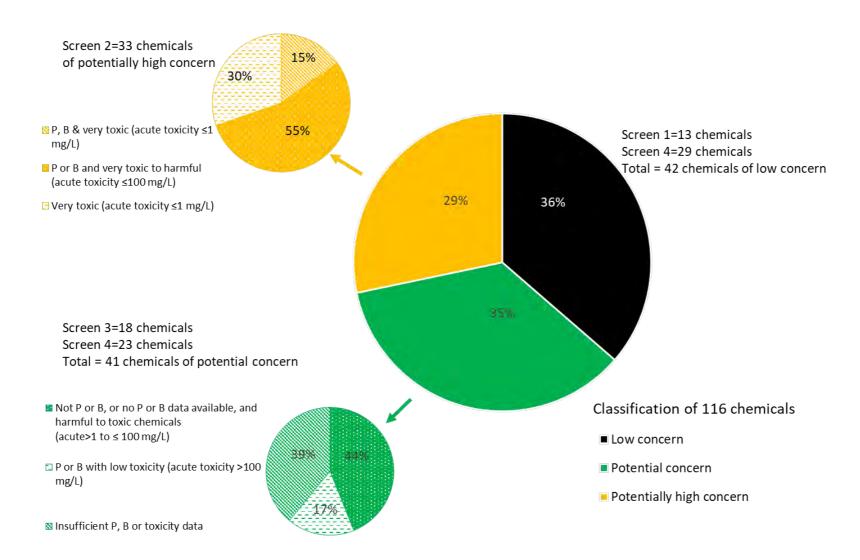


Figure 3 Tier 1 qualitative ERA of chemicals associated with shale, tight and deep coal gas operations in Australia

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 Element: GBA-ISA-247

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	P1	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 judgment (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 acryloyldimethytaurate; (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).

Chemical	CAS RN	Use	P ¹	B ²	T³
1,2,4-Trimethylbenzene	95-63-6	Solvent	##	ŧ	**
1-Benzyl methyl pyridinium chloride	68909-18-2	Corrosion in hibitor	##	ŧ	***
5-Chloro-2-methyl-4-isothiazolol-3-one	26172-55-4	Biocide	##	‡	***
2-Mercaptoethyl alcohol	60-24-2	Surfactant	##	ŧ	***
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	##	ŧ	***
Alcohols, C12-C16, ethoxylated	68551-12-2	Surfactant	##	‡	***
Amines, tallow alkyl, ethoxylated	61791-26-2	Surfactant	##	ŧ	***
C12-18-alkyldimethylbenzylammonium 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	##	ŧ	*
Pontacyl carmine 2B (acid violet 12)	6625-46-3	Tracking dye	##	ŧ	*
Heavy aromatic solvent naphtha (petroleum)	64742-94-5	Friction reducer/gelling agent	##	ŧ	**
Hydrotreated light distillate (C13-C14 isoparaffin)	64742-47-8	Friction reducer/gelling agent	##	ŧ	**

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

¹Persistence = half-life >60 d (##), half-life \leq 60 d (#); ²Bioconcentration factor = BCF >2000 or octanol/water partition coefficient = Log Kow \geq 4.2 (‡‡), BCF \leq 2000 or Log Kow <4.2 (‡); ³Toxicity = \leq 1 mg/L (***), >1 to \leq 10 mg/L (**), >10 to \leq 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	P1	B ²	T³
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	#	ŧ	***
Hydrochloricacid	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	Biocide/breaker	na	na	* * *
Tetrakis(hydroxymethyl) phosphonium sulfate	55566-30-8	Biocide	#	ŧ	* * *
Tributyl-tetradecylphosphonium chloride	81741-28-8	Biocide	na	na	* * *

¹Persistence = half-life \leq 60 d (#), not applicable (na); ²Bioconcentration = BCF \leq 2000 or octanol/water partition coefficient = Log Kow <4.2 (‡); not applicable or no data (na); ³Toxicity = \leq 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-isothiazolol-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. \leq 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 are 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 and 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 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 Kow; 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 in the 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 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 Isa 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 leach and extraction tests that allow the chemical screening of geogenic chemicals (compounds and elements) mobilised from target formations for shale gas development in the Isa GBA region during hydraulic fracturing
- identify potential inorganic and organic chemicals that could be mobilised into solution from powdered rock samples from formations in the Isa 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 for 1000 to 2500 m deep drillhole at approximately 80 °C; after removal of unknown, uncorrected, and unidentified data and methodologies in the dataset). 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 leach and extraction solutions used in the geoger	hic chemical studies
Table o composition of the leach and extractionsolutions used in the geoger	in 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 Isa GBA region were sourced from Dr Tonguc Uysal, CSIRO (Table 9). These formations (Lawn Hill Formation, Termite Range Formation and Riversleigh Siltstone) are representative of potential targets for shale gas development in the Isa GBA region (see prospectivity technical appendix (Bailey et al., 2020)). The samples were stored under dry, non-climate-controlled conditions. The rock samples were finely ground to less than 70 µm to a uniform particle size (as an upper bound for potential chemical mobilisation into solution).

