



Australian Government
**Department of Agriculture,
Water and the Environment**
Bureau of Meteorology
Geoscience Australia



Qualitative (screening) environmental risk assessment of drilling and hydraulic fracturing chemicals for the Cooper 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>.

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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.

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Cover photograph

Cooper Creek in flood, 4 km east of Windorah, March 2018.

Credit: Geological and Bioregional Assessment Program, Russell Crosbie (CSIRO)

Element: GBA-COO-2-343

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 Geological Bioregional Assessment (GBA) regions between 2011 and 2016. Of the 116 chemicals, 9 were drilling chemicals, 99 were hydraulic fracturing chemicals and 8 were chemicals used for both activities. 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 (NINCAS, 2017). A Tier 1 qualitative (screening) environmental risk assessment (ERA) of the chemicals found 42 chemicals were of 'low concern' and considered to pose minimal risk to aquatic ecosystems. A further 33 chemicals were of 'potentially high concern' and 41 were of 'potential concern'. These chemicals would require further site-specific quantitative chemical assessments to be undertaken to determine risks from specific operations 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 designed to provide an upper-bound estimates of geogenic chemical mobilisation from target formations in the Cooper GBA region and intended to guide future field-based monitoring, management and treatment options. Laboratory-based leachate tests on powdered rock samples identified several elements that could be substantially mobilised into solutions by hydraulic fracturing fluids: aluminium, arsenic, barium, cadmium, cobalt, chromium, copper, iron, lead, lithium, nickel and zinc. Priority organic chemicals such as phenols, polycyclic aromatic hydrocarbons (PAHs) and total recoverable hydrocarbons (TRHs) were also detected in extracts of powdered rock samples. 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.

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- Internal Peer Review Group: CSIRO: Anu Kumar.
- Technical Peer Review Group: Andrew Boulton, Peter McCabe, Catherine Moore and Jenny Stauber.
- State Government Science Technical Review: This group includes scientists from the Queensland and South Australian governments.

Abbreviations and acronyms

Abbreviation/acronym	Definition
AEE	Acid-extractable element
CSG	Coal seam gas
ERA	Environmental risk assessment
GBA	Geological and Bioregional Assessment
HFF	Hydraulic fracturing fluids
HCl	Hydrochloric acid
PAH	Polycyclic aromatic hydrocarbon
SGW	Synthetic groundwater
TRH	Total recoverable hydrocarbons

Units

Unit	Description
µg/g	Micrograms per gram
µg/kg	Micrograms per kilogram
µg/L	Micrograms per litre
µm	Micrometer
g	Gram
g/L	Grams per litre
KPa	Kilo pascal
Molarity (M)	Moles per litre
m/v	Mass per volume
mg/L	Milligrams per litre
mg/kg	Milligrams per kilogram
mL	Millilitres
°C	Degrees Celsius
rpm	Revolutions per minute
v/v	Volume per volume

The Geological and Bioregional Assessment Program

The \$35.5 million Geological and Bioregional Assessment (GBA) Program is assessing the potential environmental impacts of shale and tight gas development to inform regulatory frameworks and appropriate management approaches. The geological and environmental knowledge, data and tools produced by the Program will assist governments, industry, landowners and the community by informing decision making and enabling the coordinated management of potential impacts.

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

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

The GBA Program aims to:

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

The 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 Cooper GBA region are:

- Owens R, Hall L, Smith M, Orr M, Lech M, Evans T, Skeers N, Woods M and Inskeep C (2020) Geology of the Cooper GBA region.
- Lech ME, Wang L, Hall LS, Bailey A, Palu T, Owens R, Skeers N, Woods M, Dehelean A, Orr M, Cathro D and Evenden C (2020) Shale, tight and deep coal gas prospectivity of the Cooper Basin.
- Evans TJ, Martinez J, Lai ÉCS, Raiber M, Radke BM, Sundaram B, Ransley TR, Dehelean A, Skeers N, Woods M, Evenden C and Dunn B (2020) Hydrogeology of the Cooper GBA region.
- O'Grady AP, Herr A, MacFarlane CM, Merrin LE and Pavey C (2020) Protected matters for the Cooper GBA region.
- Kear J and Kasperczyk D (2020) Hydraulic fracturing and well integrity for the GBA regions.

All maps for the Cooper 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 cleanup, 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)) can have negative impacts on local and regional water quality (surface water and groundwater) and water-dependent ecosystems if not adequately controlled or managed.

Companies undertake an ERA process of gas operations that includes the identification of 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 for roles such as 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 lined pits or transported off-site to an approved treatment or disposal facility.

1.3 Hydraulic fracturing chemicals

Hydraulic fracturing involves the injection of fluids with chemicals 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; 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 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/fluid
Proppant	Holds open fractures to allow gas flow
Gelling agent/viscosifier	Alters 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 monitor 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 (i.e. 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.

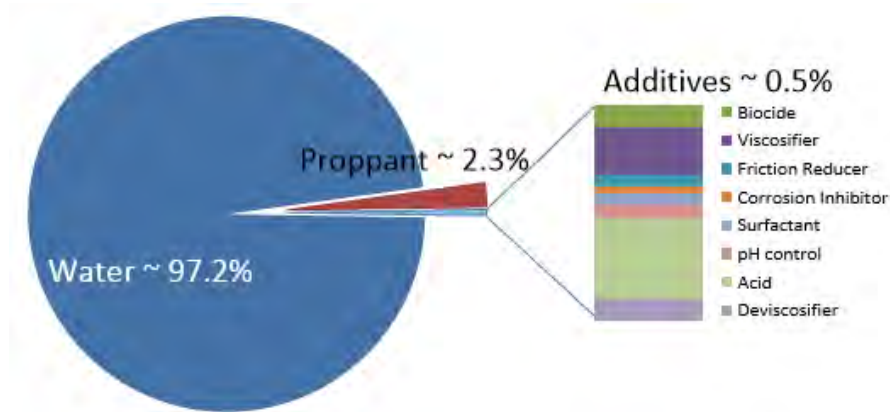


Figure 1 An example of overall percentages of water, proppant, and chemical additives in hydraulic fracturing fluid in a deep shale gas well fracturing operation in the Cooper Basin

Source: figure reproduced from Beach Energy and RPS (2012)
Element: GBA-COO-2-115

1.4 Geogenic chemicals

Concerns surrounding the use of hydraulic fracturing have mainly centred on potential effects of a range of industrial chemicals that comprise, albeit an overall small percentage (Figure 1), of the fluids. However, shale, tight and deep coal gas rocks/formations are known to contain a number of geogenic (natural) occurring chemical constituents that could be mobilised into solutions during hydraulic fracturing (Ziemkiewicz and Thomas He, 2015; Harrison et al., 2017).

Natural rock formations contain geogenic chemicals (compounds and elements) that could be mobilised into flowback and produced waters during hydraulic fracturing. These geogenic chemicals include nutrients, organics (e.g. PAHs and phenols), metals (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 and physical 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 to aquatic ecosystems from shale, tight, and deep coal gas operations in Australia. The objectives were:

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

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

2 Qualitative environmental risk assessment of chemicals

2.1 *Methods*

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

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

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

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

A tiered approach to ERA is often used to provide a systematic way of evaluating risk that is proportional to resources, complexity, and cost (Department of the Environment and Energy, 2017; USEPA, 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.

2.1.2 Data sourcing

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

Specific chemical properties of interest for Tier 1 ERA included water solubility, octanol-water partition coefficient ($\log K_{ow}$), volatility (Henry's constant), biodegradation (half-life), and bioconcentration factors (BCF=uptake of chemical into aquatic organism from water-only) (Geological and Bioregional Assessment Program, 2018). Data for some chemical properties could be estimated using the US EPA Estimation Program Interface (EPI Suite) (USEPA, 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 (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 are the chemical concentrations 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, water flea and 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 (USEPA, 2017) was used to predict acute toxicity to aquatic biota based on quantitative structure activity relationships (QSAR). The assessment also utilised chronic ecotoxicity data (where they could be sourced from the literature) using standard testing protocols as a line of evidence when best professional judgement was required (Geological and Bioregional Assessment Program, 2018).

2.1.3 Qualitative environmental risk assessment

A Tier 1 qualitative (screening) ERA was performed on drilling and hydraulic fracturing fluid chemicals identified used in shale, tight, and deep coal gas activities in GBA regions during 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 precautionary approach was applied to the evaluation of data and to the Tier 1 qualitative ERA.