Borehole	Geological unit	Sample code
AMOCO 83/1	Termite Range Formation	P84810
	RiversleighSiltstone	P84812
	RiversleighSiltstone	P84813
	RiversleighSiltstone	P84811
AMOCO 83/2	Lawn Hill Formation	P84818
	Termite Range Formation	P84819
Desert Creek	Lawn Hill Formation	P84814
	Termite Range Formation	P84815
Egilabria	Lawn Hill Formation	P84816
LH 235	Lawn Hill Formation	P84817

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 ultrapure 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) nearfull 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 μ m) organic carbon (DOC) was analysed using a Shimadzu TOC–LCSH Total Organic Carbon Analyser. Prior to analysis, 300 μ L 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 (more than 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 GBA data repository.

3.1.3.3 Organics

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.

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-Dimethyphenol	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				

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

*NEPM TRH reporting values; LOR = level of reporting

3.1.4 Leach 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 are in Table 8.

Ultrapure deionised water was sourced from a Milli-Q system (18 M Ω .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 groundwater 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.

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
Ethylenediaminetetraaceticacid (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

Table 11 In-house synthetic HFF composition

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 hours. The suspensions were then centrifuged at 3000 rpm for 3 min, and then syringe-filtered through 0.45 μ m 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 Desert Creek (Lawn Hill) 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 hours 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 the ANZECC/ARCMCANZ sediment quality guideline values (ANZECC/ARMCANZ, 2000) indicated that the samples were not particularly enriched in elements relative to these averages. Some samples contained elevated concentrations of sulfur, chromium, manganese, or mercury (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 AEE concentrations of the elements were relatively low for all samples except AMOCO 83/1 (Termite Range) which had a relatively high AEE chromium concentration. The percentages of elements present as AEE are summarised in Table 14. These ratios provide an indication of the extent to which trace elements could be mobilised from powdered rock samples into solution: boron, calcium, chromium, manganese, and phosphorus had the highest mean percentages (mean >50%).

Table 12 Tota	-		t concentr	facions in p				1		
Borehole	AMOCO 8	33/1			AMOCO	33/2	Desert Cree	ek	Egilabria	LH 235
Formation	Termite Range	Riverslei	gh Siltston	e	Lawn Hill	Termite Range	Lawn Hill	Termite Range	Lawn Hill	
Sample code	P84810	P84811	P84812	P84813	P84818	P84819	P84814	P84815	P84816	P84817
Ag	0.025	0.096	0.11	0.11	0.013	0.17	0.39	0.054	0.072	0.27
AI	2400	7200	7700	9900	3100	8100	12,000	18000	6200	12,000
As	2.4	9.3	22	20	2.4	13	25	4.5	7.8	21
В	1	19	13	24	11	22	36	12	17	17
Ва	11	25	28	38	6.7	35	93	94	65	28
Ca	2400	1100	790	2700	1000	2600	3000	3600	63000	1600
Cd	<0.04	<0.04	<0.04	<0.04	0.09	0.08	1.3	0.05	0.17	1.1
Со	2.4	4.6	12	10	0.15	12	21	13	11	22
Cr	260	29	117	88	19	69	103	100	49	68
Cu	4.6	6.9	12	19	0.8	25	73	21	19	68
Fe	6600	13,000	28 <i>,</i> 000	20,000	730	22,000	37,000	35,000	20,000	23,000
Hg	<0.1	<0.1	0.10	0.12	<0.1	<0.1	0.48	<0.1	<0.1	<0.1
к	840	4400	2600	5100	2000	4900	8300	7400	4400	4100
Mg	2000	1800	3300	3200	1200	3500	5000	6400	27000	5000
Mn	300	80	129	81	3.6	550	220	3500	950	110
Мо	0.57	0.92	4.5	7.8	0.06	6.1	8.6	0.75	0.94	20
Ni	7.8	11	17	17	12	21	39	18	16	45
Ρ	140	380	310	1200	140	350	410	480	1200	470
Pb	3.9	13	22	22	1.0	29	32	25	23	40
S	1000	10,000	20,000	17,000	20	9800	28,000	460	1700	11,000
Sb	0.26	0.75	1.3	1.3	0.04	1.3	1.3	0.72	0.70	2.1
Se	0.039	0.06	0.25	0.27	0.010	0.63	0.58	0.053	0.087	0.92
U	0.29	0.55	0.56	1.8	0.99	0.74	2.0	0.70	0.43	4.6
v	2.8	3.3	6.2	14	0.4	8.8	21	18	10	30
Zn	6.7	17	22	29	12	58	140	66	74	150

Source: Geological and Bioregional Assessment Program (2019); Bold numbers = x10 mean global crustal abundance values and/or the ANZECC Australian and New Zealand sediment quality guideline value

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

Borehole	AMOCO	33/1			AMOCO	33/2	Desert Cre	ek	Egilabria	LH 235
Formation	Termite Range	River	sleigh Silt	stone	Lawn Hill	Termite Range	Lawn Hill	Termite Range	Law	n Hill
Sample code	P84810	P84811	P84812	P84813	P84818	P84819	P84814	P84815	P84816	P84817
Ag	0.010	0.012	0.003	0.007	0.004	0.008	0.056	0.012	0.018	0.009
AI	320	1200	1500	1700	680	910	1500	2900	1300	1400
As	0.63	4.1	7.2	8.2	0.27	3.6	4.5	2.0	2.4	13
В	<1	7.7	5.8	7.5	7	11	13	10	14	4
Ва	7.1	3.1	6.3	8.1	4.1	17	25	56	39	2.9
Ca	2400	1200	820	3000	1100	2700	3100	3700	66000	1700
Cd	<0.01	<0.01	<0.01	<0.01	0.099	0.015	0.30	0.021	0.071	0.72
Со	1.4	1.2	3.2	4.0	0.12	1.9	5.0	5.4	3.8	8.9
Cr	200	15	69	39	15	44	47	72	37	27
Cu	2.2	2.4	4.8	5.7	0.53	9.2	46	10	6.1	36
Fe	2400	1600	3200	3000	260	2400	3800	6900	16000	1800
Hg	0.08	0.05	0.03	0.03	0.07	0.08	<0.03	0.06	0.06	0.11
К	350	920	680	1200	830	1500	2400	3800	1800	680
Mg	1000	730	840	1100	990	1200	1800	1000	28000	1200
Mn	270	43	45	39	2	160	114	2300	940	55
Мо	0.2	0.20	1.1	2.3	<0.1	1.1	1.6	0.4	0.5	4.1
Na	20	300	91	77	260	270	220	240	420	20
Ni	2.4	4.8	5.6	6.7	0.5	2.6	11	4.0	5.4	17
Р	130	370	280	1200	93	360	320	430	1200	440
Pb	2.1	3.3	4.8	4.8	0.50	15	15	20	15	14
S	220	1800	2900	3400	20	1700	4400	70	60	2500
Sb	0.11	0.16	0.32	0.34	0.03	0.34	0.29	0.34	0.26	0.64
Se	<0.01	0.02	0.03	0.06	<0.01	0.16	0.06	0.02	0.03	0.19
U	0.11	0.26	0.23	0.95	0.42	0.28	0.84	0.27	0.27	2.1
V	0.55	0.49	1.0	2.0	0.15	1.1	2.2	2.8	4.8	2.1
Zn	3.4	6	5	12	4.7	14	38	14	23	57

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

Source: Geological and Bioregional Assessment Program (2019); Bold = extracted chromium (Cr) high compared to mean global crustal abundance values and/or the ANZECC Australian and New Zealand sediment quality guideline value.

3.2.2 Leachate tests – inorganics

3.2.2.1 Synthetic groundwater tests

The concentrations of trace elements leached into solution by synthetic groundwater (SGW) (17 hour equilibration time) are summarised in Table 15 (Geological and Bioregional Assessment Program, 2019). In general, the concentrations of elements in solution were relatively low. The following elements showed elevated mobilisation into solution: aluminium, calcium, magnesium, silicon and sulfur. It should be noted that the leachate solution pH became alkaline by the end of the tests (typically pH 8 to 9) and this may have contributed to the mobilisation of some elements such as aluminium into solutions.

3.2.2.2 Dilute HCl tests

The mean concentration of elements leached into solution by dilute HCl (17 hour 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, cerium, cobalt, chromium, copper, iron, lanthanum, manganese, neodymium, nickel, phosphorus, lead, thallium, titanium, vanadium, yttrium, and zinc.

3.2.2.3 Synthetic hydraulic fracturing fluid tests

The concentrations of trace elements mobilised into solution by HFF (17 hr equilibration time) are summarised in Table 17 (Geological and Bioregional Assessment Program, 2019). The results are the mean of duplicate determinations. 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) included: aluminium, barium, cadmium, cerium, cobalt, copper, iron, lanthanum, manganese, neodymium, nickel, lead, yttrium, and zinc.

Higher pressure from 100 to 18,400 KPa for the leachate test using HFF resulted in higher mobilisation of elements such as thorium (x10.7), cobalt (x2.3), and boron (x2.0); and decreased mobilisation for elements such as lead (x0.1), barium (x0.1), phosphorus (x0.2), molybdenum (x0.3) and antimony (x0.3) (Table 18) (Geological and Bioregional Assessment Program, 2019).

Borehole	AMOCO 83/1				AMOCO 83/2		Desert Creek		Egilabria	LH 235
Formation	Termite Range	Riversleigh Silt	stone		Lawn Hill	Termite Range	Lawn Hill	Termite Range	Lawn Hill	
Sample code	P84810	P84811	P84812	P84813	P84818	P84819	P84814	P84815	P84816	P84817
Ag	39	13	2	6	34	4	14	22	25	3
Al	13	17	19	17	22	11	13	16	21	12
As	26	45	33	41	12	27	18	44	30	61
В	na	41	45	32	66	52	36	85	82	21
Ва	63	12	23	21	62	49	26	60	60	10
Са	100	109	104	111	110	104	103	103	105	106
Cd	na	na	na	na	106	19	23	41	42	66
Со	60	25	27	39	76	15	24	41	35	41
Cr	77	51	59	44	81	64	45	72	75	40
Cu	48	35	41	30	65	37	63	47	32	53
Fe	36	12	11	15	36	11	10	20	80	8
Hg	na	59	34	28	na	na	na	na	na	na
К	42	21	26	24	42	31	29	51	41	17
Mg	50	41	25	34	83	34	36	16	104	24
Mn	90	54	35	48	69	29	52	66	99	50
Мо	42	21	25	29	na	18	19	49	53	20
Ni	31	45	33	39	4	12	27	22	33	37
Р	93	97	90	100	66	103	78	90	100	94
Pb	53	26	22	22	49	52	47	81	65	34
S	22	18	15	20	98	17	16	15	4	23

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

Qualitative (screening) environmental risk assessment of drilling and hydraulic fracturing chemicals for the Isa GBA region | 29