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

Method	Result	Classification
Water/sediment: Test No.308: Aerobic and Anaerobic Transformation in Aquatic Sediment Systems (OECD TG 308)	>60-d half-life in water	Persistent
Biodegradability tests (OECD 301A-F)	Sufficient degradation over 10 days in a 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	$\log K_{ow} \geq 4.2$	Bioaccumulative

Source: Department of the Environment and Energy (2017)

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

Toxicity data*	Lowest acute toxicity value	Classification
3 trophic levels: <ul style="list-style-type: none"> Algae 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: <ul style="list-style-type: none"> Algae 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: <ul style="list-style-type: none"> Algae 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: <ul style="list-style-type: none"> Algae 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 Assessments, 2018). (Geological and Bioregional Assessment Program, 2018)(Geological and Bioregional Assessment Program, 2018)(Geological and Bioregional Assessment Program, 2018)Of the 116 chemicals identified, 9 were drilling chemicals, 99 were hydraulic fracturing chemicals, and 8 were chemicals used for both activities. An additional 32 proprietary chemicals (in products) were identified 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 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). 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 have been due to site-specific requirements needed for higher temperatures and pressure, geology and minerology of the formations, scale and biofilm build-up, fluid stability and viscosity, proppant transport, improve gas extraction and efficiency, and a move by industry towards 'greener, safer' options.

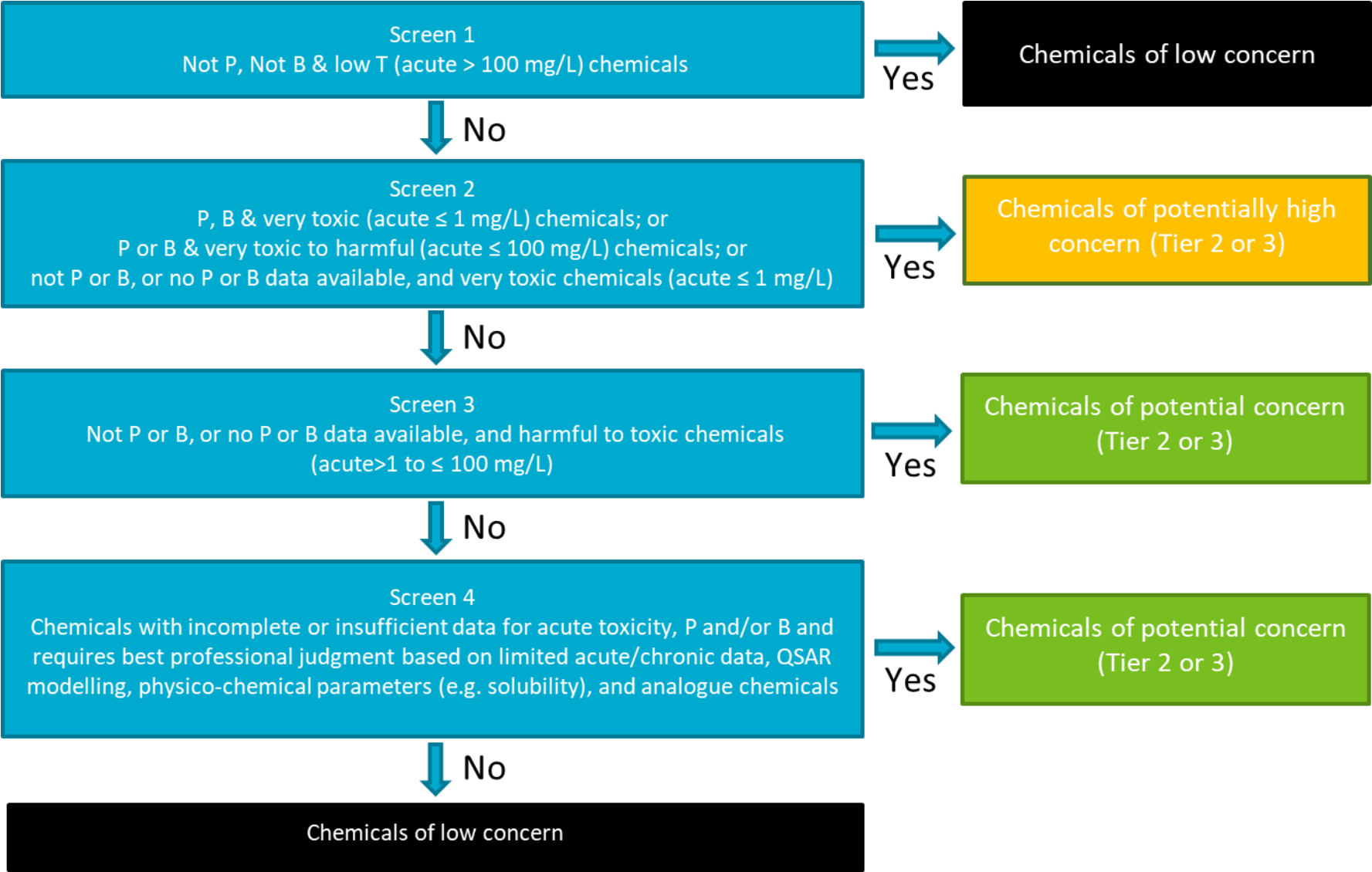


Figure 2 Decision tree framework for Tier 1 qualitative (screening) ERA of chemicals associated with shale, tight, and deep coal gas operations in Australia (P = persistent; B = bioaccumulative; T = toxic; QSAR = quantitative structure-activity relationships)

Element: GBA-COO-2-116

Table 4 Chemicals identified associated with drilling and hydraulic fracturing at shale, tight, and deep coal gas 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	Hydrochloric acid	7647-01-0*
7	2-hydroxy-N,N,N-trimethylethanaminium chloride (choline chloride)	67-48-1*	65	Hydrotreated light distillate (C13-C14 isoparaffin)	64742-47-8*
8	2-Mercaptoethyl alcohol	60-24-2	66	Hydroxypropyl guar	39421-75-5
9	2-Methyl-4-isothiazol-3-one	2682-20-4*	67	Isopropanol	67-63-0*
10	2-Propenoic acid, polymer with sodium phosphinate	129898-01-7	68	Kyanite (Al ₂ O(SiO ₄))	1302-76-7
11	2-Propenoic acid, 2-methyl-, polymer with 2-methyl-2-((1-oxo-2-propenyl)amino)-1-propanesulfonic acid monosodium salt	136793-29-8	69	Magnesium chloride	7786-30-3*
12	5-Chloro-2-methyl-4-isothiazolol-3-one	26172-55-4*	70	Magnesium nitrate	10377-60-3*
13	Acetic acid	64-19-7*	71	Maltodextrin	9050-36-6
14	Acrylamide	79-06-1	72	Methanol	67-56-1*
15	Acrylamide, 2-acrylamido-2-methylpropanesulfonic acid, sodium salt polymer	38193-60-1	73	Monosodium fumarate	7704-73-6
16	Acrylonitrile	107-13-1	74	Mullite (SiO ₂ /Al ₂ O ₃)	1302-93-8
17	Alcohols, C6-12, ethoxylated propoxylated	68937-66-6	75	Naphthalene	91-20-3
18	Alcohols C9-11, ethoxylated	68439-46-3	76	Naphthenic acids, ethoxylated	68410-62-8
19	Alcohols, C10-16, ethoxylated propoxylated	69227-22-1	77	Octamethylcyclotetrasiloxane	556-67-2
20	Alcohols, C12-C16, ethoxylated	68551-12-2	78	Orthoboric acid with 2-aminoethanol	26038-87-9*
21	Alkyl polyglycol ether	31726-34-8	79	Poly(ethylene glycol)	25322-68-3
22	Almandite garnet (Al ₂ Fe ₃ (SiO ₄) ₃)	1302-62-1	80	Pontacyl carmine 2B (acid violet 12)	6625-46-3

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

#	Chemical name	CAS RN	#	Chemical name	CAS RN
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*
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 were assessed in the National Assessment of Chemicals Associated with CSG extraction in Australia (NICNAS, 2017); Source: Geological and Bioregional Assessments, 2018

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

2.2.2 Qualitative environmental risk assessment of chemicals

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

Of the 33 chemicals identified as being of 'potentially high concern', 5 chemicals (1 biocide and 4 defoaming agents) are not likely to be easily degraded (persistent), are bioaccumulative (potentially can accumulate in organisms), and exhibit very high acute toxicity to aquatic organisms (normally 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.