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

Sb	41	21	25	25	58	26	23	47	37	30
Se	na	34	12	22	na	25	10	34	32	21
U	37	47	41	53	42	38	42	39	63	46
V	20	15	16	15	36	12	10	16	47	7
Zn	50	35	22	40	38	24	27	21	31	38

Bold = ratio of AEE to particulate element concentration > 50%; not applicable or no data (na) Source: Geological and Bioregional Assessment Program (2019)

Table 15 Dissolved elemental concentrations in SGW leachate solutions

Borehole	Units	Blank	AMOCO 83	3/1				AMOCO 83	3/2	Desert Creek	Egilabria	LH 235
Formation			Termite Range	Riversleig	hSiltstone	2		Lawn Hill	Termite Range	Lawn Hill	Termite Range	Lawn Hill
Final pH		9.5	9.1	8.4	8.0	8.6	8.9	8.7	7.8	8.8	8.9	8.2
Ag	µg/L	0.02	0.02	0.03	0.07	0.11	<0.01	<0.01	0.08	<0.01	<0.01	0.02
Al	mg/L	<0.001	0.91	0.098	0.13	0.16	0.10	0.086	0.034	0.80	0.75	0.049
As	µg/L	<0.1	4.1	2.6	1.0	11	0.5	2.8	0.4	8.2	15	11
В	mg/L	0.01	0.02	0.10	0.07	0.07	0.08	0.13	0.14	0.09	0.08	0.06
Ва	µg/L	0.2	6.5	0.2	2.0	0.2	0.8	8.7	5.7	6.5	11	0.3
Ca	mg/L	0.07	1.6	3.3	2.9	6.8	1.2	3.9	25	1.8	2.7	7.7
Cd	µg/L	0.02	<0.01	0.02	0.03	0.03	0.01	<0.01	0.15	0.01	<0.01	0.14
Ce	µg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.013	0.01	<0.01	<0.01
Со	µg/L	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.5	<0.1	<0.1	<0.1
Cr	µg/L	1	5	2	2	3	6	7	3	5	6	6
Cu	µg/L	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	0.3	<0.3	<0.3	<0.3
Fe	mg/L	<0.001	0.004	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.005	<0.001	<0.001
Hg	µg/L	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
К	mg/L	<0.01	8.7	16	18	12	12	23	~55	~50	22	9.6
La	µg/L	0.003	0.004	0.007	<0.002	<0.002	<0.002	0.003	0.002	0.004	<0.002	<0.002
Li	µg/L	<0.04	2.0	19	13	21	1.2	7.1	62	17	6.7	14
Mg	mg/L	0.01	0.80	4.2	8.1	8.8	2.1	6.1	20	0.38	1.8	8.7
Mn	mg/L	<0.001	<0.001	0.017	0.043	0.013	<0.001	0.011	0.22	0.014	<0.001	0.038

Qualitative (screening) environmental risk assessment of drilling and hydraulic fracturing chemicals for the Isa GBA region | 31

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

Borehole	Units	Blank	AMOCO 83	3/1				AMOCO 83	3/2	Desert Creek	Egilabria	LH 235
Formation			Termite Range	Riversleig	hSiltstone	2		Lawn Hill	Termite Range	Lawn Hill	Termite Range	Lawn Hill
Мо	μg/L	<0.1	1.4	4.7	17	34	0.2	17	21	3.2	7.5	116
Nd	µg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ni	μg/L	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Р	mg/L	<0.01	0.01	0.03	<0.01	0.15	0.02	<0.01	<0.01	0.05	0.04	0.07
Pb	μg/L	0.3	<0.1	0.3	0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Rb	μg/L	<0.02	11	15	23	15	8.6	27	35	71	38	7.7
S	mg/L	<0.01	7.1	52	88	59	0.16	36	~130	2.0	4.1	58
Sb	μg/L	<0.02	0.53	1.9	1.5	5.0	0.23	1.3	0.93	2.9	2.0	7.1
Se	μg/L	<0.1	0.2	0.6	1.0	0.7	<0.1	4.1	2.4	0.4	0.6	3.3
Si	mg/L	0.02	7.5	3.8	4.4	8.0	7.0	4.9	4.8	8.8	7.4	4.7
Sr	μg/L	0.7	12	1.7	3.5	<0.2	4.4	35	17	9.0	29	0.7
Th	μg/L	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01
Ті	mg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
U	μg/L	<0.004	0.72	0.43	0.047	1.8	3.6	0.86	1.6	1.0	0.48	3.6
v	μg/L	<0.1	1.5	0.5	0.2	4.6	2.6	2.6	0.3	12	10	3.4
Y	μg/L	<0.01	0.01	0.03	<0.01	0.03	0.01	0.01	0.02	0.02	<0.01	0.03
Zn	μg/L	<1	2	<1	<1	2	3	2	4	2	2	2

Source: Geological and Bioregional Assessment Program (2019)

Table 16 Dissolved elemental concentrations in dilute HCl leachate solutions

Borehole	Units	Blank	AMOCO 83/1				AMOCO 83	3/2	Desert Cre	ek	Egilabria	LH 235
Formation			Termite Range	Riversleigh Silts	Lawn Hill	Termite Range	Lawn Hill	Termite Range	Lawn Hill			
Final pH			<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Ag	µg/L	<0.01	0.26	0.33	0.11	0.18	0.07	0.32	3.3	0.93	0.92	0.70
AI	mg/L	<0.01	58	150	170	170	88	120	210	360	130	210
As	µg/L	<0.1	30	170	300	270	46	170	300	75	89	400
В	mg/L	0.12	0.23	0.62	0.57	0.59	0.54	0.71	0.90	0.85	0.72	0.63
Ва	µg/L	0.4	540	460	590	690	190	580	1700	1600	1300	430
Са	mg/L	0.08	50	24	16	59	22	58	63	77	>500	34
Cd	µg/L	<0.2	<0.2	<0.2	0.2	0.2	2.5	2.2	24	1.2	4.2	21
Ce	µg/L	<0.01	480	1600	1300	1500	2700	490	650	1300	670	800
Со	μg/L	<0.03	43	82	130	130	4	180	380	270	140	340
Cr	µg/L	<4	5100	470	1900	1200	350	1100	1400	1800	830	940
Cu	µg/L	<0.2	89	110	94	200	18	460	1400	390	340	1300
Fe	mg/L	0.003	120	190	330	220	17	310	430	700	370	340
Hg	µg/L	<1	<1	<1	<1	2	<1	<1	1	2	1	<1
к	mg/L	<0.01	26	78	51	77	50	75	140	130	84	66
La	µg/L	<0.003	270	720	560	670	1100	210	250	420	230	270
Li	µg/L	<0.2	74	200	380	260	14	76	390	640	100	410
Mg	mg/L	<0.01	42	41	73	64	29	73	99	130	>500	100
Mn	mg/L	<0.001	6.3	1.6	2.7	1.4	0.080	12	4.4	78	19	2.2

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

Borehole	Units	Blank	AMOCO 83/1				AMOCO 83	3/2	Desert Cre	ek	Egilabria	LH 235
Formation			Termite Range	Riversleigh Silts	tone	Lawn Hill	Termite Range	Lawn Hill	Termite Range	Lawn Hill		
Мо	µg/L	0.2	9.9	11	70	120	0.3	77	99	8.4	13	250
Nd	µg/L	<0.01	210	650	560	630	1200	250	320	620	420	400
Ni	µg/L	<2	89	170	200	210	27	380	610	370	230	660
Р	mg/L	<0.1	3.1	8.7	6.8	26	2.9	7.8	8.9	10	25	10
Pb	µg/L	<0.03	75	290	480	420	23	630	690	560	550	830
Rb	µg/L	<0.2	100	470	330	520	260	410	760	700	500	510
S	mg/L	<0.1	5.7	81	110	110	0.2	44	180	2.7	3.5	100
Sb	µg/L	0.2	3.0	4.3	9.2	6.7	<0.1	5.3	4.7	2.6	3.8	9.3
Se	μg/L	<0.3	<0.3	0.8	0.9	0.9	<0.3	3.6	4.1	<0.3	<0.3	5.3
Si	mg/L	0.19	87	180	160	180	130	170	190	200	170	170
Sr	μg/L	<0.4	63	190	110	180	130	340	320	250	1600	120
Th	μg/L	<0.01	53	200	160	180	340	88	170	170	160	160
Ті	mg/L	<0.01	0.09	0.24	0.29	0.32	0.03	0.09	2.0	0.99	0.23	1.0
U	µg/L	<0.01	5.5	9.8	11	30	20	11	32	12	8.2	73
V	µg/L	<0.1	58	95	160	280	13	150	470	390	230	570
Y	µg/L	<0.1	40	140	110	240	130	110	150	220	350	150
Zn	μg/L	7	140	340	340	480	250	1100	2500	1200	1300	2600

Source: Geological and Bioregional Assessment Program (2019)

Table 17 Dissolved elemental concentrations in HFF leachate solutions

Borehole	Units	Blank	AMOCO 83/1				АМОСО 83,	/2	Desert Creek		Egilabria	LH 235
Formation			Termite Range	Riversleigh Siltstone I			Lawn Hill	Termite Range	Lawn Hill	Termite Range	Lawn Hill	
Final pH		2.1	2.3	2.2	2.2	2.3	2.2	2.6	2.3	2.9	5.8	2.3
Ag	µg/L	<0.01	0.23	0.12	0.04	0.08	0.12	0.22	2.0	0.49	0.08	0.45
AI	mg/L	<0.003	7.6	16	20	15	8.9	6.6	16	15	0.013	20
As	µg/L	0.1	2.0	13	15	34	1.1	3.1	11	2.2	0.2	27
В	mg/L	0.01	0.05	0.13	0.09	0.10	0.12	0.25	0.19	0.18	0.10	0.11
Ва	µg/L	0.5	120	43	70	42	76	190	170	440	340	37
Са	mg/L	0.087	39	19	13	40	17	35	48	46	320	25
Cd	µg/L	0.19	2.6	0.59	1.5	1.5	3.0	2.9	16	2.3	3.0	16
Ce	µg/L	0.03	26	81	55	116	36	38	101	38	0.52	63
Со	µg/L	<0.1	27	25	54	52	2.0	40	74	76	39	150
Cr	µg/L	<0.3	360	67	290	97	29	32	150	40	2.4	100
Cu	µg/L	0.5	49	18	29	36	3.0	147	605	112	16	409
Fe	mg/L	0.04	28	16	41	26	3.2	126	41	82	8.4	36
Hg	µg/L	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
К	mg/L											
La	µg/L	0.017	12	27	19	34	21	15	29	12	0.41	21
Li	µg/L	0.2	11	64	90	76	2.2	10	102	57	9.8	89
Mg	mg/L	<0.02	16	11	16	17	13	36	26	13	111	21
Mn	mg/L	<0.001	4.5	0.76	0.86	0.61	0.036	7.8	1.7	51	4.6	0.93