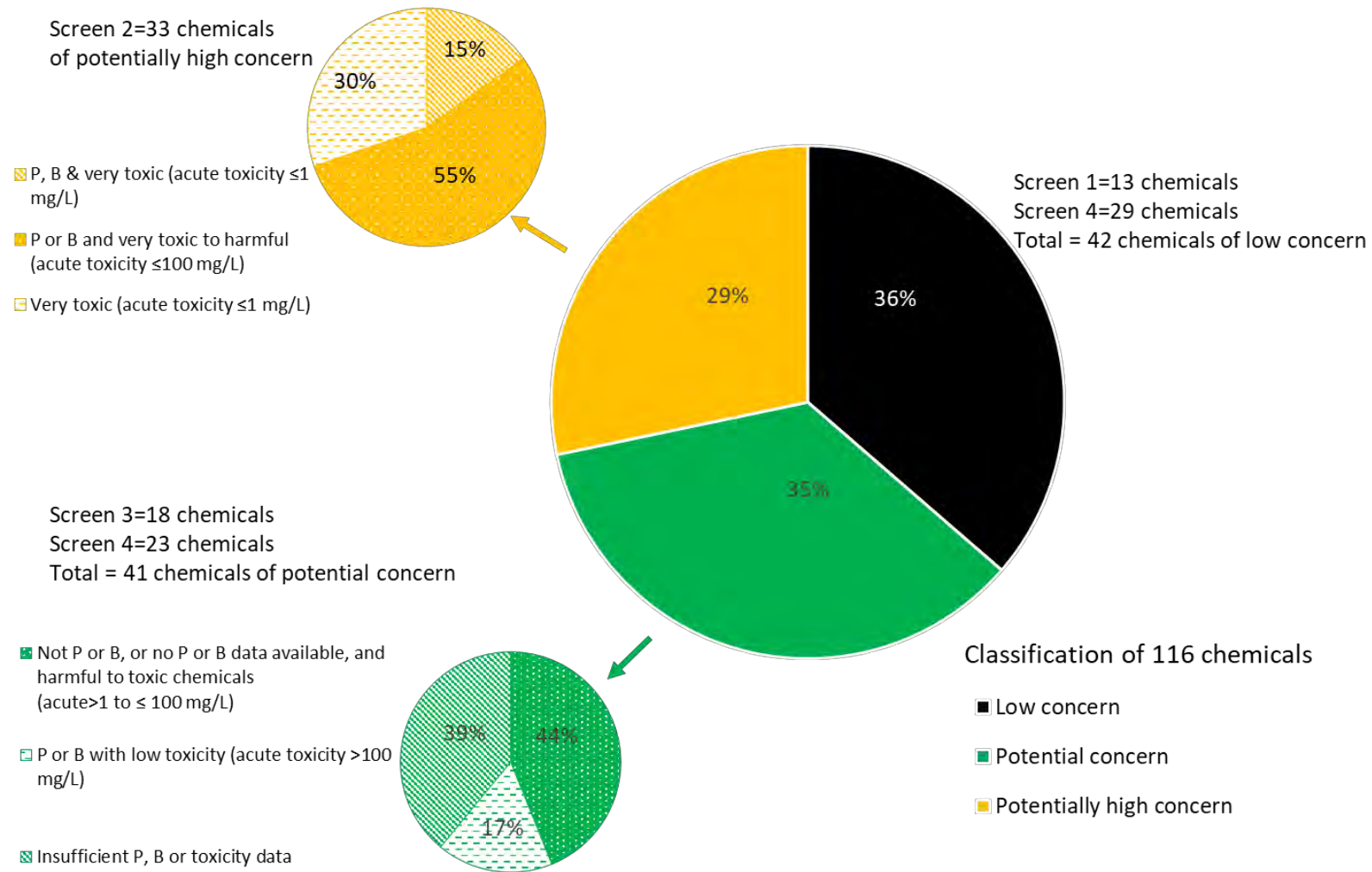


Figure 3 Tier 1 qualitative ERA of chemicals associated with shale, tight and deep coal gas operations in Australia (Refer to Figure 2 for Screen 1 to 4 details; percentage of chemicals in each category are shown in each segment; further breakdown of chemicals of ‘potential concern’ and ‘potentially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

Source: Geological and Bioregional Assessments, 2018
Element: GBA-COO-2-117

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

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

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

Source: Geological and Bioregional Assessments, 2018

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 was 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 bioaccumulation data could be sourced), but are toxic or harmful chemicals (n=18) (Screen 3), and are chemicals with incomplete data that require professional judgement (n=23) (Screen 4) (Figure 3) (Geological and Bioregional Assessment Program, 2018). These chemicals have the potential to harm aquatic ecosystems if released and may require specific control and management measures to prevent their release into the environment.

For Screen 4 (Figure 3), 7 of the 52 chemicals identified were found to be persistent or bioaccumulative, and have low toxicity (Geological and Bioregional Assessment Program, 2018). These seven chemicals are: (i) 1-benzyl quinolinium chloride; (ii) sodium acryloyldimethyltaurate; (iii) Amaranth (acid red 27); (iv) alcohols, C6-12 ethoxylated propoxylated; (v) ethylene glycol butyl ether; (vi) poly(ethylene glycol); and (vii) Tall oil (fatty acids). Since the Tier 1 ERA used mainly acute toxicity data these chemicals are considered to be of ‘potential concern’ due to their unknown effects on organisms that may occur due to long-term exposure (chronic toxicity).

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

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

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

Source: Geological and Bioregional Assessments, 2018

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

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

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

Source: Geological and Bioregional Assessments (2018)

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 content); (iii) abiotic transformations; (iv) sorption reactions; (v) performance against specific microbial species (mode of action); and (vi) cost.

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

Biocides such as glutaraldehyde (CAS RN 111-30-8) and tetrakis (hydroxymethyl) phosphonium sulfate (CAS RN 55566-30-8), which are very toxic to aquatic organisms, may pose a lower risk to aquatic organisms due to their expected rapid (i.e. ≤ 60 days) 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, bioaccumulative and highly toxic nature (Geological and Bioregional Assessment Program, 2018). The three cyclic siloxanes: octamethylcyclotetrasiloxane (CAS RN 556-67-2), decamethylcyclopentasiloxane (CAS RN 541-02-6) and dodecamethylcyclohexasiloxane (CAS RN 540-97-6), are likely to volatilise or degrade in water (via hydrolysis) but, due to their hydrophobic nature, are also likely to strongly associate with sediments/suspended solids where they can persist. Furthermore, there are currently conflicting ERAs on the cyclic siloxanes due to difficulties in conducting aquatic toxicity tests because of their volatility, making the toxicity assessments highly uncertain (ECHA, 2018; Environment Canada Health Canada, 2008; Fairbrother et al., 2015; Fairbrother and Woodburn, 2016; Government of Canada, 2012a, 2012b). 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

operations, will require a more detailed quantitative ERAs to be undertaken with realistic exposure scenarios that assess and model 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 environments.

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 the environment 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, biotransform (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 to a smaller percentage of 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 uses mainly aquatic acute ecotoxicity data representing three trophic levels – freshwater alga, water flea and 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 have effects on biota due to long-term exposure (chronic effects) in the environment. Chronic toxicity data on aquatic organisms from a range of trophic levels (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 take into account 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 are 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 is not applicable to inorganic chemicals. Studies on biodegradation are not routinely conducted for mixtures and polymers, under varying environmental conditions (e.g. oxygen concentrations, redox, salinity, and temperatures), exposure concentrations, or degradation and transformation products.
- Bioconcentration factor (e.g. fish) data were limited for the 116 chemicals and appears to be not routinely conducted using standard protocols. In the absence of BCF data, the potential for a chemical to bioaccumulate was inferred from its hydrophobicity, typically determined using its octanol-water partition coefficient (Log K_{ow} ; hydrophilic: hydrophobic nature).
- Assessments were conducted using mainly acute toxicity data for three trophic levels (fish, invertebrate, and algae) as limited chronic data could be sourced using standard testing protocols.
- There were limited ecotoxicity data available for Australian species.
- Ecotoxicity endpoints 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 mitigation measures that would substantially reduce the likelihood and consequence of the risk to aquatic organisms. A precautionary approach was applied to the evaluation of chemical and ecotoxicity data and to the Tier 1 qualitative ERA.

3 Laboratory-based leachate tests (geogenic chemicals)

3.1 Methods

3.1.1 Overview of the experimental approach

This 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 (HFF). The tests were designed to provide an upper bound estimates of geogenic chemical mobilisation from shale, tight and deep coal gas formations in the Cooper GBA region and is intended to guide future field based monitoring, management, and treatment options.

The specific aims of the study were:

- Apply laboratory batch leach tests that allow the chemical screening of geogenic compounds and elements mobilised from shale, tight and deep coal powdered rock samples during hydraulic fracturing; and
- Identify potential inorganic and organic chemicals that could be mobilised into solution from powdered rock samples from formations in Cooper 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. Tests were conducted at 80°C in order to examine elevated temperature conditions that could be present during hydraulic fracturing operations at deep shale and tight gas operations (median aquifer temperature at 1000-2500 m drill hole ~80°C; after removal of unknown, uncorrected, and unidentified data and methodologies in the dataset) (<https://ecat.ga.gov.au/geonetwork/srv/eng/catalog.search#/metadata/70604>). Exploratory studies were also conducted on the effect of pressure (that would be present in wells of shale, tight and deep coal gas operations) on geogenic chemical (element) mobilisation into solution from powdered rock samples.

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 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).

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

Leach solution	Components	Leach test conditions	Substances analysed
Dilute hydrochloric acid (HCl)	1 M HCl	80°C, 17 hours, atmospheric pressure	Elements, inorganics
Synthetic groundwater (SGW)	750 mg/L sodium chloride, 750 mg/L sodium bicarbonate	80°C, 17 hours, 100 and 18400 KPa	Elements, inorganics
Hydraulic fracturing fluid (HFF)	See Table 11	80°C, atmospheric pressure	Elements, inorganics
Organic solvents	Methanol: acetone: dichloromethane (1:2.5:2.5)	100°C, 10000 KPa	Organics

3.1.2 Powdered rock samples

Rock samples from formations in the Cooper GBA region were sourced from the South Australian Core Library (drill holes: Holdfast-1 and Encounter-1) (Table 9). The formations (Roseneath, Epsilon, Murteree, and Patchawarra) are representative of potential targets for shale, tight and deep coal gas developments in the Cooper GBA region. Six rock sections were sourced from Holdfast-1 drill core representing the Roseneath, Epsilon (x2), Patchawarra and Murteree shale formations (Figure 4) and three samples were sourced from Encounter-1 drill core representing the Roseneath, Epsilon and Murteree shale formations. The samples were stored under dry, non-climate controlled conditions. The rock samples were fine ground to <70 µm to a uniform particle size (as an upper bound for potential chemical mobilisation into solution).