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

Borehole	Units	Blank	AMOCO 83/1	083/1				/2	Desert Creek		Egilabria	LH 235
Formation			Termite Range	Riversleigh Siltstone			Lawn Hill	Termite Range	Lawn Hill	Termite Range	Lawn Hill	
Мо	µg/L	<0.1	<0.1	<0.1	0.5	4.2	<0.1	0.1	0.5	<0.1	0.5	4.5
Nd	µg/L	<0.01	20	68	48	122	30	28	85	30	0.25	71
Ni	µg/L	<0.3	36	88	102	107	18	64	191	51	41	312
Р	mg/L	<0.1	0.1	1.0	0.4	4.2	0.3	<0.1	0.5	<0.1	<0.1	0.9
Pb	µg/L	1.9	18	12	20	3.2	6.6	169	67	94	0.2	111
Rb	µg/L	151	168	227	192	219	192	265	234	365	275	179
S	mg/L	1007	1008	1030	1038	1045	996	1053	1063	987	997	1026
Sb	µg/L	0.32	0.45	0.88	1.1	1.0	0.20	0.37	0.70	0.33	0.41	1.2
Se	µg/L	<0.2	0.4	0.9	1.2	1.4	<0.2	3.2	1.4	0.5	0.4	2.8
Si	mg/L	<0.1	10	19	22	22	17	15	27	27	6.7	23
Sr	µg/L	2.1	39	63	35	58	62	177	112	121	408	35
Th	µg/L	0.02	0.14	0.30	0.21	0.13	0.03	0.30	0.81	0.09	0.00	0.23
Ti	mg/L	0.84	0.22	0.20	0.19	0.17	0.18	0.11	0.18	0.06	<0.01	0.19
U	μg/L	0.012	0.97	2.5	2.1	6.6	1.6	1.4	6.4	1.0	0.005	19
V	μg/L	<0.3	1.5	5.8	12	26	0.7	1.5	25	1.0	<0.3	42
Y	μg/L	0.004	21	78	59	133	36	30	89	46	5.2	82
Zn	μg/L	4	74	131	96	167	65	374	1300	312	160	1300

Source: Geological and Bioregional Assessment Program (2019)

Borehole	Units	Desert Creek (100 KPa)	Desert Creek (18400 KPa)	Ratio	Mobilisation Trajectory ^b	
Solution pH		2.3	2.1			
DO	mg/L		6.4			
Th	μg/L	0.81	8.7	10.7	1	
Со	μg/L	74	168	2.3	1	
В	mg/L	0.19	0.39	2.0	1	
Si	mg/L	27	50	1.8	1	
Ag	μg/L	2.0	3.5	1.8	1	
U	μg/L	6.4	11	1.8	1	
Al	mg/L	16	27	1.7	1	
Ni	μg/L	191	318	1.7	1	
Zn	μg/L	1300	2043	1.6	1	
Mg	mg/L	26	39	1.5	1	
As	μg/L	11	16	1.5	1	
Li	μg/L	102	141	1.4	1	
Cu	μg/L	605	769	1.3	1	
Ce	μg/L	101	111	1.1	\leftrightarrow	
Mn	mg/L	1.7	1.8	1.1	\leftrightarrow	
Са	mg/L	48	50	1.0	\leftrightarrow	
Cd	μg/L	16	16	1.0	\leftrightarrow	
Nd	μg/L	85	87	1.0	\leftrightarrow	
Hg	μg/L	<0.4	<0.4	1.0ª	\leftrightarrow	
Cr	μg/L	150	130	0.9	\leftrightarrow	
Se	μg/L	1.4	1.2	0.8	\leftrightarrow	
Fe	mg/L	41	35	0.8	\checkmark	
V	μg/L	25	11	0.4	\checkmark	
Ti	mg/L	0.18	0.07	0.4	\checkmark	
Sb	μg/L	0.70	0.23	0.3	\checkmark	
Мо	μg/L	0.5	0.1	0.3	\checkmark	
Р	mg/L	0.5	<0.1	0.2ª	\checkmark	
Ва	μg/L	170	13	0.1	\mathbf{V}	
Pb	μg/L	67	3.6	0.1	\checkmark	

^a half detection limit used to calculate difference; ^b Blue = increased metal mobilisation with increased pressure; Green = 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

Phenols were not detected (below level of reporting limits) in powdered rock sample extracts sourced for this study. Targeted PAHs were detected in six of ten powdered rock sample extracts (Table 19) (Geological and Bioregional Assessment Program, 2019). The other targeted PAHs were all below their respective levels of reporting in sample extracts (Table 10). Of the 15 PAHs targeted for analysis, a maximum of eight PAHs was detected in any one powdered rock sample extract (Desert Creek, Lawn Hill Formation; P84814) (Table 19). The most common identified PAHs in sample extracts were pyrene and fluoranthene (five of ten extracts), chrysene (four of ten extracts) and phenanthrene (three of ten extracts) (Table 19). Highest concentrations of PAHs were found in extracts from Desert Creek Lawn Hill (chrysene 105 mg/kg; phenanthrene 40.6 mg/kg), AMOCO 83/2 Termite Range (pyrene 34.9 mg/kg; phenanthrene 20.5 mg/kg), and AMOCO 83/2 Lawn Hill (chrysene 31.9 mg/kg).