Table 9 Rock sections sourced for testing from Holdfast-1 and Encounter-1 drill cores in Cooper GBA region

Sample description	Drill hole	Drill core no.	Formation
R2183300 offcuts 4,5,6	Holdfast-1	R-2183300	Roseneath
R2183302 offcuts 3 & 5	Holdfast-1	R-2183302	Epsilon
R2183305 offcuts 3,4	Holdfast-1	R-2183305	Epsilon
R2183309 offcut 2	Holdfast-1	R-2183309	Patchawarra
R2183306	Holdfast-1	R-2183306	Murteree shale
Epsilon formation (deep coal)	Holdfast-1	R-2183303	Epsilon
Encounter P84828	Encounter-1	2074444	Roseneath
Encounter P84831	Encounter-1	2074452	Epsilon
Encounter P84836	Encounter-1	2074462	Murteree shale

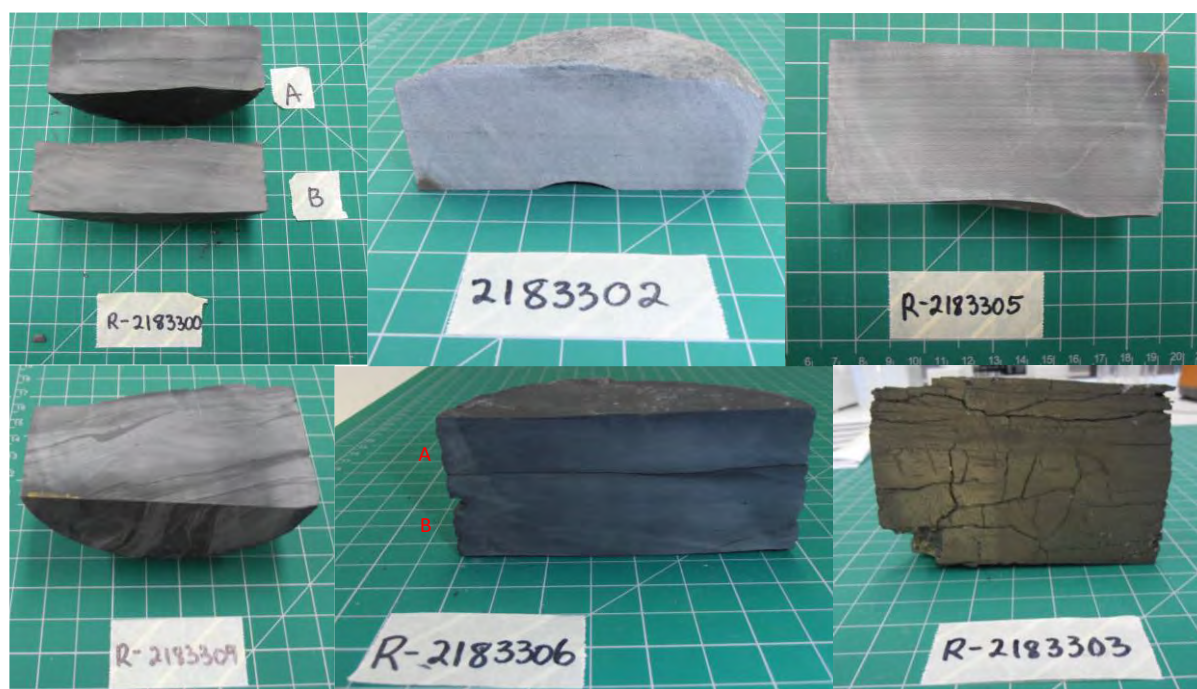


Figure 4 Photographs of the rock sections from the Holdfast-1 drill core used to generate powdered rock samples

Source: Photos from D. Heryanto, CSIRO

Element: GBA-COO-2-314

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 nitric acid and 3 mL HCl was added, then heated in a microwave oven (MARS Xpress 6, CEM) to 175°C for 16.5 minutes. Sample digests were then diluted with ultra-pure deionised water and analysed for inorganic elements by a combination of inductively coupled plasma-atomic emission spectrometry (ICP-AES) (Varian 730-ES, Australia) and inductively coupled plasma-mass spectrometry (ICP-MS) (8800, Agilent Technologies, Japan) using matrix matched standards. The results are reported on a dry weight basis. Certified reference materials (ERM-CC018, European Reference Materials; OREAS-25a, Ore Research and Exploration Australia) were included in each digestion batch. Replicate analysis and spike recoveries were carried out on selected samples.

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

Acid-extractable element (AEE) concentrations were also determined on powdered rock samples. The acid-extractable metal fraction gives an indication of the fraction of particulate metals that may be amenable to mobilisation under environmental conditions. Approximately 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 hour 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 analysis and spike recoveries were carried out on selected samples.

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

3.1.3.2 Inorganic element analysis

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

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

3.1.3.3 Organics analysis

Extracts were analysed for a range of priority (targeted) organic compounds: 14 substituted phenols, 15 PAHs, and TRH fractions (C10 to C40) (Table 10) at the National Measurement Institute (NATA accredited facility).

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

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

*NEPM TRH reporting values; LOR = limits of reporting

3.1.4 Leachate test protocol – inorganics

3.1.4.1 General test conditions

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

Ultrapure deionised water was sourced from a Milli-Q system (18 MΩ.cm conductivity, Millipore, Australia). Plasticware used for element analyses was acid-washed prior to use by soaking for a minimum of 24 hours 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) at respective 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.

Table 11 In-house synthetic HFF composition

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

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

The leach tests were based on those developed by CSIRO for the investigation of geogenic chemicals mobilisation 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 minutes, and then syringe filtered through 0.45 µm filter cartridges (Minisart, Sartorius Stedim, Germany). If sample masses permitted, duplicate leach tests were performed. The tests also included a blank treatment (no solids added).

3.1.4.2 Synthetic groundwater

Leach tests were conducted using SGW in order to determine the concentration of easily mobilised trace 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.

Leachate tests on Holdfast-1 Roseneath (2183300) and Encounter-1 Murteree Shale (2074462) were also conducted at 80°C and elevated pressure (18400 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 20000 KPa. The reactor was pressurised with nitrogen doped with oxygen in order to maintain aerobic conditions.

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 cleanup 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 atmospheric pressure.

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. 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). 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 minutes. Approximately 10 mL 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).

The concentration of >60 trace elements were determined in the powdered rock samples (Geological and Bioregional Assessment Program, 2019). The particulate concentrations of commonly occurring trace elements are summarised in Table 12. The concentrations of many trace elements were quite variable and typically ranged by over one order of magnitude across the rock samples. Comparisons of the trace elemental data with the mean global crustal abundance values (Taylor, 1964) and the ANZECC/ARMCANZ sediment quality guidelines (ANZECC/ARMCANZ, 2000) indicated that the samples were not particularly enriched in trace elements relative to these averages. The only exceptions identified were for chromium (264 mg/kg) in Holdfast-1 Epsilon 2183302 and copper (120 mg/kg) in Holdfast-1 Patchawarra 2183309.

The AEE concentrations of commonly occurring trace elements are summarised in Table 13 (and 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 for Holdfast-1 Epsilon (2183302) and Holdfast-1 Patchawarra (2183309) which had elevated AEE chromium and copper concentrations, respectively. The percentage of

trace elements present as AEE are summarised in Table 14. The ratios provide an indication of the extent to which trace elements could be mobilised from powdered rock samples into solution: barium, calcium, chromium, lead, phosphorus and sodium had the highest mean percentages (mean >50%).