The highest concentrations of TRHs were associated with the >C16 to C34 NEPM TRHs (54 to 134 mg/kg; 41 to 46% TRHs) and TRHs C15–C28 (26 to 105 mg/kg; 19 to 34% TRHs) fractions for all rock samples (Table 19) (Geological and Bioregional Assessment Program, 2019). Targeted analysis of PAHs represented a small fraction of the total organic geogenic compounds identified in the sample extracts (i.e. less than 0.1% for all samples analysed) (Table 19). The absence of volatile compounds found 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 HCI and HFF mobilised the highest element concentrations into solutions compared to SGW. This demonstrates the role that acidity and chemical constituents of hydraulic fracturing fluid (e.g. chelating agents, surfactants, solvents, etc.) can play in mobilising elements from powdered rocks. The elements showing substantial mobilisation (greater than 50-fold median increase compared to SGW) in hydraulic fracturing fluid include: aluminium, barium, cadmium, cerium, cobalt, copper, iron, lanthanum, manganese, neodymium, nickel, lead, 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.

Borehole	AMOCO 83/1				AMOCO 83/2		Desert Cree	k	Egilabria	LH 235
Formation	Termite Riversleig Range		h Siltstone		Termite Range	Lawn Hill	Termite Range	Lawn Hill	Lawn Hill	
Sample code	P84810	P84813 P84812		P84811	P84819	P84818	P84815	P84814	P84816	P84817
PAHS										
Benz(a)anthracene	<2	<2	<2	<2	<2	<2	<2	2.4	<2	4
Benzo-(b)&(k)- fluoranthene	<5	<5	<5	<5	<5	17.9	<5	21.9	<5	<5
Benzo(ghi)perylene	<5	<5	<5	<5	<5	<5	<5	18.1	<5	<5
Chrysene	<5	<5	<5	<5	13	31.9	<5	105	<5	5.3
Dibenz(ah)anthracene	<5	<5	<5	<5	<5	7.4	<5	10	<5	<5
Fluoranthene	<2	<2	<2	<2	7.9	3.2	7	<5	5.5	3.5
Indeno-(1,2,3-cd)- pyrene	<5	<5	<5	<5	<5	2.7	<5	5	<5	<5
Phenanthrene	<5	<5	<5	<5	20.5	<5	8.4	40.6	<5	<5
Pyrene	<5	<5	<5	<5	34.9	<5	6.1	22.3	5.3	16.6
TRHs										
TRH C10–C14	1,581	5,273	5,608	5 <i>,</i> 840	6,518	4,420	1,756	15,029	1,514	4,200
TRH>C10-C16*	2,325	8,788	9,346	9,976	10,941	7,613	4,214	23,856	2,660	6,853
TRH C15–C28	25,572	32,642	37,385	34,065	65,180	51,572	93,655	104,967	85,928	37,851
TRH>C16–C34(F3)*	55,793	55,240	58,414	53,531	93,114	78,585	128,775	133,594	116,617	64,108
TRH C29–C36	19,760	8,788	9,346	9,976	17,924	15,472	25,755	23,856	20,459	16,580
TRH>C34–C40(F4)*	30,221	19,585	18,459	17,276	25,606	24,558	32,779	26,242	26,597	26,528

*NEPM TRH reporting values; phenols were below reportable limits; Source: Geological and Bioregional Assessment Program (2019)

Higher pressure led to increased mobilisation into solutions of elements such as thorium, cobalt, and boron; and decreased mobilisation for elements such as antimony, barium, phosphorus, lead, and molybdenum. 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 Isa GBA region.

Targeted priority organic compounds such as PAHs and TRHs were detected in extracts of powdered rock samples from formations in the Isa GBA region (Geological and Bioregional Assessment Program, 2019). However, the majority of the organic geogenic compounds extracted 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 upperbound 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 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 that could reduce the concentrations of industrial and geogenic chemicals in the environment.

4 Conclusions

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 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 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 Isa GBA region identified many elements that could be substantially mobilised by hydraulic fracturing fluids including aluminium, barium, cadmium, cerium, cobalt, copper, iron, lanthanum, manganese, neodymium, nickel, lead, yttrium, and zinc. Phenols were not detected (below reporting limits) in powdered rock sample extracts. Priority organic chemicals such as PAHs and TRHs were detected in sample extracts from 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

4 Conclusions

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 assessment of chemicals associated with shale, tight and deep coal operations in GBA regions identified knowledge gaps including:

- 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 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 endpoint data are currently not available for groundwater organisms (e.g. stygofauna).
- 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.
- There is limited information on the fate, transformations and toxicity of chemicals present in hydraulic fracturing fluids, and flowback and produced water (individual chemicals and mixtures) in the environment.
- The majority of organic compounds present in sample extracts (TRH fraction) 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.

5 Knowledge gaps

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

6 Recommendations

The following are recommendations to improve ERA of chemicals and understanding in 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 groundwater-dependent ecosystems (GDEs) should be collected prior to shale, tight and deep coal gas developments.
- Assessments should be undertaken into 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.
- Direct toxicity assessments of hydraulic fracturing fluids, flowback and produced water should be undertaken to determine no-effect concentrations using a range of aquatic organisms 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.