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

Drill hole	Holdfast 1						Encounter 1		
	Roseneath	Epsilon	Epsilon	Patchawarra	Murteree shale	Epsilon	Roseneath	Epsilon	Murteree shale
Drill core no.	2183300	2183302	2183305	2183309	2183306	2183303	2074444	2074452	2074462
Al	9500	3000	10000	7800	580	21000	12000	4000	6800
Ag	0.11	0.032	0.028	0.050	0.060	0.16	0.10	0.031	0.089
As	5.0	8.0	8.3	19	4.9	5.4	4.8	3.0	2.8
B	2.8	0.6	1.1	1.2	<0.2	5.5	4.2	1.3	1.9
Ba	140	26	58	61	854	260	250	100	180
Cd	0.29	0.09	0.03	0.15	0.09	0.23	0.33	0.09	0.19
Ca	970	530	240	300	380	1400	2100	1500	820
Co	18	11	4.9	13	26	18	17	15	16
Cr	60	264	116	116	3.1	71	37	97	33
Cu	68	33	16	120	29	55	48	14	37
Fe	55000	56000	18000	16000	2000	50000	50000	61000	26000
Hg	<0.1	<0.1	<0.1	<0.1	0.46	<0.1	<0.1	<0.1	<0.1
K	3600	910	1900	2100	360	6300	4800	2800	3500
Mg	4700	13000	3300	2900	130	5300	5200	8300	4400
Mn	1000	1500	300	150	27	760	1200	1000	260
Mo	0.83	0.45	0.49	0.36	2.7	1.0	0.97	0.87	0.81
Na	250	63	150	130	-	280	47	240	510
Ni	34	35	17	28	35	36	45	25	29
P	210	71	46	100	150	650	800	200	250
Pb	35	8.4	8.2	13	20	41	39	16	31
S	350	79	69	110	700	320	330	87	180
Sb	0.59	0.16	0.19	0.41	0.31	0.80	0.55	0.20	0.62
Se	1.0	0.05	0.01	0.11	0.12	0.48	1.5	0.13	0.32
U	0.51	0.12	0.032	0.29	0.13	1.4	2.0	0.69	0.89
V	14	5.6	4.3	4.9	7.5	28	18	10	12
Zn	110	63	65	97	97	122	106	66	102

Source: Geological and Bioregional Assessment Program (2019); Bold numbers: Chromium (Cr) and copper (Cu) enriched in samples

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

Drill hole	Holdfast 1						Encounter 1		
	Roseneath	Epsilon	Epsilon	Patchawarra	Murteree shale	Epsilon	Roseneath	Epsilon	Murteree shale
Drill core no.	2183300	2183302	2183305	2183309	2183306	2183303	2074444	2074452	2074462
Al	835	352	614	718	1666	45	1138	963	897
Ag	0.010	0.010	0.010	0.005	0.013	<0.001	0.010	0.008	0.007
As	0.87	3.5	5.4	8.1	0.74	0.14	1.9	1.8	1.4
B	<1	<1	<1	<1	<1	<0.4	<1	<1	<1
Ba	85	19	32	30	73	523	147	63	83
Cd	<0.1	<0.1	<0.1	<0.1	<0.1	<0.01	<0.1	<0.1	<0.1
Ca	576	345	219	293	1220	160	1894	1024	627
Co	4.1	3.3	1.5	3.4	3.6	0.55	13	7.0	5.6
Cr	35	184	84	84	39	<0.2	21	81	23
Cu	27	16	9.1	91	20	0.84	31	4.2	11
Fe	11500	18000	2480	3100	11300	140	9750	29800	6410
Hg	<0.004	<0.004	<0.004	0.004	<0.004	0.09	<0.004	<0.004	<0.004
K	691	313	364	492	976	28	817	699	656
Mg	859	3790	343	403	843	14	1000	3910	1150
Mn	242	560	104	48	186	<4	226	488	67
Mo	0.4	<0.3	<0.3	<0.3	0.3	0.32	0.7	0.5	0.3
Na	188	70	133	117	176	26	365	217	419
Ni	5	11	6	7	5	0.20	19	9	6
P	117	68	48	77	479	68	750	224	193
Pb	20	6.1	5.7	6.4	29	6.3	26	11	20
S	38	23	27	21	32	150	94	28	41
Sb	0.32	0.09	0.10	0.23	0.33	<0.04	0.38	0.11	0.38
Se	0.09	<0.02	<0.02	0.03	0.07	<0.01	0.53	0.03	0.07
U	0.12	0.065	0.024	0.069	0.43	0.017	1.5	0.28	0.34
V	1.8	1.6	0.60	0.78	2.6	0.08	2.2	4.2	2.0
Zn	8	10	15	22	14	2	24	20	18

Source: Geological and Bioregional Assessment Program (2019)

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

Drill hole	Holdfast 1	Holdfast 1	Holdfast 1	Holdfast 1	Holdfast 1	Holdfast 1	Encounter 1	Encounter 1	Encounter 1	Mean	Std. Dev.
Formation	Roseneath	Epsilon	Epsilon	Patchawarra	Murteree shale	Epsilon	Roseneath	Epsilon	Murteree shale		
Al	9	12	6	9	8	8	9	24	13	11	5
As	17	44	65	43	14	3	40	58	50	37	21
Ba	61	72	56	49	28	61	59	63	46	55	13
Ca	59	65	91	98	87	42	90	68	76	75	18
Co	23	30	30	27	20	2	72	47	36	32	19
Cr	58	70	72	73	56	na	56	84	69	67	10
Cu	40	50	56	76	36	3	66	30	29	43	22
Fe	21	32	14	19	23	7	20	49	25	23	12
Mg	18	29	10	14	16	11	19	47	26	21	12
Mn	24	37	35	32	24	na	19	49	26	31	10
Mo	43	na	na	na	33	12	75	61	39	44	22
Na	75	112	89	90	63	na	na	90	82	86	15
Ni	15	31	35	26	13	1	43	36	22	25	13
P	56	95	104	77	74	45	94	112	77	82	22
Pb	59	73	70	48	69	31	68	65	64	61	13
S	11	30	39	19	10	21	29	32	23	24	10
Se	9	na	na	26	15	na	36	22	21	21	9
U	25	56	76	24	30	13	72	41	38	42	22
V	13	28	14	16	9	1	12	40	17	17	11
Zn	8	16	23	23	11	3	23	30	18	17	9

Bold = ratio of AEE to particulate element concentration > 50%; not applicable or no data (na)

Source: Geological and Bioregional Assessment Program (2019)

3.2.1 Leachate tests – inorganics

3.2.1.1 SGW tests

The concentrations of elements leached into solution by SGW (17-hour equilibration time) are summarised in Table 15 (Geological and Bioregional Assessment Program, 2019). In general, the concentration of elements in solution were relatively low. The following elements showed elevated mobilisation into solution: aluminium, arsenic, barium, calcium, magnesium and sulfur. It should be noted that the leachate solution pH became alkaline by the end of the tests (typically 9.0) and this may have contributed to the mobilisation of some trace elements such as aluminium and arsenic into solution.

Higher pressure from 100 to 18400 KPa for the leachate tests using SGW resulted in a significant increase in the concentrations of aluminium, arsenic, lithium, phosphorus, and sulfur mobilised into solution (Table 16) (Geological and Bioregional Assessment Program, 2019). Increased pressure also led to a decrease in the mobilisation of elements such as barium, calcium and magnesium into solution (Table 16).

3.2.1.2 Dilute HCl tests

The mean concentration of elements leached into solution by dilute HCl (17-hour equilibration time) are summarised in Table 17 (Geological and Bioregional Assessment Program, 2019). Acidification of the rock samples led to increased mobilisation (compared to SGW) of a range of elements into solution including: arsenic, aluminium, barium, cadmium, chromium, cobalt, copper, iron, lead, nickel, and zinc.

3.2.1.3 Synthetic HFF tests

The concentrations of elements mobilised into solution by HFF (17-hour equilibration time) are summarised in Table 18 (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 substantially released into solution were generally much higher in HFF than in the SGW indicating the role of industrial chemicals present in the HFF in mobilisation. The elements showing substantially increased mobilisation into solution (compared to SGW) were: aluminium, arsenic, barium, cadmium, cobalt, chromium, copper, iron, lithium, nickel, lead, and zinc. Figure 5 illustrates the differences found in mobilisation of selected elements from powdered rock samples due to the leachate test solutions. In most cases the highest elemental concentrations in solutions were found in the dilute HCl leachate tests (compared to SGW and HFF).

Table 15 Dissolved elemental concentrations in SGW leachate solutions

	Drill hole	Blank	Holdfast 1	Holdfast 1	Holdfast 1	Holdfast 1	Holdfast 1	Holdfast 1	Encounter 1	Encounter 1	Encounter 1
	Formation		Roseneath	Epsilon	Epsilon	Patchawarra	Murteree shale	Epsilon	Roseneath	Epsilon	Murteree shale
	Drill core no.		2183300	2183302	2183305	2183309	2183306	2183303	2074444	2074452	2074462
DOC	mg/L	---	---	2.9	2.1	---	---	---	---	---	---
Ag	µg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Al	µg/L	0.6	1050	795	1700	1650	1300	360	800	955	1150
As	µg/L	<0.1	12	27	77	160	14	16	5	5	15
B	µg/L	<4	12	9	12	13	18	9	18	14	16
Ba	µg/L	0.13	35	6	10	7	9	1450	39	8	16
Be	µg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ca	µg/L	40	1100	490	430	340	395	315	710	780	395
Cd	µg/L	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Co	µg/L	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	1	<0.1	<0.1	<0.1
Cr	µg/L	<1	<1	<1	<1	<1	<1	<1	<1	<1	2
Cu	µg/L	<0.2	1	2	1	1	1	1	1	1	1
Fe	µg/L	<2	4	3	3	5	4	<2	3	<2	3
Hg	µg/L	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
La	µg/L	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Mg	µg/L	14	365	890	195	225	335	81	490	1100	310
Mn	µg/L	0.13	1	1	1	1	1	2	2	2	<0.1
Mo	µg/L	<0.03	10	1	2	2	11	14	6	4	8
Ni	µg/L	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	1	<0.4	<0.4
P	µg/L	<10	33	18	25	51	67	<10	35	15	42