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, http://waterquality.gov.au/anz-guidelines/Documents/ANZECC-ARMCANZ-2000-guidelines-vol1.pdf.
- 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.

- Bailey AHE, Bradshaw BE, Palu TJ, Wang L, Jarrett AJM, Orr M, Lech M, Evenden C, Arnold D, Reese B, Skeers N, Woods M, Dehelean A, Lawson C and Hall L (2020) Shale gas prospectivity for the Isa 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.
- 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-csgextraction-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 and 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.

- 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: Isa GBA region. [tabular]. Viewed 20 June 2019, https://repo.bioregionalassessments.gov.au/metadata/94F838CA-38DA-40AD-8386-14958898C29D. GBA data repository GUID: 94F838CA-38DA-40AD-8386- 14958898C29D.
- Government of Canada (2012a) Siloxane D4 (Cyclotetrasiloxane, octamethyl-) CAS Registry Number 556-67-2. Viewed 03 September 2018, https://www.canada.ca/en/healthcanada/services/chemical-substances/challenge/batch-2/cyclotetrasiloxaneoctamethyl.html.
- Government of Canada (2012b) Siloxane D5 (Cyclopentasiloxane, decamethyl-): CAS Registry Number 541-02-6. Viewed 03 September 2018, https://www.canada.ca/en/healthcanada/services/chemical-substances/challenge/batch-2/cyclopentasiloxanedecamethyl.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 shalehydraulic fracturing fluid interactions. Applied Geochemistry 82, 47–62. Doi: 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 methanogenicanaerobic 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/imapassessments/tier-ii-environment-assessments/cvms.
- 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.
- Pepper R, Anderson A, Ashworth P, Beck V, Hart B, Jones D, Priestly B, Ritchie D and Smith R (2018) Final report of the scientific inquiry into hydraulic fracturing in the Northern Territory. Viewed 08 March 2019, https://frackinginquiry.nt.gov.au/inquiry-reports/final-report.
- 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: 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-suitetm-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: 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 https://w3id.org/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.

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

<u>activity</u>: 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 lifecycle 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.

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

<u>aquifer</u>: 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

<u>aquitard</u>: 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.

<u>asset</u>: 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.

<u>bed</u>: 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

<u>bore</u>: 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.

<u>casing</u>: 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

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

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

<u>cleat</u>: 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

<u>coal seam gas</u>: 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).

<u>conceptual model</u>: 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 under standing. 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.

consequence: synonym of impact

<u>conventional gas</u>: 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.

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

<u>dataset</u>: 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).

<u>deep coal gas</u>: 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.

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

<u>discovered</u>: 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.

<u>dome</u>: 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

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

<u>effect</u>: 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).

<u>endpoint</u>: 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.

<u>extraction</u>: 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.

<u>field</u>: 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.

<u>flowback</u>: 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.

flowback water: the fluids and entrained solids that emerge from a well during flowback

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

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

fracking: see hydraulic fracturing

<u>fracture</u>: 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.

<u>free gas</u>: 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.

<u>geogenic chemical</u>: a naturally-occurring chemical originating from the Earth, for example, from geological formations

<u>geological formation</u>: 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

<u>groundwater</u>: 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.

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

<u>hydraulic fracturing</u>: 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.

<u>hydraulic fracturing fluid</u>: 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.

<u>hydrocarbons</u>: 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

<u>impact</u>: 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.

<u>impact mode</u>: 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

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

<u>kerogen</u>: 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.

likelihood: probability that something might happen

<u>lithology</u>: the description of rocks, especially in hand specimen and in outcrop, on the basis of characteristics such as color, mineralogic composition and grain size

material: pertinent or relevant

<u>methane</u>: a colorless, odorless gas, the simplest parafin 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.

<u>migration</u>: 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 Mohorivicic discontinuity (seismic reflector) at the base of the crust

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

<u>oil</u>: a mixture of liquid hydrocarbons and other compounds of different molecular weights. Gas is often found in association with oil. Also see Petroleum.

Stage 2: Chemical screening technical appendix

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.

<u>permeability</u>: 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.

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

<u>petroleum system</u>: 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.

<u>play</u>: 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.

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

<u>potential effect</u>: 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 byproduct 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 byproduct of shale and tight gas resource development, whereas 'co-produced water' refers to the large amounts of water produced as a byproduct of coal seam gas development.

<u>production</u>: 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

<u>proppant</u>: 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

<u>reserves</u>: 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

<u>reserves, proved</u>: 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.

<u>reservoir</u>: 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

<u>ridge</u>: 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)

<u>risk</u>: the effect of uncertainty on objectives (ASNZ 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.

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

<u>seal</u>: 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.

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

<u>sedimentary rock</u>: 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.

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

<u>shale</u>: 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

<u>shale gas</u>: 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.

Glossary

siltstone: a sedimentary rock composed of silt-sized particles (0.004 to 0.063 mm in diameter

<u>stress</u>: 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

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

<u>structure</u>: 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

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

<u>tight gas</u>: 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

<u>trap</u>: 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.

<u>unconventional gas</u>: 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.

<u>well</u>: 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'.

<u>well barrier</u>: 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 barrier failure: when a single, specific barrier fails to contain fluids (remaining barriers maintaining containment)

<u>well integrity</u>: 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

Glossary

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