	Drill hole	Blank	Holdfast 1	Holdfast 1	Holdfast 1	Holdfast 1	Holdfast 1	Holdfast 1	Encounter 1	Encounter 1	Encounter 1
	Formation		Roseneath	Epsilon	Epsilon	Patchawarra	Murteree shale	Epsilon	Roseneath	Epsilon	Murteree shale
	Drill core no.		2183300	2183302	2183305	2183309	2183306	2183303	2074444	2074452	2074462
Pb	µg/L	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	1	<0.1	<0.1	<0.1
S	µg/L	21	1500	690	720	670	1200	915	2100	555	1150
Sb	µg/L	<0.03	5	1	1	4	5	1	2	1	5
Se	µg/L	<0.1	9	1	<0.1	1	4	0	13	1	3
Th	µg/L	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
U	µg/L	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
V	µg/L	<0.4	9	3	5	6	10	2	8	5	9
Zn	µg/L	3	1	4	2	3	3	3	<1	3	<1

Source: Geological and Bioregional Assessment Program (2019)

Table 16 Effect of pressure on mobilisation of dissolved elemental concentrations in SGW leachate solutions

Drill hole	Units	Holdfast 1			Encounter 1		
Formation		Roseneath			Murteree shale		
Drill core no.		2183300	2183300	Difference	2074462	2074462	Difference
Pressure	KPa	100	18400		100	18400	
Ag	µg/L	<0.01	<0.01	na	<0.01	<0.01	na
Al	µg/L	400	2500	2100	430	2450	2020
As	µg/L	2.8	12.7	9.9	4.57	18.68	14
B	µg/L	<4	<4	na	5.3	8.9	3.6
Ba	µg/L	62.2	25.7	-37	26.6	22.2	-4.4
Be	µg/L	<0.01	<0.01	na	<0.01	<0.01	na
Ca	µg/L	1050	805	-245	380	385	5.0
Cd	µg/L	<0.1	<0.1	na	<0.1	<0.1	na
Co	µg/L	0.19	0.11	na	<0.1	<0.1	na
Cr	µg/L	<1	<1	na	<1	<1	na
Cu	µg/L	0.27	0.28	0.01	0.3	<0.4	-0.10 ^a
Fe	µg/L	<2	13.7	13 ^a	<2	11.8	11 ^a
Hg	µg/L	<0.4	<0.4	na	<0.4	<0.4	na
La	µg/L	0.003	0.001	-0.002	<0.001	<0.001	na
Li	µg/L	17.2	34.8	18	20.2	39.7	20
Mg	µg/L	555	195	-360	410	215	-195
Mn	µg/L	1.34	0.68	-0.66	0.5	0.5	na
Mo	µg/L	6.14	9.63	3.5	5.1	7.7	2.6
Ni	µg/L	0.49	<0.4	-0.29	0.4	<0.4	-0.20 ^a

Drill hole	Units	Holdfast 1			Encounter 1		
Formation		Roseneath			Murteree shale		
Drill core no.		2183300	2183300	Difference	2074462	2074462	Difference
Pressure	KPa	100	18400		100	18400	
P	µg/L	<10	40.0	35 ^a	14.8	56.8	42
Pb	µg/L	<0.3	<0.3	na	<0.3	0.1	-0.05 ^a
S	µg/L	800	1650	850	840	1200	360
Sb	µg/L	2.36	4.21	1.9	2.6	5.0	2.4
Se	µg/L	4.25	9.01	4.8	1.6	3.5	1.9
Sr	µg/L	5.59	4.41	-1.2	3.5	3.8	0.30
Th	µg/L	<0.1	0.12	0.07 ^a	<0.1	<0.1	na
U	µg/L	0.02	0.08	0.06	<0.001	<0.001	na
V	µg/L	1.40	9.87	8.5	2.5	9.8	7.3
Zn	µg/L	<1	3.31	2.8 ^a	1.5	2.7	1.2

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

Source: Geological and Bioregional Assessment Program (2019)

Table 17 Dissolved elemental concentrations in dilute HCl leachate solutions

Drill hole		Blank	Holdfast 1	Holdfast 1	Holdfast 1	Holdfast 1	Holdfast 1	Holdfast 1	Encounter 1	Encounter 1	Encounter 1
Formation			Roseneath	Epsilon	Epsilon	Patchawarra	Murteree shale	Epsilon	Roseneath	Epsilon	Murteree shale
Drill core no.			2183300	2183302	2183305	2183309	2183306	2183303	2074444	2074452	2074462
Ag	µg/L	<0.01	0.62	0.56	0.44	0.35	1.21	0.02	0.63	0.53	0.58
Al	mg/L	<0.01	115	66	165	130	175	6	120	61	69
As	µg/L	<0.3	59.5	125	145	305	56.0	10.8	54.9	47.6	41.1
B	µg/L	48	66.2	25.0	28.4	35.9	99.1	<10	78.1	44.8	44.8
Ba	mg/L	<0.001	2.02	0.45	0.75	0.93	2.03	14.1	3.37	1.45	2.22
Be	µg/L	<0.02	28.4	5.4	13.3	12.6	28.3	12.2	31.3	19.3	22.5
Ca	mg/L	0.004	18.9	10.3	4.4	5.8	27.4	4.3	40.1	28.5	15.8
Cd	µg/L	<0.2	5.49	1.14	0.34	2.35	3.98	0.25	5.80	1.39	2.98
Co	µg/L	<0.1	355	210	88	240	350	43	350	280	300
Cr	µg/L	<1	935	4300	1900	1900	915	11	540	1600	500
Cu	µg/L	<0.2	1000	615	280	1900	880	64	750	235	710
Fe	mg/L	<0.01	1000	1000	340	310	985	54	950	>1000	485
Hg	µg/L	<0.3	0.34	0.30	0.79	0.53	0.40	<0.3	0.35	<0.3	<0.3
In	µg/L	<0.03	1.01	0.21	0.23	0.45	0.88	0.09	1.11	0.41	0.87
K	mg/L	<0.004	29.3	11.8	15.2	20.3	38.2	2.1	35.3	27.2	27.3
La	µg/L	<0.01	63.6	47.9	20.8	73.8	117.7	5.0	90.7	67.4	87.7
Li	µg/L	<0.1	185	120	365	215	250	9	175	57	130
Mg	mg/L	0.000	88.2	270.0	58.4	57.1	98.0	3.4	95.8	160.0	84.6
Mn	mg/L	<0.001	19.9	30.9	5.9	3.0	15.6	0.7	22.6	20.2	5.1
Mo	µg/L	<0.2	11.6	5.3	3.6	3.7	13.0	9.0	14.3	10.3	9.0

Drill hole		Blank	Holdfast 1	Holdfast 1	Holdfast 1	Holdfast 1	Holdfast 1	Holdfast 1	Encounter 1	Encounter 1	Encounter 1
Formation			Roseneath	Epsilon	Epsilon	Patchawarra	Murteree shale	Epsilon	Roseneath	Epsilon	Murteree shale
Drill core no.			2183300	2183302	2183305	2183309	2183306	2183303	2074444	2074452	2074462
Na	mg/L	<0.1	4.37	1.70	2.94	2.63	4.31	0.59	8.53	5.02	9.17
Ni	µg/L	<1	610	710	300	535	630	27	895	525	500
P	mg/L	<0.02	4.21	1.63	1.09	2.08	10.86	1.57	15.58	4.39	4.40
Pb	µg/L	<0.03	625	165	150	270	690	180	675	275	505
S	mg/L	<0.2	1.33	0.61	0.63	0.62	1.33	3.50	2.34	0.69	1.14
Sb	µg/L	<0.2	2.31	1.60	<0.2	1.24	2.44	0.53	1.88	1.10	2.83
Se	µg/L	<1	2.85	<1	<1	<1	1.43	<1	6.40	<1	1.18
Th	µg/L	<0.01	45.5	17.0	7.1	20.6	60.8	2.3	120.0	58.8	37.1
U	µg/L	<0.01	7.2	2.7	1.4	3.5	14.5	0.6	34.6	10.0	10.4
V	µg/L	<1	225	115	69	87	290	28	250	210	180
Zn	µg/L	<1	1950	1200	1200	1700	2150	625	1900	1250	1800

Source: Geological and Bioregional Assessment Program (2019)

Table 18 Dissolved elemental concentrations in HFF leachate solutions

	Drill hole	Blank	Holdfast 1	Holdfast 1	Holdfast 1	Holdfast 1	Holdfast 1	Holdfast 1	Encounter 1	Encounter 1	Encounter 1
	Formation		Roseneath	Epsilon	Epsilon	Patchawarra	Murteree shale	Epsilon	Roseneath	Epsilon	Murteree shale
	Drill core no.		2183300	2183302	2183305	2183309	2183306	2183303	2074444	2074452	2074462
pH	-	2.0	3.1	4.3	2.3	2.4	3.2	2.1	3.3	4.1	3.1
Ag	µg/L	<0.01	0.7	<0.01	0.3	0.3	1.3	0.02	0.7	0.1	0.6
Al	mg/L	<0.01	5.4	<0.01	29.2	21.0	8.4	0.6	4.8	<0.01	6.1
As	µg/L	0.04	3.3	0.0	3.1	11.3	3.2	3.6	1.4	0.2	1.4
B	µg/L	<3	17.5	7.0	3.7	4.7	7.9	<3	4.9	9.2	8.8
Ba	µg/L	<0.3	125	115	145	120	140	96	130	180	135
Be	µg/L	0.02	14.0	1.3	8.9	7.8	13.0	5.4	13.0	3.7	12.2
Ca	mg/L	0.07	9.8	4.7	2.5	3.2	6.5	2.6	10.9	11.5	6.8
Cd	µg/L	<0.1	2.2	0.4	0.3	1.8	1.5	0.3	2.1	0.4	1.4
Co	µg/L	<0.1	220	89	46	120	175	42	220	125	185
Cr	µg/L	2	26.3	9.4	368	194	33.1	1.9	9.6	2.3	22.5
Cu	µg/L	<0.4	445	36	195	1350	350	38	280	16	200
Fe	mg/L	0.002	310	275	89	99	245	28	245	295	190
Hg	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
La	µg/L	0.002	4.7	1.1	2.5	3.5	8.4	0.1	7.1	3.4	1.8
Li	µg/L	<0.1	86.2	8.5	83.2	62.1	108	6.1	81.9	31.7	82.8
Mg	mg/L	<0.03	26.3	123.9	19.7	19.3	21.8	1.9	32.4	69.4	45.2
Mn	mg/L	<0.001	8.2	16.6	4.4	1.9	5.7	0.4	8.2	8.7	2.6
Mo	µg/L	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Ni	µg/L	0.8	255	275	160	240	185	18	425	175	250

	Drill hole	Blank	Holdfast 1	Holdfast 1	Holdfast 1	Holdfast 1	Holdfast 1	Holdfast 1	Encounter 1	Encounter 1	Encounter 1
	Formation		Roseneath	Epsilon	Epsilon	Patchawarra	Murteree shale	Epsilon	Roseneath	Epsilon	Murteree shale
	Drill core no.		2183300	2183302	2183305	2183309	2183306	2183303	2074444	2074452	2074462
Pb	µg/L	2.3	57.7	0.4	58.4	63.1	67.7	87.4	28.1	1.7	54.1
Sb	µg/L	0.18	0.3	0.2	0.1	0.2	0.3	0.2	0.2	0.2	0.2
Se	µg/L	18	16.5	14.0	12.7	15.6	16.5	30.0	21.1	18.7	29.0
Th	µg/L	0.01	0.1	0.1	0.1	0.1	<0.01	0.1	0.1	0.1	0.1
U	µg/L	0.002	0.6	<0.001	0.4	0.7	0.4	0.2	1.2	0.1	0.4
V	µg/L	<0.1	0.6	<0.1	2.1	2.8	0.8	4.2	0.2	<0.1	2.3
Zn	µg/L	<3	735	260	725	1150	735	280	695	345	770

Source: Geological and Bioregional Assessment Program (2019)

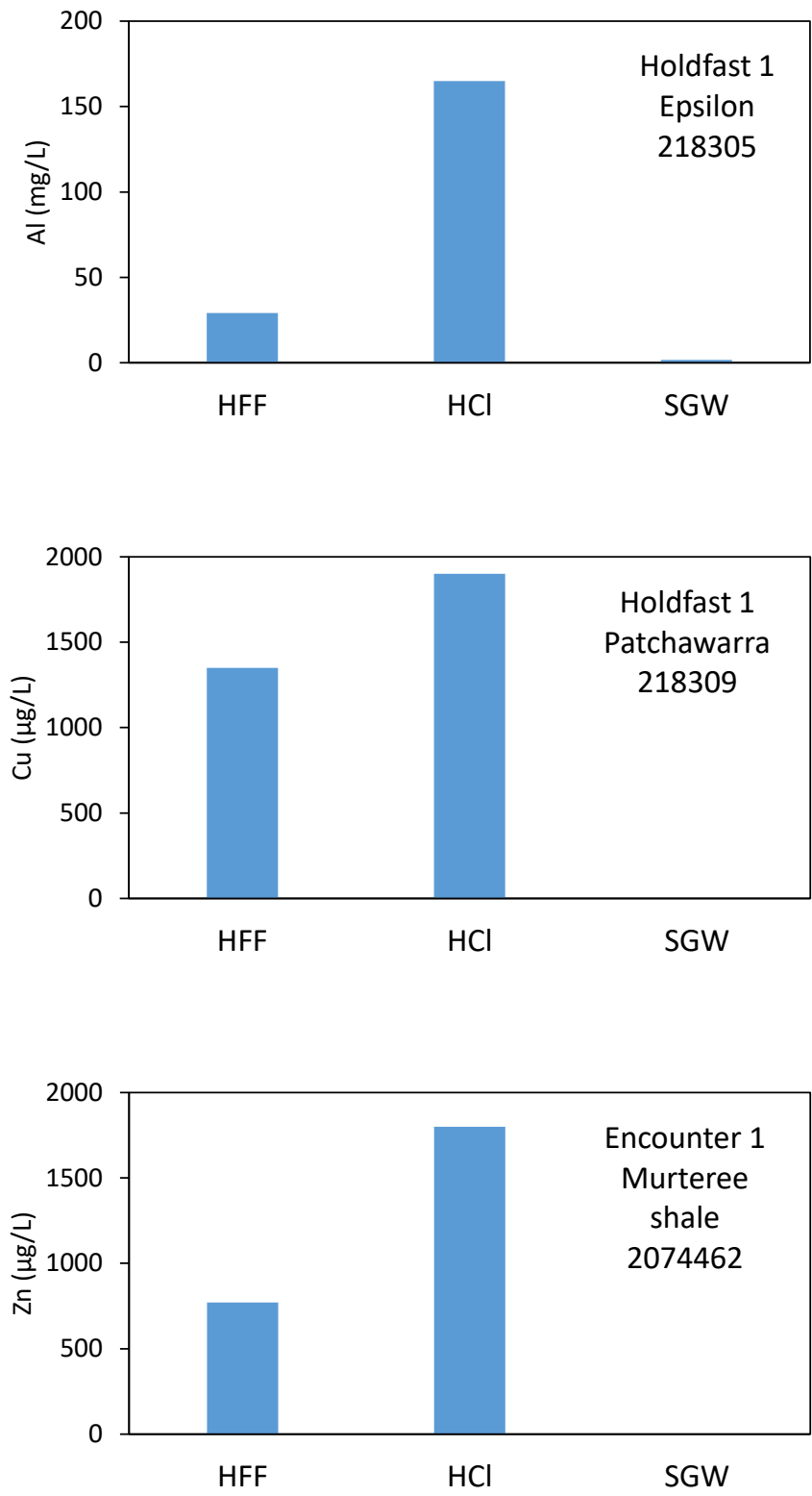


Figure 5 Comparison of aluminium (Al), copper (Cu), and zinc (Zn) concentrations in different leachate test solutions (HFF = hydraulic fracturing fluid; HCl = dilute hydrochloric acid; SGW = synthetic groundwater)

Source: Geological and Bioregional Assessment Program (2019)
 Element: GBA-COO-2-315

3.2.2 Extracts – organics

Phenol (33.6 - 54.9 µg/g) and PAHs were detected in 6 of 9 sample extracts from powdered rock samples (Table 19) (Geological and Bioregional Assessment Program, 2019). The other targeted phenols and PAHs were all below their respective concentrations of reporting in sample extracts (Table 10). The most common identified PAHs in sample extracts were benzo(ghi)perylene and phenanthrene (3 of 9 extracts) (Table 19). The deep coal sample from Holdfast-1 Epsilon contained the highest number of PAHs (n=7) and concentration in sample extracts e.g. benzo(ghi)perylene (318 mg/kg), indeno-(1,2,3-cd)-pyrene (101 mg/kg), and benzo(ghi)perylene (66.2 mg/kg).

The highest concentration of TRHs were found to be associated with the TRH C15-C28 (75 to 245 mg/kg; 32 to 53% TRHs) and >C16-C34 NEPM TRH (52 to 129 mg/kg; 24 to 44% TRHs) fractions for all rock samples (Table 19) (Geological and Bioregional Assessment Program, 2019). Targeted analysis of phenols and PAHs represented a small fraction of the total organic geogenic compounds (based on TRHs) present in the sample extracts (i.e. ~0.17% for deep coal sample from Holdfast-1; <0.04% for the other 8 samples analysed) (Table 19). The absence or low concentrations 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. The majority of organic compounds in sample extracts (as TRHs) were unidentified and their potential risk (individuals and mixtures) to aquatic environments is unknown. A study by Maguire-Boyd and Barron (2014) found the composition of chemicals based on their carbon content varied between shale gas regions and the majority of organic chemicals were present in the >C6 fractions. Similarly, solvent-extracted shale samples from the United Kingdom were found to have organic chemicals predominantly in the C14-C29 fraction, reflecting both the maturity of the shales as well as their algal origins (Wright et al., 2015).

3.3 Discussion

The leachate tests conducted with dilute HCl and HFF generated the highest inorganic elemental concentrations in solutions compared to SGW. This demonstrates the role of acidity and chemical constituents of HFF (e.g. chelating agents, surfactants, solvents, etc.) can play in mobilising elements from powdered rocks in formations. The inorganic elements showing substantially increased mobilisation in HFF were: aluminium, arsenic, barium, cadmium, cobalt, chromium, copper, iron, lithium, nickel, lead, 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 required to determine the underlying relationships between trace element content and physico-chemical properties of the rock formations and fate of chemicals in the HFF.

Higher pressure led to increased mobilisation into solutions of elements such as aluminium, arsenic, lithium, phosphorus, and sulfur; and decreased mobilisation for elements such as barium, calcium and magnesium. 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 HFF and mobilisation of geogenic chemicals from powdered rocks in shale, tight and deep coal formations in the Cooper GBA region.

3 Laboratory-based leachate tests (geogenic chemicals)

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

Drill hole	Holdfast 1						Encounter 1		
Formation	Roseneath	Epsilon	Epsilon	Patchawarra	Murteree shale	Epsilon	Roseneath	Epsilon	Murteree shale
Drill core no.	2183300	2183302	2183305	2183309	2183306	2183303	2074444	2074452	2074462
PAHs									
Benz(a)anthracene	<2	<2	<2	17.9	<2	27.8	<2	<2	<2
Benzo-(b)&(k)-fluoranthene	<5	<5	<5	56.6	<5	318	<5	14.2	<5
Benzo(ghi)perylene	<5	<5	<5	<5	<5	66.2	<5	<5	<5
Chrysene	<5	<5	<5	21.7	<5	<5	5.8	<5	<5
Fluoranthene	<5	<5	<5	5.7	<5	21.6	<5	<5	<5
Indeno-(1,2,3-cd)-pyrene	<5	<5	<5	<5	<5	101	<5	<5	<5
Phenanthrene	<2	<2	8.3	<2	<2	40.6	<2	<2	5.6
Pyrene	<5	<5	<5	<5	<5	15.4	<5	<5	<5
Phenols									
Phenol	39.8	33.6	47.8	65.9	<5	61.8	<5	<5	56.1
TRHs									
TRH C10 - C14	13 129	10 403	22 629	14 613	11 864	18 086	15 958	15 193	<100
TRH>C10 - C16*	13 552	10 739	18 167	14 142	13 395	17 203	11 288	13 233	21 993
TRH C15 - C28	194 816	167 796	191 229	245 121	176 043	198 500	105 091	156 832	74 871
TRH >C16 - C34(F3)*	102 914	88 261	99 758	128 689	92 997	102 779	51 767	84 787	104 352
TRH C29 - C36	39 175	36 076	34 262	45 960	36 548	35 068	20 434	33 082	19 420
TRH >C34 - C40(F4)*	13 510	12 048	10 167	14 094	11 060	10 543	7 356	10 733	14 460

*NEPM TRH reporting values

Source: Geological and Bioregional Assessment Program (2019)

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

3 Laboratory-based leachate tests (geogenic chemicals)

4 Conclusions

A total of 116 chemicals were identified for use in drilling and hydraulic fracturing at shale, tight and deep coal gas operations between 2011 and 2016. Of the 116 chemicals identified, 9 were drilling chemicals, 99 were hydraulic fracturing chemicals, and 8 are chemicals used for both activities. Fifty-eight percent of the chemicals identified in the current study were not assessed in the National Assessment of Chemicals Associated with CSG extraction in Australia.

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 'potential high concern' and 41 are of 'potential concern'.

The chemicals of potential and potentially high concern would require further site-specific chemical assessments to be undertaken 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 industry adapts to site-specific conditions, improve gas extraction efficiency, and endeavours to use 'greener, safer' options. A Tier 1 qualitative (screening) ERA for all new chemicals (or chemical not previously assessed) used in shale, tight and deep coal operations in Australia could determine whether these new chemicals represent an environmental risk ('Yes/No'). For identified chemicals of environmental risk, Tier 2 and 3 quantitative ERAs can assess 'what', 'where' and 'how great' is the risk.

Laboratory-based leachate tests on powdered rock samples collected from formations in the Cooper GBA region identified several elements that could be substantially mobilised into solutions by hydraulic fracturing fluid: aluminium, arsenic, barium, cadmium, cobalt, chromium, copper, iron, lead, lithium, nickel and zinc. Priority organic chemicals such as phenols, PAHs and TRHs were detected in extracts of powdered rock samples. Targeted analysis of phenols and PAHs represented a small fraction of the total organic geogenic compounds (based on TRHs) present in the sample extracts. The majority of organic compounds in sample extracts (as TRHs) were unidentified and their potential 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 (in consultation with government agencies) of gas operations that includes the identification of 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. Despite undertaking these detailed ERAs, there is still public concern surrounding potential environmental impacts of hydraulic fracturing, in particular 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 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 for all new chemicals (or chemical not previously assessed) used in shale, tight and deep coal operations in Australia could determine whether these new chemicals represent a potential environmental risk ('yes/no'). For identified chemicals of potential concern, Tier 2 and 3 quantitative ERAs can assess 'what', 'where' and 'how great' is the risk.
- Tier 1 qualitative ERA relies mainly on aquatic acute ecotoxicity data representing three trophic levels – freshwater alga, water flea and 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.
- There are limited public data available on the composition and concentration of chemicals in hydraulic fluids, flowback and produced water, and wastes (e.g. muds, brines, etc.) from shale, tight and deep-coal operations in Australia.
- There is limited understanding of the fate and transformations of chemicals present in hydraulic fluids and flowback and produced waters (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 to aquatic environments is unknown.
- There are limited ecotoxicity data available on drilling and hydraulic fracturing chemicals for Australian species and ecotoxicity endpoints are currently not available for groundwater organisms (e.g. stygofauna).
- Despite the very low likelihood of a well integrity failure or failure of surface infrastructure (ponds, tanks, 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 to water quality (i.e. localised event) and the adequacy of control and management plans to prevent environmental impacts.

6 Recommendations

The following are recommendations to improve ERA of chemicals at shale, tight and deep coal operation in Australia:

- Chemical assessments for shale, tight and deep coal gas operations in Australia should consider following the ERA framework developed by Australian Government Department of Energy and the Environment for CSG exploration (Department of the Environment and Energy, 2017);
- The chemicals identified in a Tier 1 screening ERA as ‘potentially high concern’ and ‘potential concern’ would need to undergo further site-specific assessment with realistic environmental conditions and exposure scenarios (Tier 2 and 3 quantitative ERAs);
- Consideration of site-specific groundwater related risks of chemicals due to hydraulic fracturing in the event of unlikely release of fluids due to well integrity failure and pond/tank leakage (residual risk reduction);
- Comprehensive baseline surface water and groundwater quality data in targeted aquifers, used for irrigation and drinking water, and for ground water dependent ecosystems collected prior to shale, tight and deep coal gas developments.
- Public disclosure of chemicals and water quality monitoring data before, during and after hydraulic fracturing would provide greater community and government confidence in drilling and hydraulic fracturing (Development of National Register of Chemicals for Shale, Tight and Deep Coal Gas Operations in Australia);
- Further research needs to be undertaken into determining the composition and concentration of unknown organic compounds present in flowback and produced waters and their potential effects on aquatic organisms, management and treatment; and
- Direct toxicity assessments of hydraulic fracturing fluids, flowback and produced water would, in conjunction with chemical analyses, provide information to determine no-effect concentrations and for safe dilutions/treatment options.

Public concern about potential environmental impacts on water quality from hydraulic fracturing remains heightened. In particular, the community is concerned about potential impacts on water quality from the mixture of industrial chemicals used and geogenic chemicals that could be mobilised during shale, tight and deep coal gas resource development. The independent collection and open and transparent reporting of water quality data at future 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.

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Glossary

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

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

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

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

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

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

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

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

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

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

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

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

consequence: synonym of impact

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

hydraulic fracturing: also known as 'fracking', 'fracing' or 'fracture stimulation'. This is a process by which geological formations bearing hydrocarbons (oil and gas) are 'stimulated' to increase the flow of hydrocarbons and other fluids towards the well. In most cases, hydraulic fracturing is undertaken where the permeability of the formation is initially insufficient to support sustained flow of gas. The process involves the injection of fluids, proppant and additives under high

pressure into a geological formation to create a conductive fracture. The fracture extends from the well into the production interval, creating a pathway through which oil or gas is transported to the well.

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

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

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

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

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

likelihood: probability that something might happen

material: pertinent or relevant

methane: a colourless, odourless 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.

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

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.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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